A handbook of
chemical manipulation

Charles Greville Williams

A HANDBOOK

OF
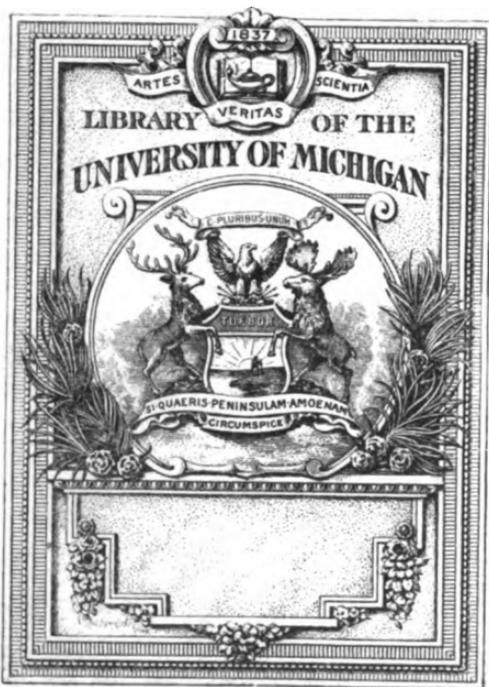
CHEMICAL MANIPULATION.

A HANDBOOK

4988

OF
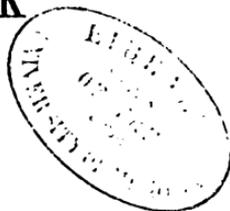
CHEMICAL MANIPULATION.

By C. GREVILLE WILLIAMS,

LECTURER ON CHEMISTRY IN THE NORMAL COLLEGE, SWANSEA,
LATE PRINCIPAL ASSISTANT IN THE LABORATORY
OF THE UNIVERSITY OF GLASGOW.

TO

THOMAS ANDERSON, M.D., F.R.S.E.,

&c.   &c.   &c.

REGIUS PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GLASGOW.

DEAR DR. ANDERSON,

The three years during which I had the privilege of assisting in your researches, were the happiest I have yet known. You must regard the dedication of this Work as a small mark of my appreciation of the numerous acts of kindness which made that time pass only too rapidly.

Ever faithfully yours,

C. G. WILLIAMS.

PREFACE.

THE only work in our language specially devoted to Chemical Manipulation has long been out of print, while probably at no time has a guide to the Student in his experiments been more needed.

Within the last few years modes of manipulating have undergone many changes, and a vast number of processes, involving the use of complex apparatus, have been invented. Chemistry is doubtless in a transition state; eventually, and, as it approaches perfection, processes will be simplified, and we shall obtain reactions by more simple and direct methods. Possibly, although we dare scarcely hope it, we may eventually rival the fabled simplicity of the Rosicrucian, and, by the aid of a few simple vessels, obtain far more beautiful compounds than we now procure with all our elaborate appliances.

Manipulation is to chemistry what Bacon conceived mathematics to be to science, and as such " should know her place ;" nevertheless the importance of manipulation cannot be overrated. The good, and therefore successful manipulator, will do far more work than he who is deficient in that respect, and his researches will be of a higher order. The time expended by an awkward or clumsy operator in merely attaining accuracy, will be devoted by the skilful chemist to the exploration of new fields.

It often happens that the Student, earnestly desirous of pursuing chemical researches, is prevented from attending

a laboratory or school of chemistry; the following pages are especially intended for persons so situated. To those who are so fortunate as to have the advantage of regular instruction, the work will still be found a useful companion in the laboratory.

On several occasions descriptions have been quoted at length (*vide* pp. 60, 324, 332 and 448). The author of a process is generally best able to describe it accurately and clearly.

Considerable space is devoted to certain reactions employed in researches; a careful perusal of that portion of the work will be to the Student's advantage, more especially to those undertaking investigations.

The illustrations have been engraved by Mr. George Pearson from original drawings, made in most cases from the instruments themselves. For a few of them the Author is indebted to his friend, Mr. Galletly, and one or two were copied from photographs.

It has been the Author's earnest desire to give every chemist his due; if, therefore, the names of inventors of apparatus or processes have anywhere been omitted, such omission has been accidental.

The numerous Tables which have been added will, it is hoped, be found to increase the usefulness of the work.

Laboratory, Normal College, Swansea,
September 22, 1857.

CONTENTS.

SECTION XXII.

Gas Manipulation.

SECTION XXIII.

Manipulation connected with
Organic Analysis.

CHEMICAL MANIPULATION.

1. IT is not often that a building is to be specially erected for the purposes of chemical research: it will be necessary, therefore, in most instances, to alter one already existing; but it is essential for the completeness of the plan about to be detailed, to presuppose the laboratory built purposely. The matter contained in this section must be understood as applying solely to a laboratory of research, unconnected with any School of Medicine, University, or other place where the science is taught. In order that the following descriptions may be more easily apprehended, a plan of a laboratory, and an elevation of a student's workingbench, will be inserted at the end of the volume.

2. It is more convenient for the laboratories to be on a ground floor than on several storeys, as will be readily seen when we consider the facility with which furnaces can be built without the necessity of springing arches for their support, the much greater safety in the event of fire or other accident, and the ease with which heavy or large articles can be brought in or removed. Nevertheless it is the opinion of many that the dryness of an upper floor more than compensates for any slight trouble of access. Balances, air-pumps, and other apparatus of metal soon become injured by the damp frequently found in rooms level with the ground.

3. Unless it is intended for several persons to work together, it is better not to have an experimental laboratory too large, for it

B

will generally be found that one of moderate size is kept in better order than a very large one; the fact of there being plenty of room frequently inducing carelessness in putting things away, a procedure which cannot be too strongly reprobated, whereas, on the other hand, if there be not too much space, it becomes absolutely necessary to the operator's comfort and progress that everything which may be no longer in use should be restored to its proper place.

4. Those who have not been accustomed to experimental pursuits, can scarcely conceive how frequently an operation is dependent for success upon the readiness with which the hand can be placed upon an instrument, while a careless person is constantly exposed to the mortification of finding an experiment which has perhaps cost much labour, entirely spoiled from the impossibility of adding an ingredient, or performing some apparently trifling operation, at the exact instant required.

5. The apparatus required in an experimental laboratory of the present day is very different, and in general far less bulky than in those of even a few years ago. The furnaces especially have been modified, while the greatly increased facilities for the use of gas have to a certain extent rendered chemists independent of them. Every laboratory ought to have three or four gas-furnaces of different sizes and patterns, as will be described in the section on Lamps. Several yards of vulcanized india-rubber tubing will also be required, to enable them to be arranged upon any part of the tables or floor. They can be attached to any of the gas-pipes, and when not in use may be kept in a special place out of the way of injury.

6. The laboratory, as will be seen by a glance at the Plan and explanation, is lighted by windows all down one side; and at one end there is another large window, in front of which is placed a glass case fitting very tight and containing three balances, each being also in its own lantern, so that they are doubly protected from the corrosive vapours which float about the laboratory. No chemical laboratory can, however, be considered as at all approaching completeness, unless another room is especially

appropriated to the balances, air-pumps, and other delicate instruments.

7. All down one side is placed the chief working bench, at one end of which is a desk in which will be contained paper, the note book, and various et ceteras which are necessarily kept free from dirt; it is advisable to allot one of the drawers of the desk to the various test papers, cut into slips, and kept in well-corked tubes ready for use. Above the desk will be two or three shelves, for those works of reference which are constantly in use in the laboratory; and above these may be placed a shelf for containing some of the less bulky and more valuable reagents. The books for reference may perhaps with greater propriety be kept in a cupboard in the balance room.

8. At the extremity of the long bench, next the desk, should be fixed a small vice, which will be in everyday use during the construction or repair of apparatus. A few pairs of scissors or shears should be suspended against the wall near this spot, which should also be close to the drawers containing the tools. At the other extremity of the bench to the vice, is placed a four- or six-gallon stone barrel with a tap of the same material, containing distilled water, and beneath it a pan to contain the droppings. This will, from its proximity to the operator during his work, be found far more convenient than having it over the sink, which would involve passing to the extremity of the laboratory frequently. The presence of the barrel will not prevent the necessity of having one or two Gmelin's washing-bottles, of about a pint capacity, within easy reach, they being constantly in use for washing precipitates and applying small quantities of water.

9. At intervals of every few feet down the working benches, are gas-pipes projecting a few inches above the surface; they afford great facilities for the performance of several operations simultaneously, and as each is terminated by a screw or "thread," they may have attached any of the gas-jets mentioned in the section on Lamps.

10. The two tables in the centre are very strong and heavy, so as not to be easily vibrated; they are, however, capable of being

removed when required to make room for any particular operation. The larger of the two has an apparatus affixed, which enables it to sustain a filter-stand to hold the calico and other bags, so often required for filtering large quantities of liquid. This is accomplished by having two slips of wood sliding in mortises immediately under the top of the table, supporting a board pierced with holes to receive the bags. In addition to this contrivance, several small filter-stands should be provided, in order to prevent the unnecessary use of retort stands, which are more advantageously appropriated to operations with retorts and flasks, and to experiments requiring heat. The shape and modes of construction of the most convenient apparatus of this kind will be mentioned in its proper place. Near that portion of the laboratory where the filtrations are carried on, will be placed the receptacle for filtering-paper, which is so arranged as to show all the different sizes of ready-cut filters at a glance.

It is recommended, if possible, to appropriate some special part of the laboratory to filtrations when they are on a larger scale than usual, because being generally a long and in many cases a tedious operation, it is desirable not to occupy the space allotted to general work.

11. On the other side of the laboratory, opposite to the general working-bench, is placed a large arch or hood of masonry, under which, on a slight rise, are placed the furnaces; but where a manufactory which contains powerful furnaces is connected with the establishment, it is recommended to dispense with them altogether in the experimental room, and, instead, to have one on Luhme's or some analogous principle, and to replace the hot-air cupboard of the table-furnace by one heated with gas. Nevertheless, as this is not always a convenient arrangement, a furnace of the kind last named is represented in the Plan of the laboratory. A few chauffers will be found necessary, from the facility with which they can be moved to any part of the laboratory. The hood must have its flue quite independent of those belonging to the furnaces, which may be placed under it, or their draught would be entirely spoiled; and it is desirable to have an

arrangement in the form of a damper placed in it, so as to enable the operator to regulate the current of air, and at times to close it altogether, especially if the flue be straight, in which case inconvenience would be occasioned in wet weather by the descent of blacks and rain.

12. Where organic analyses are frequently being made, it is advisable to have the means of using two combustion-furnaces side by side, for the convenience of performing two analyses simultaneously, unless Hofmann's gas-furnace is used, when, from the rapidity with which combustions can be made, it becomes unnecessary. The large quantity of white ash and charcoal dust which attends the use of the ordinary combustion-furnace, makes it important to perform the operation under the hood or chimney shown in the Plan, unless another room can be used for the purpose, which is very desirable.

As, in many laboratories, these analyses are of everyday occurrence, it is important to afford every facility to the operator, by placing all the materials and utensils required, within reach, and always keeping a supply of combustion-tubing clean and dry.

In a convenient place at one end of the room, the square water-bath for drying precipitates, &c. must be placed; and as, in an active laboratory, this instrument is every day in use, and is often required to contain a considerable number of preparations, it can scarcely be too large.

13. At the end of the laboratory opposite the balances will be seen a vapour chamber or cupboard, having free access to the atmosphere. Beneath may be a furnace, serving to heat a small sand-bath; the chief use of this apparatus is to receive vessels emitting vapours, which, from being corrosive or unpleasant, it is desired to prevent floating about the laboratory. The sand-bath enables us to apply heat when required, as in dissolving gold or platinum, preparing chlorine, &c.

14. At the end nearest the balance-case is a moveable sky-light, which will often be in use to remove the vapours with which the laboratory is unavoidably filled in the progress of some experiments, and which renders the power of rapidly removing

the air an object of great importance. It will be seen that no special arrangement is made for carrying away the hot and vitiated air produced by combustion of the gas, for its influence is so small in comparison with the odours and other exhalations constantly emitted during the progress of experiments, that it may be altogether disregarded.

15. The laboratory should be well provided with cupboards and shelves, of which it would be difficult to have too many. In all laboratories of research there is a constant accumulation of specimens of valuable or rare products; these should be neatly arranged and labelled; one of the large cupboards will probably be the most convenient place for their retention, in the event of there being no museum attached to the establishment.

16. In most establishments there is some operation which is more frequently in requisition than any other; for instance, in one, alkalimetrical analysis will probably be of almost everyday occurrence; in some laboratories metals are constantly being examined for their purity, or ores for the per-centage of their constituents; in others, on the contrary, the analyses of manures, or operations connected with organic research, are the staple occupations; whatever, therefore, the most frequently recurring source of employment may be, everything else ought to be made subservient to it, and every facility afforded for its ready and perfect performance.

17. A good store of test-solutions should always be kept ready, and the various burettes, beakers, basins, &c. should, immediately after use, be cleaned and put in convenient situations, that they may be at hand for the next series of experiments.

18. The barometer, with a good thermometer of small range but very open degrees, should be kept near the place where the gaseous nitrogen determinations are made, so as to indicate the temperature and pressure on the spot. It is advisable to note these data every day, at stated times, and to become as familiar as possible with all the peculiarities and best methods of observing the indications of the two instruments.

19. One particular part of the laboratory, preferably under one

of the benches, should be appropriated to dirty apparatus intended to be cleaned; and it must be distinctly understood that no vessels or utensils should be taken away to be washed, no matter what their appearance, unless placed here. The best arrangement, perhaps, for this purpose, is to have three trays with rather deep rims sliding upon beadings, so as to be easily capable of removal when full.

20. The blowpipe table, so useful for the construction and repair of glass apparatus, especially the preparation of combustion-tubes, finds a place near the chief working-bench, as indicated in the Elevation. A convenient contrivance for glass-working will be found in its proper section.

21. A considerable number of retort-stands are indispensable in an active laboratory; they should vary in height from 14 inches to 4 feet; the latter are intended to stand upon the floor, and should have large and heavy bases to them. The rings should be numerous, and a few sizes will be found sufficient, varying from 2 to 9 or 10 inches diameter. It is important that only two sizes of rods should be in use, one for the large and the other for the table stands, so that the rings may be used indifferently for any one of the set of stands to which they belong. In the same manner, the threads of all the screws should, in every possible case, correspond; this will greatly facilitate the arrangement of the complicated systems of apparatus which are sometimes necessary.

22. Several small wooden hoops should be provided, some of which fit moderately tight into one another; they answer a twofold purpose, namely, as supports for hot flasks or dishes and other apparatus, which would be endangered by being put down on a rapid conductor of heat; and also as sieves, by taking two, one of which fits inside the other, stretching muslin over the smaller, and then pressing the larger one over it so as to keep the muslin tight; these sieves are the more convenient, as it is easy to wash the material, and also to have it of different degrees of fineness, without occupying so large a space as would be required by several of the ordinary kind.

23. At the end of the laboratory, over the barrel of distilled water, is placed the rack for glass tubes. Probably the most convenient form is that made on the principle of the racks used by decorators for keeping their stock of paper-hangings. It is also desirable to have a long box fastened against the wall, preferably under one of the shelves, to contain combustion-tubing. The box should be about 6 feet 6 inches long, and the cover may be attached by a leathern hinge, somewhat in the manner of a candle-box. It is made so long because the combustion-tubes are usually sold in six-foot lengths, and it is not advisable to cut them until the tubes are being made. The method of making them will be found further on. The tubes, when finished, are, from the peculiarity of their shape, extremely fragile; the smallest carelessness in moving them is almost sure to break off the long thin point. It is advisable, therefore, to keep them on two iron brackets fixed into the wall about 16 inches apart, all the tails being at the same end, and turned downwards; they should each have a cork placed in the aperture to prevent ingress of dust. As they are very quickly made, it is better to do so when required than to keep a large stock, and so run the risk of breakage.

24. Places should be provided in the drawers under the benches for the hammers, files, anvils, and other tools constantly required. One drawer should be assigned to the blowpipe apparatus, with its agate mortar, lamps, &c. The various Wedgwood mortars should have a place assigned them on a shelf near the sink. The iron mortar on a block will generally be kept in the store-room, if there be one attached, its size and weight rendering its presence inconvenient in the laboratory. The stock of porcelain crucibles will also find a place in the same cupboard with the beakers, retorts, flasks and dishes.

25. It has probably been observed, that throughout the previous descriptions it has in most cases been taken for granted that the laboratory has to be confined to one room; if, however, the operator has the use of a second or even a third, much advantage will be found to accrue from such an arrangement. The

balances, air-pumps, and other delicate instruments, will then be kept out of the danger, which they otherwise incur, of being injured by the corrosive vapours of the laboratory, which in time will find their way through even the double cases which protect them. It is therefore most desirable that whenever such fumes are flying about, every means of ventilation at hand should without delay be put in action. The close chamber previously alluded to (§ 13), will afford the means of preventing the contamination of the air of the room during the performance of experiments which will go on by themselves; but there are some operations which from their nature are necessarily carried on on the tables or benches. There are, however, few cases in which the fumes cannot be conveyed into the open air by the use of a little contrivance; when it is impossible, the only remedy is either to make the experiment under the hood (§ 11), or to open the skylight and windows, and by this means establish a current of air through the chamber.

26. In some laboratories the pneumatic trough is in very frequent request; where this is so, it is best to have it on a table near the sink, and at some distance from the fire.

The mercurial trough is best kept covered over, on a table provided with a groove and raised edge, so that any mercury spilled may be swept with a card into a receptacle for the purpose.

If it is possible for each working-bench to have a sunk basin and plug, with a tap to supply water, which can, when required, be attached to a flexible pipe so as to cool the Liebig's condensers, such an opportunity must not be neglected; if, however, the pressure is insufficient to enable it to enter the lower part of the last-mentioned instrument and escape by the upper end, it will be useless for this purpose.

Where the laboratory is attached to a public institution, the working-places for the students may be arranged in the manner shown in the Elevations. The rest of the laboratory arrangements will be best seen by reference to the engravings and accompanying descriptions.

SECTION II.

FURNACES.

27. It is not intended to notice more than a very small portion of the furnaces that have been invented by chemists at different times. Their number is immense; even the first chemists, the adepts, had furnaces of almost every pattern that fancy could suggest, or complicated, yet mostly useless, processes require.

The Athanor was perhaps their masterpiece; it was intended to afford a steady heat, adapted for digestion or distillation, for a very long period, sometimes for many months. This was effected by a contrivance at once simple and ingenious: it consisted in having an air-tight tower, with a close-fitting lid at the back of the furnace, immediately connected with the fireplace; this held the charcoal in such a manner, that, as it burnt in the grate, it descended in the tower and replenished the fire.

28. The operations of modern chemistry do not generally require a long-continued heat to be applied to retorts or vessels for digestion; and where it occurs, gas is by far the most economical and convenient fuel. Lately, however, it has become necessary in some researches to expose substances in sealed tubes to 212° or higher for many hours, sometimes even for a week or more; and it is advisable in such cases, especially where regard is had to economy of time, to keep up the heat to the highest point, whatever that may be, during the whole period, instead of letting the temperature fall during the night. Gas, as being so easily regulated, will prove the most convenient source of heat in these experiments; where it is not to be had, considerable difficulty is generally found in constructing an arrangement which shall dispense with the operator's attention during the night. The manipulations connected with this subject will be found in the section on Pressure tube operations.

29. The first furnace which presents itself is that which is ordinarily in use in the laboratory, and which may be either on

Brande's or Luhme's principle. The former is generally used, and as it frequently happens that it has to be placed in a room

Fig. 1.
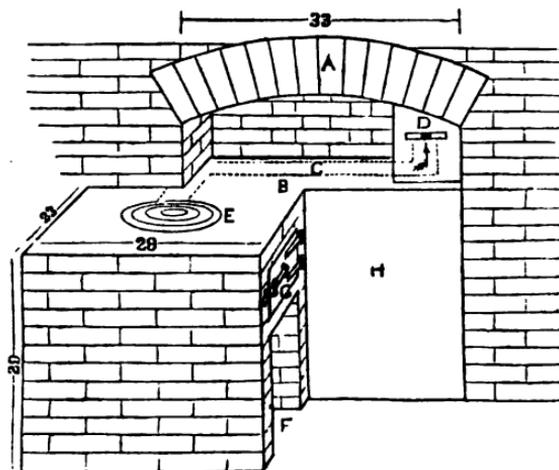
where there is a fireplace, and economy of space being usually of importance, a modification will be described which has been found extremely convenient in practice. The figures indicate the dimensions at the parts where they are attached: A is the arch of the fireplace; B the sand-bath under the arch; C the flue, indicated by the dotted lines; D the damper; E the rings by which the aperture over the fireplace is enlarged or contracted; F the ashpit, which may very conveniently have a door to regulate the draught; G the fire-door; H the hot closet, the roof consisting of an iron plate, between which and the top plate the flue runs between two courses of bricks. The upper plate, both outside and inside the arch, is in one piece. The rings fit easily into each other, in the manner indicated by the sections (figs. 2 and 3); if they fitted exactly, the expansion on heating would cause them

Fig. 2.

to adhere. The space between each ring is somewhat exaggerated, for the sake of distinctness. They may be procured in

sets of the chemical instrument makers,
or it is easy to have a wooden pattern
made, and get them cast, in places
where they are not procurable ready

Fig. 3.

made. The price is very trifling. This furnace will give heat
enough to melt several ounces of copper with ease, and by nearly
closing the damper and opening the fire-door, a gentle heat fit
for distillation or evaporation may be obtained. The fire-bars are
loose, and fit into notches in iron bearings (fig. 4) built into the
wall of the furnace at each end. By
this means it is easy to replace a bar
when destroyed. Several contrivances
for distilling in different ways with
this furnace will be described in the

Fig. 4.

section on Distillation. The hot chamber is convenient for drying
preparations, precipitates, &c. The temperature of course varies
with the fire in the furnace, but from 100° to 150° may be taken
as an average. It has an iron grating about half-way between
the floor and the top, which is useful to support capsules, bottles,
funnels, with their filters, &c. put in to dry.

It is advisable, in constructing this furnace, to have a slip
of iron 1½ inch high, placed in such a manner as to con-
fine the sand to that portion of the iron plate which is beneath
the arch. In order to obtain a sufficient draught, and yet not
to prevent the possibility of using a hood, several contrivances
are applicable.

In that given, the chimney to the fireplace is closed by slates
about 30 inches from the top of the plate, and the furnace-flue is
carried into another chimney running parallel with the first; by
this means the pipe of the hood is enabled to play into the fire-
place chimney without injuring the draught of the furnace.

The hood is not represented in the engraving; it projects com-
pletely over the furnace, its lower edge being about 3 feet 6 inches
from the iron plate.

It will be seen that an arrangement of this kind has many ad-
vantages: it occupies little room, from the sand-bath being under

the arch, while the light which comes laterally is quite sufficient
for every purpose.   Crucible operations are conveniently exe-
cuted, from the great facility which the rings offer to the in-
gress and egress of the vessels; moreover, by placing a sheet
of talc over the centre hole, after removal of the small stopper,
the whole operation can be watched without distress to the face
and eyes.

Evaporation is readily performed in Berlin or other porcelain
dishes over the naked fire, on a ring of the proper size; or even,
when it is wished to proceed more slowly, by placing the basin
on the top of the rings, the stopper being in its place.   In some
sublimations, when considerable heat is required to be applied
to flasks, two or three rings may be removed, and a sand-pot
introduced of one of the shapes shown in figs. 5 and 6.   They

Fig. 5.

Fig. 6.

are made of cast iron, and may be obtained of the instrument
makers at a very low price.   In the section on Distillation, a
method will be given for converting pots of this kind into retorts
for destructive distillation, and for preparing sulphurous acid on a
large scale.

Several evaporations may be conducted simultaneously at dif-
ferent parts of the plate and sand-bath, so that any temperature
may with facility be commanded, from the melting point of copper
or gold, and even, with care, cast iron, to the evaporation of an
alcoholic solution, or, in the closet, the drying of the most delicate
organic preparations.

There is one disadvantage which this furnace possesses, namely,
that it offers no means for performing the numerous tube opera-
tions which it is so frequently necessary to resort to even in
some of the least complex researches.   In these cases, great use

may generally be made of the sheet-iron combustion-furnace represented below.

Fig. 7.
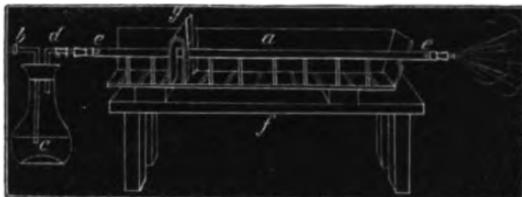
30. The cut represents the method of reducing copper turnings used in the ultimate analysis of organic substances containing nitrogen; a is the combustion-furnace, of sheet iron, seen in section. In figure 8, a is the front end, b a sectional view of the anterior extremity, showing the position of the supports, and c a screen to confine the fire to the parts required. The details of the method of using this instrument will be found in its proper place.

The length of this furnace, to be practically useful, should not be less than 30 inches by 4 inches high, and 3½ broad at the bottom, increasing to 5 inches at top. Where considerable heat is required, as in the reduction of somewhat refractory substances, it is merely requisite to fan the ignited charcoal with a piece of cardboard; or a long parallelogram of sheet iron, ending in a chimney, as in fig. 9, may be employed. Instead of

Fig. 8.

Fig. 9.
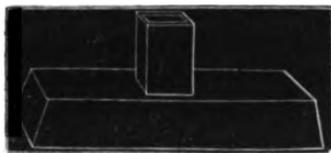
the latter, a couple of the chimneys belonging to chauffers may be used, as they will raise the heat sufficiently for all the purposes to which the furnace is likely to be applied.

31. Where a very intense heat is required to be given to the tubes, one of Luhme's furnaces may be employed, which, from

its extreme adaptability to most chemical operations, will be described. It in many cases renders the brick furnace, shown in fig. 1, unnecessary. The first section, fig. 10, represents the body of the furnace, which is lined with fire-clay, and has apertures on each side for the passage of a tube. These holes are capable of being closed by the small doors shown open. Fig. 11 shows the body of the furnace with its fire- and ashpit-doors closed. The three projections seen at the top, are to allow of a large pan being placed over the fire without destroying the draught.

Fig. 10.   Fig. 11.   Fig. 12.
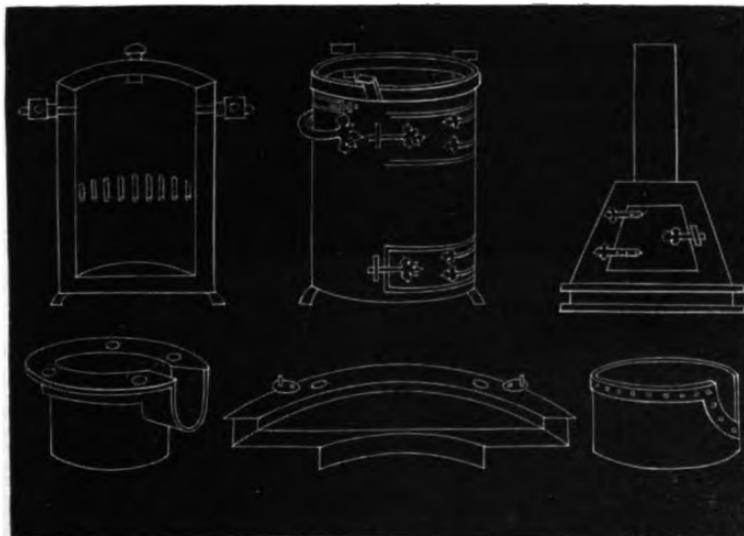
Fig. 13.   Fig. 14.   Fig. 15.

The chimney, fig. 12, which fits on over the body, has a door to allow of the introduction of fuel. Fig. 13 is a sand-bath adapted to distillations with retorts; it rests when in use on fig. 15; the broad depression in fig. 13, intended to allow of the passage of the neck of the retort, fitting into the corresponding notch in fig. 15. Four apertures on the top of fig. 13 allow of the escape of the hot air, so that the combustion is only slightly

impeded by its use.   Fig. 14 is a section of a broad shallow sand-bath, adapted to digestions and many other operations.   When in use it rests on the top of fig. 11.   The products of combustion pass between the double pieces of which it is composed, and escape by four apertures in the rim, two of which are seen in the engraving; they are capable of being closed by small move-able pieces of metal, so as to form, in connexion with the fire- and ashpit-doors, a perfect control over the temperature.   The fur-nace just described, and which I have had in use for a long time, I have always been accustomed to feed with the London gas-coke.   That kind which is obtained in Scotland, and some-times elsewhere, which leaves an ash almost equal in bulk to the coke itself, is of course useless, and in such a difficulty, char-coal, although a very expensive fuel, must be used.

In most laboratories of research, such furnaces as the two just described will be sufficient for the performance of all the operations likely to be undertaken; but it nevertheless some-

Fig. 16.
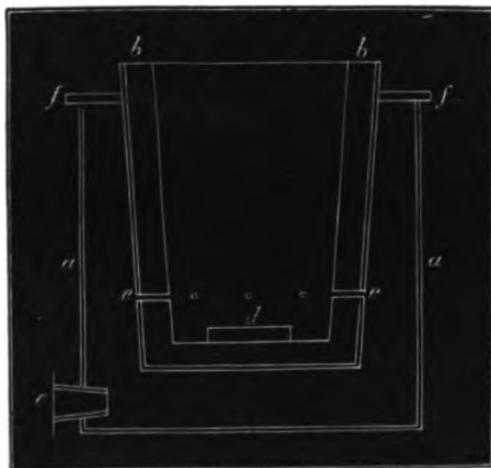
times happens that experiments requiring a very intense heat are necessary; when such is the case, recourse must be had to a

blast-furnace. The most convenient and powerful of these is that of Sefström. It consists of a thick sheet-iron cylinder, $a\,a$ (fig. 16); on the top of this is a strong iron ring, ff, which is intended to support a second cylinder, $b\,b$, which drops into it; this has six tubes, ⅝ths of an inch in diameter, fastened into it, which are intended to conduct the air from the vacant space. They are 2¼ inches long, and are, as is likewise the rest of the cylinder, covered with fire-clay. The tube c, which projects at the bottom of the outer case, is intended to admit the nozzle of a pair of powerful bellows. The proper composition for lining the surface is prepared by patiently mixing fresh Stourbridge clay with a little horse-dung, and adding about a sixth of a powder made by pulverizing old crucibles. The composition must not be applied too moist, and is to be allowed to dry spontaneously.

It is generally found on drying that cracks have been formed, which must be filled up with a little more of the composition. When *quite* dry, a gentle fire is made in the furnace, and gradually increased to the highest pitch by a vigorous application of the bellows; it is then allowed to cool, and the surface of the clay is usually found to be vitrified from the intense heat. The crucible is always supported in the furnace about 3 inches from the bottom. A piece of brick or an old crucible, as at d, fig. 16, resting on a thin stratum of sand, to prevent it from adhering to the lining, forms perhaps the best support.

Staffordshire coke should be used, from its small tendency to produce a fluid slag, which would fill up the tubes, and so prevent the ingress of the air. By means of this furnace may be obtained the most powerful heat which can be applied to crucibles in laboratories*. In fact, its power is greater than the resistance offered by the best vessels: it not unfrequently happens that a good Hessian crucible is completely fused; this is more likely to happen with common gas-coke than with the Staffordshire, as the slag produced from the furnace acts as an

* The improved apparatus of M. H. Sainte-Claire Deville, by means of which even platinum may be melted and volatilized, will be described in the Appendix.

energetic flux. This description of furnace was especially valuable at a time when, in mineral analyses, fusions with carbonate of baryta were often necessary.

The platinum crucibles are to be imbedded in magnesia contained in a good Hessian or London crucible, as, if exposed to the naked fire, they would be readily destroyed by the slag; even if they escaped this, they would soon be rendered rotten and useless by the sulphurous and other vapours which are invariably present in an active state in the atmosphere of a blast-furnace.

It is scarcely necessary to caution the chemist against the danger arising from the performance of an operation evolving such an intense heat and abundance of sparks, in an unprotected or unsafe place. It is advisable, where the full power of the furnace is required, to have a good fire at hand, in order to replenish with bright red-hot fuel, as great reduction of temperature would arise from feeding it with cold coke. In ordinary experiments this will not be necessary, as, from the intensity of the heat, operations performed with it are usually soon finished, and frequently without the necessity of adding any fresh fuel. The furnace will be found of service in the reduction of iron ores on the small scale; also in the formation of alloys of the more refractory metals.

32. It was intended to give an illustration of Aikin's blast-furnace, formed from large black-lead crucibles, but the superiority both in point of economy and durability of the one just mentioned will render such a description unnecessary, and enable us to devote the space to the consideration of some other convenient and more frequently used furnaces.

33. In establishments where fused potash, nitrate of silver, chloride of zinc, and similar preparations are made, the little furnace about to be described is, from its simplicity and cheapness, very useful; it may be used also for distillations, and small crucible experiments. It is, however, less applicable for distillations than other operations, because there is no fire-door; the fuel being introduced at the aperture in the plate, which is closed by rings, c, fig. 17, like the furnace first described. The

heat is regulated by a damper, *d*, in the usual manner. The chief peculiarities are in the arrangement of the grates and the shape of the fireplace; for it will be seen there are notches at different heights supporting square rods on which fire-bars may be placed, as at *b b b*, to adapt the furnace either for crucible operations, distillations or fusions, in pans on the rings. Those bars not in use, are to be removed and the holes to be closed by brick or iron stoppers; and, if a very intense heat be required, the interstices, if any, may be made good with a little Stourbridge clay. As the ends of the bars project from the furnace, they may be removed with a pair of tongs, and the fire is thus immediately extinguished. The bars are of the usual shape and lie side by side, the square piece at the ends preventing them from lying so close as to injure the draught. Fig. 18 gives a view of the bars

Fig. 17.

as seen when looking down into the furnace, and also a side section. This arrangement, when playing into a tall chimney, forms an intensely powerful wind-furnace, and that at a very small cost, as it can be erected by any workman. It should be lined with fire-bricks. It will be seen that the fireplace is made slightly conical, so as to allow the easy descent of the fuel. The addition of a fire-door of course makes the fur-
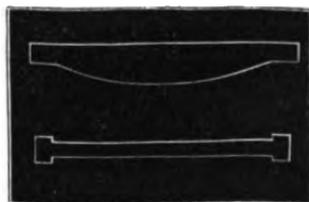
Fig. 18.

nace fit for distillation with retorts, &c. The top is formed by a plate of wrought iron pierced for the rings; or if cast, it should be made with a flange to fit them accurately. This furnace may

also be used for cupellations by placing the cupel on the exit of
the hot air, as at *a*; and the progress of the experiment may be
watched from the ring-hole by removing the stopper *c*.   In this
operation a piece of red-hot coke may be placed on the cupel, in
such a manner as to concentrate the heat on the assay without
preventing the access of the air.

It is necessary to observe, that the furnace, if intended for ope-
rations requiring a very powerful heat, should be constructed of a
different size to what it would be if only used to evaporate and
fuse the chemicals alluded to, or similar preparations.   Even then,
however, the same relative proportions may be preserved.

Considerable care and attention is requisite in using powerful
furnaces, to obtain a temperature adapted to the operation.   It
may be taken as a rule, generally, that there is more danger of
heating a crucible too highly than too little.   Carelessness in this
respect is often the cause of much disappointment and annoyance
to persons unaccustomed to the necessary manipulations.

34. Where many consecutive crucible operations of the same
kind are to be performed, as, for instance, in the preparation of a
considerable quantity of a fused chemical product, much advantage
is often gained by not permitting the crucible to cool.   If, in
making crude nitrite of potash by fusing nitre, we first melt the
salt in an iron basin to expel the water, and then put it into a
previously warmed common English crucible, and gradually raise
the temperature to bright redness, we shall often find, on pouring
out its contents, that the crucible is uninjured, and if immediately
returned to the fire may be refilled with the dried salt, and the
operation continued in the same manner until many pounds of
the nitrite have been made.   If, on the contrary, the damp nitre *
be placed in a cold crucible, and the latter be at once introduced
into the fire, it is sure to be destroyed, and, in all probability, the
contents lost.   It is therefore advisable to put the crucibles intended
to be used, on the top of the furnace for an hour or so before they

* Commercial saltpetre, although apparently dry and containing no water
of crystallization, always retains a considerable amount between the layers of
the crystals.

are wanted, to ensure their complete dryness and to prevent too
rapid change of temperature, on being put into the fire. When
crucibles or stoneware retorts are required to be luted, as is the
case when they are to be exposed to a long-continued or violent
heat, a very convenient mixture for the purpose is composed of
sifted Stourbridge clay well mixed with a little damp horse-
dung to which a small quantity of a strong solution of borax has
been added. It is to be evenly applied over the outer surface
with a knife. The vessel should then be placed on a moderately
warm part of the furnace until perfectly dry, and the cracks
which will probably have formed must then be filled up and the
drying be repeated. Further directions for the application of
luting will be found in the section on Distillation at a high
temperature.

35. One of the most con-
venient and often used sub-
stitutes for the furnace is the
sheet-iron chauffer, fig. 19.
It is intended to burn char-
coal, and, when used with the
additional chimney, it gives a
very good heat, quite sufficient
for the decomposition of sili-
ceous minerals by the improved
processes of Lawrence Smith,
and others. To adapt it for
tube operations it is provided with holes opposite each other,
which are capable of being closed by means of small pieces of
sheet iron moving on a rivet. The grate is supported by
three projecting pieces of sheet iron riveted on. The small
door at the top is for the purpose of enabling fuel to be added
without removing the chimney. By means of an iron triangle
placed over the chauffer, after the chimney is removed, we at
once adapt it to distillations and evaporations. The smallest
dimensions practically convenient are 6 inches in diameter and
the same in depth, the grate being placed immediately above the
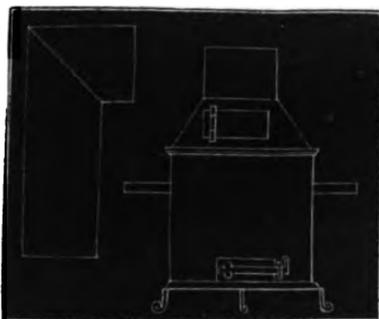
Fig. 19.

door, which is 2¼ inches high by about 3½ long.   One of the
advantages connected with it, is the facility it affords to operations
requiring its presence on the tables or other parts of the labora-
tory.   When placed upon any wooden substance it is supported
by a tile, which prevents any danger from the heat.

Its use, to contain a supply of red-hot charcoal during the pro-
cess of organic analysis in laboratories not possessing a complete
arrangement for the purpose, will be alluded to in the section
devoted to that subject.   A furnace of this description is far more
convenient than any substitute made from "blue pots," which are
recommended in many chemical works.   The latter invariably
crack after one or two operations, are more troublesome to con-
struct, much heavier, and, in fact, less eligible in every respect.
Sometimes, however, the French clay-chauffers may, from their
convenience of form and cheapness, be used with advantage;
and the better class of them may
be used a considerable time be-
fore any serious injury occurs.
They should be bound with strips
of iron, or wire, in several places,
in order to keep them together
when fissures make their ap-
pearance.

36. It has been said that the
furnace represented in fig. 17
may be used for cupellations, but
when an apparatus especially
adapted to this process is de-
sired, that depicted in fig. 20 is
perhaps as convenient as any.
It is made, preferably, of sheet
iron lined with fire-clay.   Those
constructed entirely of an earthen
material, are liable to the disad-
vantage alluded to in the case of
the crucible-furnaces made from blue pots.   It consists, essentially,

Fig. 20.

of a chamber either square or cylindrical, provided with three apertures: one, *a*, to admit the muffle, fig. 21; another, *b*, to introduce the fuel; and a third, *c*, to regulate the draught. The muffle, *d*, is seen to be supported at one end by the edge of the aperture in the furnace, and at the other by a projection opposite to it. The small gallery, *e*, placed round the chimney, is intended

Fig. 21.

to support the newly-made cupels during the process of drying, sufficient heat for which is obtained partly by radiation and partly by conduction. The muffles are small earthen ovens pierced on the sides to enable a current of air to play on the assay, by which means the more oxidizable metals are converted into a state which enables them to be absorbed by the cupel.

The best fuel for a small assay-furnace is charcoal in moderate-sized pieces mixed with somewhat smaller fragments of coke or well-sifted cinders. The cupels are formed by mixing finely sifted bone-ashes with just sufficient water to enable the powder to adhere; it is then pressed into a cupel-mould, fig. 22, the superfluous mass being removed by a knife; and the stamper, *á*, being introduced, a smart blow is given by a mallet, and, on reversing the mould, a little pressure enables us to remove the cupel, which

Fig. 22.

must be thoroughly dried before use. In fig. 22, in addition to the stamper, *a*, and the mould, *b*, a ring, *c*, is introduced; this is, however, only used where the unnecessary complication of having *b* made in two pieces, to facilitate the removal of the cupel, is adopted; the ordinary arrangement, which requires only the two parts *a* and *b*, is by far the best. The division of *c* into two pieces, and keeping them together by a ring during the time the cupel is being formed, appears to be an imitation of Plattner's mould for crucibles. The details of the process of cupellation are of course foreign to a book on manipulation, as they would afford sufficient
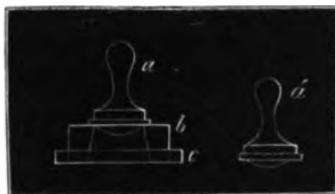
material for a treatise on that subject exclusively*; but we may
mention, that it is founded on the non-oxidizability of gold and
silver; if, therefore, we expose a mixture of these metals on a
cupel, with the addition of a certain quantity of lead, to a cur-
rent of air at a high temperature, the less valuable metals pre-
sent are converted into oxides, which, being fluxed by the excess
of fusible oxide of lead, become fluid, and are absorbed by the
cupel. At the end of the operation, therefore, we have the pure
metal (or a mixture, if both gold and silver be present) in the
state of a globule on the cupel; it is then removed and weighed.
If silver be present, the resulting button is again subjected to
the operations of quartation and parting, the details of which are
to be found in the work mentioned in the note, and also in most
manuals of chemistry.

37. It must be remembered, that, in furnaces of the ordinary
kind, the maximum heat is about $1\frac{1}{2}$ or 2 inches above the bars;
the crucible should therefore be supported on a piece of brick, or
another crucible inverted, by which means it will acquire much
more heat than it would if put directly on the bars.

38. It is sometimes required to construct a furnace that shall
heat an exceedingly large sand-bath; and as it is, of course, an
object to accomplish this end with as small an expenditure of fuel
as possible, the flue is made to wind backwards and forwards, so
as to deprive the current of air and smoke of as much heat as
possible; the bricks at the end of each turn are capable of being
removed, so as to enable the flue to be cleaned without taking the
plate off. A sand-bath of this description is extremely valuable
in numerous operations, especially for sublimations which are to
be performed at a gentle heat; such, for instance, as the manu-
facture of pyrogallic acid, much used of late years in photography.
By the arrangement alluded to, all gradations of temperature,
from a dull red to a gentle digesting heat, may be obtained; more-
over, the flue is provided with a damper, which enables us to
increase or lessen the fire at will.

* For information on these points, the reader is referred to Mitchell's
' Manual of Practical Assaying.'

SECTION III.

LAMPS.

39. The extreme cleanliness, and great facility with which the heat of lamps can be regulated, render their possession, under one or other of the numerous forms which fancy or necessity has created, quite indispensable to the experimental chemist. It is to be observed that much difficulty is often found by the inexperienced operator in selecting the most really useful form of lamp for general use, and, as is so frequently the case, under very different circumstances, the most simple is likewise the most generally efficacious.

As in all towns of any importance gas is to be had at a moderate cost, it becomes for many reasons by far the best and most economical fuel. In the first place, with moderate care, there is no waste, there is also no spilling of oil, no evaporation of spirit, no trimming of wicks, no tendency to derangement in the mechanism, and therefore no trouble in obtaining precisely the most eligible amount of flame. Gas as a fuel is therefore most strongly recommended for general use instead of either oil or spirit.

40. Several kinds of gas-lamps are in use in laboratories, and all of them have excellencies in one way or another. The first and most simple is the common Argand burner, a vulcanized india-rubber pipe connecting it with a supply-pipe. The burner is generally supported upon a heavy foot, as in fig. 23. It has two taps, one at the supply-pipe and one at the burner. The effect of the second is to enable us to use the gas at some distance from the supply-pipe, without the necessity of going from the lamp to regulate the flame, an important thing where, from the opacity of the chimney, which must

Fig. 23.

be of copper or brass, it becomes impossible to adjust the flame
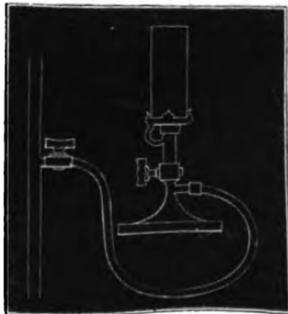
c

without being sufficiently close to look down into it. It is also necessary to have a tap at the supply-pipe as well as the burner, in order to facilitate the removal of the latter for the purpose of cleaning, &c. without causing escape of gas. The great command which the operator has over this arrangement makes it the most generally useful of any. From the smallest blue flame to a heat sufficient to raise to dull redness a moderately large platinum crucible may be obtained. The next method, where the gas mixed with air is burnt on the top of wire-gauze, is far less easily regulated, but is, nevertheless, extremely valuable in cases where a powerful temperature is desired, as in the fusions which occur in the analysis of siliceous minerals, the ignition of precipitates, the combustion of the platinum and gold double salts formed by the different bases, with a view of ascertaining their atomic weights; also in the determining the quantities of baryta, lead, and silver in the salts formed by the union of those substances with the organic acids* &c. The simplest way to construct a lamp of this kind, is to take a piece of wire-gauze of moderate fineness and press it over the chimney, b, fig. 24, until it is folded down sufficiently, and then to pinch the creases with a pair of pliers until they take the shape seen from the top at c: this will have the effect of drawing the gauze tight over the chimney; the points are then to be folded against it as at d, and the ring, a, is then to be put over the whole to keep it in its place. The gas is turned on for a few seconds before a light is applied, otherwise the mixture is so explosive that the flame passes through the gauze.

Fig. 24.

When alight, and the proportion of air and gas properly regulated, it is observed that a pale blue flame is obtained, showing the absence of solid carbon. Moreover, if we place a basin or other vessel over it, no soot is deposited. In the Argand lamp, where

* In these latter experiments, it is better to commence by heating gently over the Argand lamp, fig. 23, until all volatile matters are expelled, and to finish by ignition over the Bunsen's burner, fig. 30.

the combustion is, chemically speaking, less perfect, the flame, if allowed to play on the bottom of a vessel, immediately deposits carbon, causing inconvenience, not only by the soiling of the vessel, but also by preventing the due access of heat.

41. Another, and, in some cases, more convenient method of burning coal-gas with air is represented in fig. 25, where a gas-pipe, fixed to a table, as alluded to in the description of the laboratory (§ 9), is seen to open beneath a funnel-shaped tube; by this means a blue flame of great intensity may be obtained, in which, equally with the last arrangement, all the carbon is oxidized; moreover, the flame is more compact, and, by a little management, may be obtained in a form admirably adapted for the ignition of platinum crucibles, and many other purposes. The neck of a broken glass retort supported by a clip, or even by a wire, answers every purpose. This instrument is, it is believed, the contrivance of Mr. Remington.

Fig. 25.
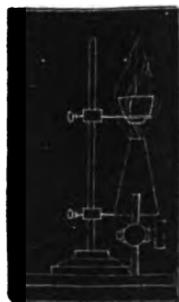
42. A neat gas-burner, on the same principle, is shown in fig. 26; the description of the first renders a second unnecessary. Dr. Lionel Beale has described a gas-furnace (fig. 27) for heating common earthen crucibles: he states that it is capable of raising 10 or 12 ounces of oxide of copper to redness, and of fusing silicates with carbonate of soda. He also states that the tube in which the coal-gas mixes with the air should not be less than 9 inches in height and 3 in diameter. The gas comes from a small tube in the lower part, and burns with the air on the surface of wire-gauze. Just above the gauze there are several small holes. The crucible is supported by pieces of iron, projecting from a wide iron ring made to fit the furnace, and which can be replaced by others adapted to crucibles of various sizes. The upper part of the body of this furnace can be removed when required, and there is a small door in it to enable the operator to watch the process going on within. The next method of applying gas to chemical operations which claims our attention, is the gas-

furnace represented below.   It is made of sheet iron, and has two
rows of holes, about $\frac{1}{2}$ an inch in diameter, pierced in it, one at

Fig. 28.

Fig. 26.   Fig. 27.
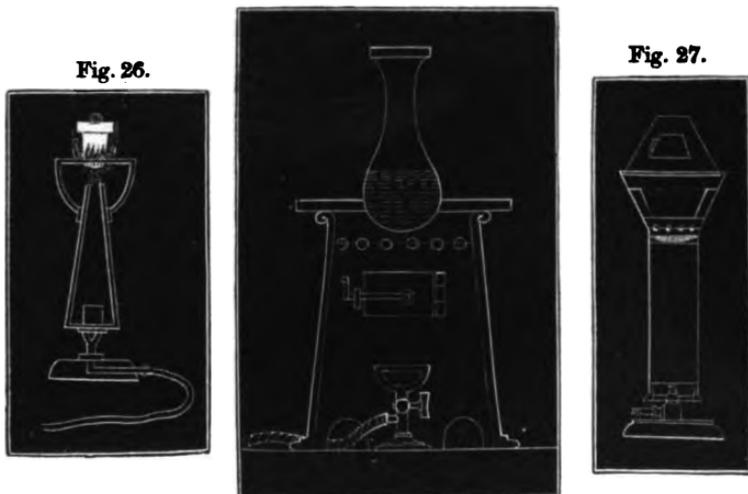
the top and the other at the bottom ; the former is necessary to
allow the exit of the heated air, in case the whole of the superior
aperture becomes closed by a retort or basin, &c.   It is advisable
sometimes to have a plate of talc adapted to the door, in order to
facilitate the regulation of the flame by enabling the operator to
see it without opening the apparatus.   The burner consists of a
large ring pierced with holes, and may be made either to rest on
three projecting slips of iron, or on a foot, in the manner shown
in fig. 28.   The top is adapted to a series of sheet-iron rings of
various sizes, which serve to support the vessels over the flame.
This instrument is of great use in the laboratory of research, from
the ease with which varieties of temperature can be obtained, and
still more especially from the fact that a uniform heat may be
maintained for any length of time with very little superintendence.
A furnace for heating a small sand-bath is shown in fig. 29.   It
is particularly adapted to analytical operations, from the ease with
which the heat is capable of being regulated.

A burner of a very convenient kind for mixed gas and air* has lately been introduced; it consists (fig. 30) of a brass tube, $a\,b$, of

Fig. 29.   Fig. 30.
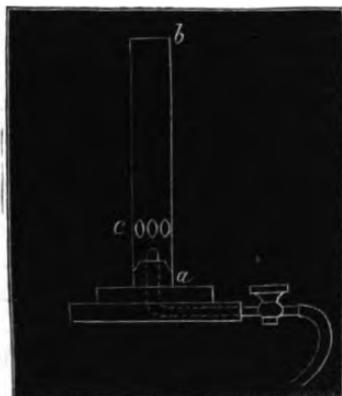
about $\frac{4}{5}$ths of an inch in diameter, sliding at a on a fish-tail burner; the air enters by holes at c, the amount being regulated by means of a small slide, which closes them wholly or partially as may be required.   The nature of the aperture by which the gas enters is well adapted for causing it to mix with the air, notwithstanding the small size of the tube $a\,b$.

43. The admirable contrivance of Dr. Hofmann for obviating the necessity for the use of charcoal in organic analysis, an instrument which must greatly influence the progress of organic chemistry, from the rapidity with which it enables us to make extremely accurate analyses, will be described in the section on Manipulation in Organic Analysis.

44. Chemists who have the misfortune to be unable to procure gas for the laboratory will necessarily be obliged to use oil or spirit, and, where economy of fuel is of secondary importance, methods may be adopted which will prevent the operator from feeling any great inconvenience from the substitution; nevertheless, so considerable are the advantages of gas over any other

* Said to be invented by Bunsen.

source of heat on the small scale, that an effort should be made to procure it.

45. The number of lamps which have been invented at different times is almost as great as that of furnaces; it would, therefore, be hopeless to attempt describing them all, and, in fact, very few are really serviceable in practice. Oil-lamps are now but little in request, the heat they give being less powerful, and the combustion, unless great care is used, less perfect than with alcohol or wood-spirit. We are therefore obliged frequently to trim the wicks and clean the instruments, if we would avoid the annoyance of having vessels exposed to the flame blackened by smoke. Sometimes, however, there are occasions when (gas being absent) they are necessary; but this only happens when an extremely gentle heat is required for a considerable time, as, for instance, in the solution of refractory substances, distillation of volatile liquids, drying precipitates, &c. In all these instances the most simple form of lamp is quite sufficient, and it is doubtful if anything would answer the purpose better than that kept for use with the blowpipe. It is quite unnecessary to describe the oil Argand lamp, its construction being so nearly similar to that of the spirit-lamp with circular wick (fig. 31); of course the water-chamber may be omitted; in every other respect the same model may be taken. A few cotton threads gathered together at the lips of a small evaporating basin filled with olive oil may often be used, and, under some circumstances, is an extremely useful substitute for a proper lamp. The operator will find no difficulty in forming an impromptu oil-lamp, if required, from the various pieces of metal, &c. which are generally at hand in all laboratories. When required for giving light to the apartment, the construction so much used now, called the Moderateur, will be found economical and convenient. Colza, or refined rape oil, is the best fuel for it.

46. *Spirit-Lamps.* The ordinary glass spirit-lamp is so common that a description of it is unnecessary; it may be mentioned, however, that, as ordinarily sold, they almost invariably have the cap made too short, so that when placed on the lamp the wick is

compressed. This ought to be provided against by selecting one with a cover sufficiently high. The use of brass wick-holders is liable to many objections. In the first place, they become greatly heated and endanger the splitting of the glass. But the chief objection is the corrosive action which the fuel generally used as a substitute for spirits of wine in this country, exerts on the alloy of which the wick-holder is made; we frequently therefore find a cupreous deposit on platinum vessels when exposed for any length of time to the flame, a circumstance of great importance in many cases, and one which ought to be carefully guarded against. The stoneware wick-holders to be procured at the chemical instrument makers, and first introduced, it is believed, by Mr. J. J. Griffin, are admirable substitutes for the ordinary metal ones; in default of this, a piece of glass tube may be advantageously used. An effective spirit-lamp may at any time be constructed out of a vial having a tube passing through the cork, a cover being formed from a test-tube inverted over the wick, and fitting with moderate tightness on the superior extremity of the cork.

47. The spirit-lamp with the circular wick figured in section in the margin (fig. 31), is a necessary piece of apparatus in all laboratories where gas is not to be ob-
tained. The construction is obvious; it has, however, a peculiarity which deserves attention, namely, the water-chamber *a*, which is seen to surround the wick-holder, thereby preventing the spirit from becoming heated during long operations. It is, however, re-commended to have the wick elevated by a circular screw, as in the ordinary

Fig. 31.

Argand table-lamps, instead of the rack-work placed on one side (fig. 31), a mode of elevating and depressing the wick which has many disadvantages. The lamp invented by Berzelius (fig. 32) is much used, and has the spirit-chamber placed at some distance from the wick-holder, by which means the heating of the spirit is prevented; but, from occupying so much space, this arrangement
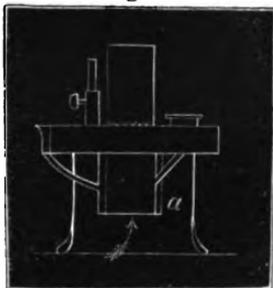
is perhaps scarcely so convenient as the water-chamber.   A cir-
cular spirit-lamp, to be generally useful, ought to be able to heat
a platinum crucible of one ounce capacity and contents to full
redness, so as to enable the operator to fuse the more easily de-
composable silicates with carbonate of soda or the other fluxes
recommended in works on the analysis of minerals; these opera-
tions may, however, be performed with a charcoal furnace similar
to fig. 19.   The modes of rendering even the more refractory
minerals soluble have been so far improved by J. Lawrence Smith[*]

Fig. 33.
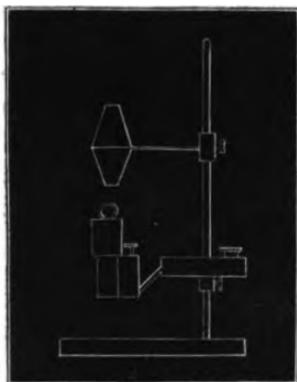
Fig. 32.

and others, that it is seldom necessary to use Sefström's blast-
furnace.   Where the full powers of a lamp are required to be
exerted, the crucible jacket, fig. 33, is necessary; it will be seen
that the crucible is supported on three knife-edges; the arrange-
ment is such that the flame is made to act on the crucible in a
manner well adapted to economize the heat and avoid loss by
radiation.

[*] Chemical Gazette, vol. xi. p. 252.

SECTION IV.

BLOWPIPE APPARATUS.

48. This little instrument has become absolutely indispensable to the chemist; perhaps there is no single appliance made use of in the science which has so wide a field of usefulness; its value is not only found in mineral, but also in organic research; in fact so extended has the subject of blowpipe manipulation become, that a separate treatise would be necessary were we to enter upon it at anything like the length it undoubtedly deserves. Of all the manuals extant which treat of the blowpipe, that of Professor Plattner is the most elaborate and useful, so much so that a chemist could scarcely be said to be a good blowpipe analyst unless tolerably familiar with its contents; the treatises of Berzelius and Children may also be consulted. Under these circumstances it will not be necessary to enter at any great length upon the subject, but the following paragraphs may at least serve as an introduction to the more extended works alluded to. The philosophy of a candle-flame is familiar to all who have studied elementary chemistry, and is undoubtedly foreign to a work on manipulation; we shall therefore proceed to describe the blowpipe itself. The different fancies of chemists have produced a considerable number of them, each, possibly, having some particular merit adapted to the circumstances under which it was invented; however, out of all these there are but two or three in general use.

Fig. 34.

It will be found, that for all purposes for which a mouth blowpipe is applicable, that of Black is the best and cheapest. It consists of a tube of tin plate (fig. 34) about 7 inches long, $\frac{3}{4}$ inch broad, tapering to a quarter, where a small mouthpiece is soldered, to increase the operator's command over

c 5

the instrument. At the wider end is inserted a small cylindrical tube of brass, about 2 inches long, supporting the nozzle, which may be of brass or platinum. The tube is slightly conical at the end where the jet is fixed, and the latter is thus made to fit on without a screw, which would soon be injured by the high temperature to which it is exposed, and render it difficult to be removed for the purpose of cleaning. It is absolutely necessary to a good blowpipe that the nozzle should be drilled from a solid piece of metal, in the form represented on a larger scale in the section fig. 34. One of the chief merits of Black's instrument, is the efficient manner in which it condenses and retains the water derived from the breath, and renders its ejection upon the heated assay impossible.

The moveable trumpet-shaped mouthpiece may sometimes be used with advantage in long and fatiguing operations; it is, however, seldom necessary.

Wollaston's blowpipe consists of three tubes, capable of being connected or of being taken asunder and then packed one inside the other.

Cronstedt, who was perhaps the first who endeavoured to prevent the moisture of the breath from reaching the assay, contrived an instrument having a bulb in the middle capable of being opened in order to remove the condensed moisture. It is an expensive, although far from convenient form, and if, by any chance, held vertically, the moisture escapes.

The lamp generally used with the blowpipe is of very simple construction. The wick, which is about an inch long by one-eighth wide, stands $\frac{1}{4}$ inch above the holder, fig. 35. A cover is made to screw over it, to prevent dust from accumulating on the wick. The construction of the wick-holder will be seen by reference to the engraving, and the cotton is to be cut parallel to it, the lower end being away from the operator while blowing. The air is propelled along the wick in the direction of its greater axis. To a person of moderate dexterity, the manipulations connected with ordinary blowpipe analysis, will prove very easy, but considerable experience will be necessary to enable the student to detect in complex mixtures, substances whose reactions are not

very decided. Nevertheless, the value of the instrument is so
great, and so many otherwise troublesome problems in qualitative
analyses may . be rapidly and decisively solved by it, that no

Fig. 35.
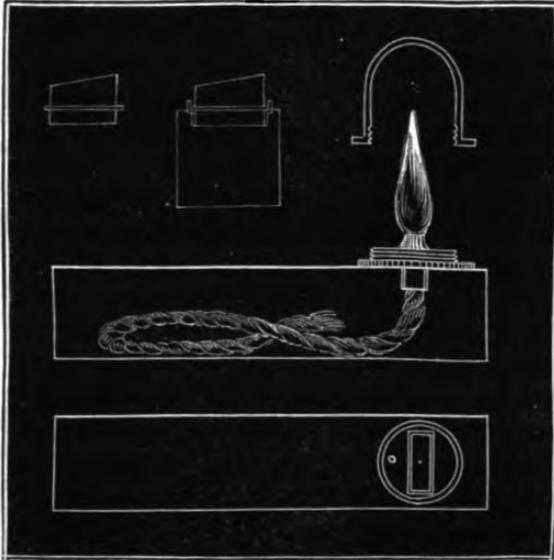
labour should be spared to acquire facility in its management. It
may be mentioned, that the blowpipe is not intended entirely to
supersede the humid method of analysis; it is rather to be con-
sidered as an adjunct; for instance, we will suppose a piece of
type-metal to be under examination: its brittleness will at once
lead to a suspicion of the presence of antimony or bismuth, but
it is wished to ascertain which of these, and what other metal may
be present. It is heated with nitric acid until converted into a
white powder, evaporated to a small bulk, water added, and the
liquid filtered; the precipitate on the filter is washed and heated
with carbonate of soda on charcoal in what is termed the reducing
flame; a brittle button of metal is obtained, which may be further
examined on a fresh piece of charcoal: its colour is almost a pure
white; we therefore are led to believe in the absence of bismuth,
which has a pinkish tinge; but, to be certain, we heat it in the oxida-

ting flame; white fumes are given off, which, when condensed, have no tint of red or orange; we therefore conclude the absence of bismuth. The solution may now be examined: sulphuric acid is found to produce a precipitate; it is therefore added in excess, and the precipitate filtered off, washed and reduced in the same manner as the last; a malleable globule is obtained, conclusive of the presence of lead. In fact, the precipitation by sulphuric acid is sufficient, but it is always satisfactory to obtain the pure metals where it can be done so easily. The first globule of antimony may, moreover, be examined for tin or arsenic if necessary.

49. The above sketch is not given as the best mode of analysing the alloy alluded to, but merely as the first case that suggested itself, of a real experiment, where the agency of the blowpipe was made use of to obtain a rapid result. There are many metals whose reactions before the blowpipe are so marked that their presence may be ascertained almost instantly, while by the ordinary course of analysis, a long and troublesome series of operations are necessary before a decided answer can be given; among these may be mentioned manganese, arsenic, iron, chromium, cobalt, tin, titanium, and several others.

50. The first thing to be acquired in blowpipe practice, is the power of keeping up a continuous blast or current of air for some time; to effect this, the enlarged orifice of the instrument is to be placed between the lips, and the mouth filled with air until the cheeks become distended like a trumpeter's; it will soon be found, that, by making a motion with the tongue, somewhat like that which is done in uttering the syllable "tut," a fresh supply can be given as often as may be required; during this time the breathing is carried on by the nostrils.

51. The next step is to produce either the oxidizing or reducing flame at will; and by attending to the following instructions, the operator cannot fail to succeed after a little experience. The oxidation flame is generally considered easier to obtain than the reducing; we will therefore commence with a description of the method of producing it. The lamp being trimmed, so that the wick is parallel with the holder, and quite free from any strag-

gling fibres, is to be lit, and the wick so adjusted that the flame
may be clear and brilliant; if we now take a blowpipe with a
moderate-sized orifice, and hold it in such a position that the jet
shall be just inside the flame, and about the tenth of an inch
above the wick, the flame will not only be deflected, but consider-
ably altered in its characters; two parts being more especially
conspicuous, viz. an internal blue cone, and a yellow halo-like
flame at the end. It is in this exterior yellow part that the
power of oxidization resides; and, if a globule of tin about the
size of a mustard seed, be placed in it for a short time, it will
swell, and finally become converted into a white earthy-looking
matter, the peroxide of tin. If, on the contrary, we use an instru-
ment with the aperture rather less than in the last experiment,
and withdraw the jet a little, so that it may be on the outside
of the flame, and then blow rather powerfully, we shall find
that, although deflected, the flame is less altered in its general
characters than in the previous case, the chief part of it consist-
ing of a large and highly luminous cone, containing a consider-
able portion of strongly ignited carbon, precisely in the condition
most adapted for assimilating oxygen, and becoming converted
into carbonic acid; and if we expose to it, upon charcoal, the
cauliflower-looking mass of peroxide of tin which we obtained in
the first experiment, we shall find that the highly ignited carbon
will combine with its oxygen, and it will be reduced to the me-
tallic state. To reduce peroxide of tin on charcoal without the
assistance of a flux, is a test of moderate proficiency in the use of
the instrument.

52. *Supports for Substances before the Blowpipe.*—Having ac-
quired facility in the two operations which are in request every
time the blowpipe is used, we turn our attention to the supports
necessary when an assay is to be exposed to the flame. The three
substances most used for this purpose are charcoal, platinum,
and clay.

The first is generally resorted to when a deoxidizing power is re-
quired, although, in certain cases, it is admissible where oxidation
is to be effected; the two latter are employed if a substance is to

be brought to a higher state of oxidation, or is merely to be fused. Good pine charcoal is, perhaps, the best that can be used, but the laboratory charcoal-box generally contains pieces which by a little use of the saw may be made fit for blowpipe experiments. It must be remembered that the sides only should be used, and that pieces which have bark on them should be carefully avoided, as they emit showers of sparks which scintillate and fly about in a very annoying and even dangerous manner.

53. Platinum is used as a support in three different states, namely, as wire, foil, or small spoons. The first of these is re-presented in figs. 40 and 41, bent into the shapes in which it is

Fig. 36.   Fig. 37.

Fig. 38.   Fig. 39.

Fig. 40.

                           Fig. 41.
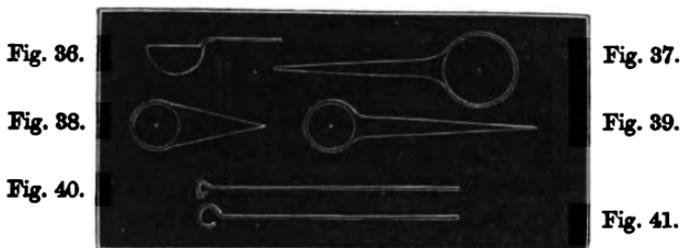
generally used to support a bead of borax or microcosmic salt to which a small portion of the assay is to be added. The whole is then to be exposed, first to the reducing and then to the oxidating flame; the changes of colour produced in this manner, generally afford a clue to the class of substances to which the assay belongs, and frequently enable us to pronounce with certainty as to the presence of one and sometimes several of its ingredients.

54. Platinum spoons are employed in blowpipe experiments, to contain mixtures of siliceous minerals and fluxes, where it is intended to bring a substance insoluble *per se* into a condition to be acted on by solvents in cases where the dry method alone is insufficient to enable us to ascertain with certainty the composition of the assay. They may be made of the sizes and shapes of those represented in figs. 36, 37, 38, and 39; the handle may either be held with a pair of pincers, during exposure to the flame, or be fixed in a support of wood with a hollow brass fe-

rule, through which a screw is passed to fix the platinum handle, as in fig. 42. It is likewise well adapted to hold the platinum

Fig. 42.
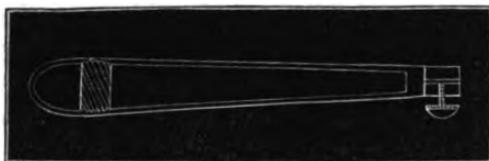
wires, and is made hollow in order to contain them when not in use. A very convenient support for platinum wires is the small ivory instrument used by ladies for containing and fixing crochet-hooks. It is much like the holder in the engraving, but differs in the arrangement by which the hooks are grasped.

There are a few precautions necessary to be observed in using platinum vessels, which may with propriety be introduced in this place. For instance, if a reducible metallic oxide be heated with any substance capable of removing its oxygen (as oxide of lead with charcoal powder, or other organic matter), or, if a reducible oxide be exposed on the platinum wire to the reducing flame, the support is almost certain to be destroyed; such substances must, therefore, be heated on charcoal or clay supports. When a bead has been fused in the loop of a platinum wire, it should not be removed by mechanical means, but the wire should be thrown into a small vessel of water until the bead is dissolved. An exception to this rule occurs when a bead fused in the loop of a platinum wire is observed to be coloured before addition of the assay; in such case the bead must be sharply heated; and then, if the wire be dexterously jerked against the anvil, or any other hard or steady substance, the melted mass will fly off, and must be replaced by a fresh portion until a colourless bead is obtained. Where a silicate has been fused in a platinum spoon, and it is wished to remove the mass, it is generally admissible to boil it with hydrochloric or nitric acid, but we must carefully avoid the presence of both together, or, in fact, of any substances capable of generating chlorine; as the vessel would be more or less attacked, and thus cause a twofold injury, namely,

damage to the vessel and, what is sometimes more serious, intro-
duce platinum into the analysis. Where a silicate has been fluxed
in a platinum spoon with any of the mixtures to be found in
analytical manuals, and difficulty is found in extracting the fused
mass, the spoon should be suspended by a platinum wire near
the top of a glass of water, and left for a few hours; it may then,
in most cases, be removed without difficulty. If this procedure
is insufficient, acids must be resorted to.

55. *Platinum foil.*—Platinum, in the state of thin sheets, is
much less useful in blowpipe experiments than either spoons or
wire; nevertheless, it may sometimes be employed with advantage,
as in testing for manganese by fusion of the assay with soda,
with or without the addition of nitre, according as the metal is
more or less plentiful in the specimen.

In organic chemistry, platinum foil has many uses, especially
for supporting salts, &c. in the flame of a lamp during combus-
tion, in order to ascertain the presence of inorganic substances.
It is also used to form the platinum trays used in organic analysis
in the process by oxygen gas, to be alluded to further on. In
cases where a platinum crucible is not at hand, an extempore one
may be constructed, by folding a piece of the foil in the same
manner as for a filter. The electro-negative element of Grove's
battery is constructed of this metal in foil, and it usually forms
the electrodes of batteries used in the decomposition of liquids, &c.

56. *Clay Supports.*—An excellent method of forming small
basins and crucibles will be found in Plattner's treatise; it will
be unnecessary, therefore, to describe it here; moreover, basins
of extreme thinness, and in every way adapted for blowpipe
experiments, are now imported from the Continent, and may be
procured of the instrument-makers.

57. *Forceps.*—A pair of platinum-pointed forceps is indispen-

Fig. 43.
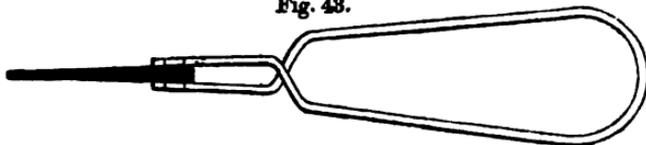
Fig. 45.
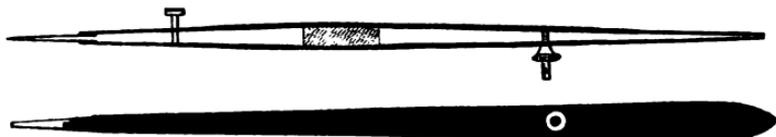
Fig. 44.

sable to the blowpipist; they are made of the various kinds represented in the woodcuts.   The first, fig. 43, is merely steel wire bent in the form depicted, and having small beaks of platinum riveted on.   The second form is more expensive, but far more convenient and strong; they are those usually used, and are made to open by pressing the knobs.   Another pair, the invention of Mr. S. Highley, Jun., seen in section and plane, fig. 45, resembles the first, save that it only possesses one knob.

58. There are many other instruments used in blowpipe analysis, some of which will be found in their places among the apparatus used in the humid method; the greater part are chiefly intended for quantitative blowpipe operations, a method of research very little practised in this country, and not having sufficient advantages over the usual methods to be likely to supersede them.

59. *Self-acting Blowpipes.* — The principle upon which most of these instruments are constructed, is that of directing a jet of vapour of alcohol or wood-spirit through a flame, which latter is generally that which heats the spirit.   In order to fulfil these conditions the vessels figured on the next page are employed; the first (fig. 46), generally known as the Russian blast-lamp, consists of a double case, *a a,* to hold spirit; on one side of the interior is fastened a tube reaching nearly to the top, and bent at the bottom, where it passes out of the double case and rises about half an inch above the bottom of the inner chamber; its end should have a

blowpipe-nozzle attached to it; *d* is an aperture to introduce spirit into the double case, which should not be filled to more than two-thirds of its capacity, otherwise a portion is liable to find its way into the exit-pipe during the time the lamp is being used, by which means a jet of ignited spirit is ejected, which may cause much inconvenience. It has a handle to facilitate its re-

Fig. 46.

moval from place to place. During use, *d* is closed moderately tight with a cork, which acts as a safety-valve; if, therefore, the jet becomes choked, the cork is blown out and prevents the destruction of the lamp, which might be attended with serious consequences. When required to be used, spirit is, as we have said, introduced into *a a*, and a certain portion is placed in the inner chamber, *b*, so as to cover the bottom to the depth of half an inch. If the last-mentioned spirit is now ignited, that in the chamber *a a*, will soon enter into ebullition, and a stream of vapour will make its exit from *c*, and, immediately igniting, forms a powerful jet of flame capable of heating large platinum vessels to a brilliant red heat; the flame is, moreover, adapted for heating the German glass in making combustion-tubes, when no other form of blowpipe is at hand. The mode of using the second contrivance (fig. 47) is almost obvious from the figure: a hollow globe, *a*, half-filled with spirit, having a blowpipe, *b*, attached, is fixed above a lamp, *c*, opposite the wick of which the exit of the pipe is placed. On lighting the lamp, almost the same phenomena occur as in the Russian instrument. A cork safety-valve is inserted
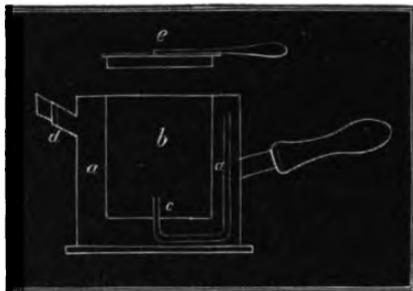
Fig. 47.

at *d*, the screw-cap being previously removed. When placed in circumstances in which a blast-lamp was not at hand, I found the

following a useful and powerful substitute. The body of the lamp is formed out of a tin bottle, and a hole pierced in the side has a small tube soldered in, to act, when fitted with a cork, as a safety-valve and a place to insert the spirit. A jeweller's blowpipe is cut in half, and the bent portion inserted vertically in the neck of the bottle, the nozzle of a Black's blowpipe being fixed at the aperture. It may be supported above a gas-burner or oil-lamp. A portion of lamp-cotton is placed in an evaporating basin, and held in its position by a bent wire, and the basin being filled with olive-oil, and the wick adjusted to the aperture, we have an apparatus simple in the extreme, and not easily surpassed in power: combustion-tubes may be easily prepared at such a lamp in a very short time, even when of large calibre and made of the most refractory glass.

60. *Table Blowpipes.*—Any laboratory where experiments are carried on with even moderate activity, must possess one of these pieces of apparatus. So many instruments of different kinds are constantly being made from glass, that no one who has ever had one at his command will willingly dispense with its services. One of the most convenient of these is the blowpipe contrived by Herapath; it is represented in fig. 48, where *a* is a flexible tube attached to a stopcock, *b*, which communicates with a tube, *c d*, bent at right angles at *d*, where a T-shaped tube, *e f g*, slips on by means of the piece *f*. The blowpipe jet, *h i*, passes into the longer arm of the T-piece, and fits somewhat tightly; *k l* is a second piece of flexible piping terminating in a mouthpiece. On turning on the gas, it passes in the direction marked by the arrows, and is to be inflamed at *e*. On blowing with the mouth, or by means of a pair of bellows, into the flexible tube, *k l*, the ignited gas takes the form of a blowpipe flame of great power, the nature of which is entirely under control by means of the stopcock, *b*, and also by regulating the quantity of air thrown in from the lungs or bellows. As the T-shaped piece is freely moveable at *f*, the jet may be directed to any position, and the apparatus becomes well adapted for the ignition of platinum crucibles, &c.[*]

[*] I have had one of these (made by Mr. E. G. Wood, of Cheapside, Lon-

It is mounted on a heavy foot, and being connected with the gas

Fig. 48.
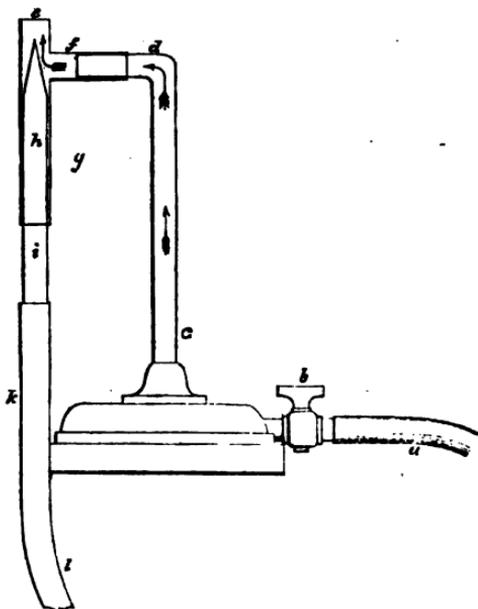
supply by means of the flexible tube, *a*, it may be readily adjusted upon the laboratory table.

Blowpipes of other kinds are also procurable at the instrument makers, worked by bellows set in motion by the foot; the aperture for the exit of the air should end in a tube of about a quarter of an inch in diameter, to allow of jets formed from glass tube being adapted to it. They are accompanied by a gas-jet of rather peculiar form, intended to supersede the necessity of an oil-lamp. The water-pressure blowpipes of Tilley or Toft are also very effectual; they may be procured, with directions for use, from the makers of chemical instruments.

don) in use for some time, and have found it to answer so well, that I prefer it to any other I have yet used, excepting the bellows blowpipe, with the water-pressure arrangement.

SECTION V.

BATHS.

61. There are numerous instances, in almost every department of chemistry, where it is necessary to apply heat, but in a gradual and gentle manner; in all these cases it is advantageous to be aware of the actual temperature of the exsiccating medium. In fact, by the skilful use of a few very simple instruments, we have it in our power to apply any heat, from that which is scarcely perceptible to the hand, to a bright red. There are many substances which it is necessary to obtain in a dry state, but which are decomposed by the slightest elevation of temperature: instances of this kind will be noticed in the section on Operations preparatory to Weighing. Where the application of a very gentle and uniform heat is necessary, as sometimes happens in certain researches, we use ether or alcohol, or their vapour at the boiling-point, under ordinary pressure, as the medium of communication. Under such circumstances, an apparatus like that in the margin may be used, the shape, size, and arrangement, varying according to the nature of the operation.

Fig. 49 represents a glass or metal vessel to contain the spirit, provided with a tube-funnel, by which to add more if required. The exit-pipe for the vapour of the spirit leads to a vessel of cold water containing ice, where, being condensed, it returns to the chamber to be cohobated again and again. A small test-tube is represented as converted into a retort, and containing the substances to be distilled. Heat may be applied by means of a lamp.

Fig. 49.

Water-baths are made in several different ways, some of porcelain, others of metal. Fig. 50 is simply a hemispherical cup of porcelain or earthenware, with another

having flanged edges hang-
ing within it. Fig. 51 is a
filter-drier, of porcelain,
made in one piece; it has
an aperture which serves
the threefold purpose of a
handle, a place to insert the

Fig. 50.   Fig. 51.

water, and an exit for the steam. Fig. 50 may be made of
metal, preferably copper, having a number of concentric rings of
different diameters, to adapt it to various-sized dishes. The rings
are socketed in the same manner as the furnace-rings represented
in section in fig. 2, only, of course, very much thinner. Fig. 52
is a bath, or rather hot-air chamber, of very different construction;
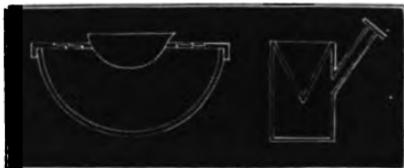
it consists of a double box of
copper, the water being con-
tained between the two. The
latter is inserted through
an aperture provided for the
purpose.   The other hole is
intended to enable the ope-
rator to keep a thermometer
inside the bath, to indicate
the temperature. The chim-
ney on the right serves to
create a draught. The sub-
stances to be dried are placed
in capsules, supported on

Fig. 52.

shelves placed within the chamber.   By keeping a small piece of
tube in the aperture by which the water is introduced, and reach-
ing to the bottom of the double chamber, we may always ascertain
the depth of water, by closing it with the finger after it has been
plunged in, and then withdrawing it, somewhat in the manner of
a wine-taster; the height of the water in the tube of course cor-
responds to that in the chamber.
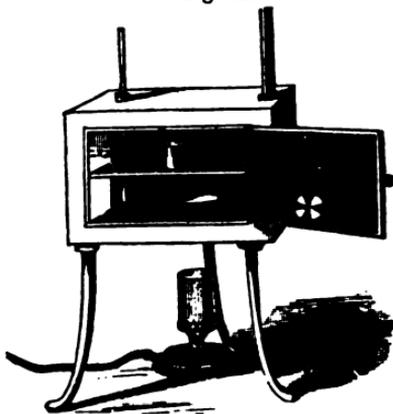
All these water-baths may be heated by placing them upon a
tripod or retort-stand over a lamp. Those of porcelain require

more care than the others, and are preferably heated on the sand-bath. When it is required to expose substances to a temperature above 212°, but still below a red heat, the bath may be filled with linseed oil, or a solution of the chlorides of calcium or zinc: the retort or flask to be heated, should be immersed in the fluid to about two-thirds its depth. For temperatures above that at which oil or the saline bath alluded to can be conveniently used, fusible metal is sometimes, though rarely, employed; in general, it is much more convenient to employ a hot-air bath, such as will be found in the section on Distillation. Moreover, the heat of the latter can, by management of the fire, be rapidly raised or lowered; but the fusible metal requires a considerable time to fall even a few degrees; and is inconvenient, from the rapidity with which oxide is formed at high temperatures; and if it be attempted to prevent this by a layer of grease, the odour becomes so disgusting when it approaches the decomposing point, that it forms a serious objection to its use. The same inconvenience is found in oil-baths, unless care be taken to prevent the heat rising too high. It is sometimes advisable, where a water-bath is to be raised to 212° rapidly, to have a thin layer of oil upon the water, to retard evaporation; and, of course, the heat rises more rapidly than it would without this precaution. Where a given fixed temperature is required, the heat must be regulated by keeping a thermometer immersed either in the bath, or perhaps preferably in the retort, or other vessel in which the liquid under examination is contained. When it is intended to use steam as the heating agent, the apparatus figured in the margin (fig. 53), contrived by Dr. Ure, may be conveniently employed. Its construction is obvious: the apertures are intended to hold flasks, capsules, or other vessels to be exposed to the heat.

Fig. 53.

It will be seen that, from the steam-chamber being placed above the boiler, the condensed water is raised over and over again.

Fig. 54.

A water- or steam-bath may at any time be constructed in the laboratory, by placing one capsule over another, the lower one being partly filled with water, fig. 54.   Fig. 55 represents a very convenient water-bath for many purposes.   It consists of a rectangular tin-plate or copper box, somewhat hollowed up in the spot where the lamp a is stationed.   It is provided with six apertures, which may be covered,

Fig. 55.
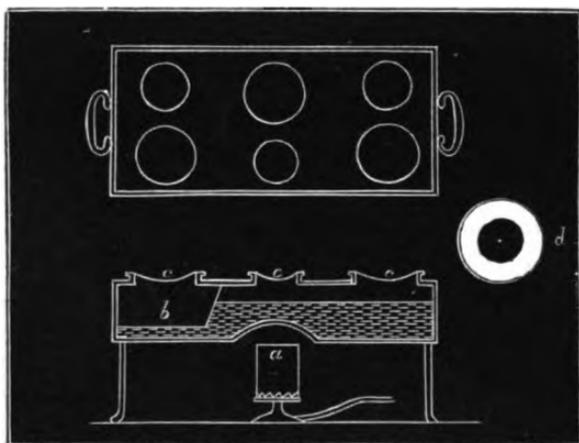
if necessary, by pieces of metal plate, or watch-glasses; or evaporating basins may be placed over them.   These apertures are represented in the section at $c\,c\,c$; metal plates, d, provided with apertures of different sizes, may be used to contract the holes if required.   One of the openings communicates with the box, b, intended to contain preparations for desiccation.   The apparatus is neat, but less convenient for laboratory use than the square chamber-bath, fig. 52.   In all these arrangements, of course care must be taken that the bath does not boil dry.

In using baths for various operations, it is often advantageous to be enabled to employ a fluid of known boiling-point, and, for this purpose, the following Table will be found useful:—

TABLE OF BOILING-POINTS OF SATURATED SOLUTIONS OF VARIOUS SALTS.

	Boiling-point.
Chloride of calcium	355° Fahr.
Acetate of soda	256 ,,
Nitrate of soda	246 ,,
Sal-ammoniac	236 ,,
Common salt	224 ,,
Cream of tartar	214 ,,

62. It will be seen that, in the above Table, solutions have been selected which, with the exception of the first, give boiling-points, as nearly as could be obtained, 10° above each other; and, as a certain amount of heat is always lost before it reaches the contents of the vessel immersed in the bath, it is an advantage to select fluids, the boiling-points of which increase in a ratio a little more than the 10°, as more than the difference will be lost from the reason stated. The above solutions have been chosen, because, in fractionating volatile substances, it is usual to separate the products by differences of temperature equal to 10° Fahr.

Fig. 56.

It will be proper in this place to describe the ingenious device of Mr. Kemp for enabling the flame of a gas-burner to be so regulated as to allow of a constant temperature being maintained for any length of time. A glass tube, *a b c*, fig. 56, formed into a reservoir at *c*, is partly filled with mercury, the rest being occupied by air. A brass piece, *d e f*, is cemented at the top. This latter consists of a stuffing-box, *d*, through which the tube, *f*, descends, and is capable of motion up and down. The gas enters by *e*, and to reach the burner has to

D
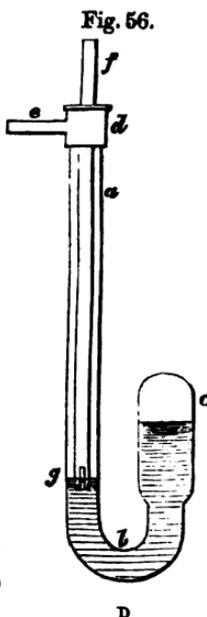
pass down the glass tube, up the brass pipe, and out of the flexible pipe which connects the apparatus with the gas-lamp. The bulb, c, is to be immersed in the fluid of the bath to be heated, and the tube, f, is to be so adjusted in the mercury, that a slit which is made in it at g just allows sufficient gas to pass to keep the bath at the required temperature. If now the gas should, from the other lights in its vicinity being extinguished, or other causes, flow faster than before, and cause a larger flame, the air in the reservoir, c, expands, and elevating the mercury in the tube, decreases the aperture by which the gas reaches the burner. The instrument is therefore on the principle of the air-thermometer. To allow of complete contact between the end, g, and the mercury, the brass at the extremity is platinized.

This apparatus has been used for some time in the laboratory of the University of Glasgow, in various researches, particularly in investigating the action of nitric acid on narcotine[*], and it has been found to answer perfectly.

* Transactions of the Royal Society of Edinburgh, vol. xx. part 3. p. 359.

SECTION VI.

HEAT MEASURERS.

THERMOMETERS. PYROMETERS.

63. In chemical research there are few things of more import-
ance than the accurate measurement of temperatures; in fact,
when we consider that the theories of chemistry, as now received,
more especially the organic part, are, to a great extent, founded on
the relations of substances to heat, we shall see that one of the
most important things to a chemist is the unimpeachable accuracy
of his thermometers. The laws of expansion of gases, by which
we calculate the results of experiments on the specific gravity of
vapours, the theory of the rise of boiling-point in liquids as the
carbon atoms increase, and lowering of the same by the addition
of hydrogen, facts which promise to have the most important
bearings upon all the ramifications of chemical philosophy, are
entirely dependent for their experimental verification on the cor-
rectness of our means of measuring minute variations of tempe-
rature. Moreover, the actual practice of ordinary chemistry shows
frequent instances of the importance of an intimate acquaintance
with the manipulations connected with heat-measurers. Fractional
distillation is sometimes the only means we have of separating
substances from each other; and it is also possible, in some in-
stances, to effect a more or less perfect disjunction of bodies having
different points of volatility, by keeping the mixture at a steady
temperature, by which means we may expel the more volatile, and
thus obtain both in a state of comparative purity. In the section
on Distillation, we shall notice some points of this kind.

64. To construct a thermometer of even moderate approxima-
tion to accuracy, is a matter of far more difficulty than would be
supposed from the directions to be found in some works on this
subject. The difficulties alluded to are almost entirely of a prac-
tical description, and relate to peculiarities in the details of the

D 2

process which would not suggest themselves to many persons. It is therefore strongly advised that the student should not attempt the construction of these instruments, even if he has obtained considerable proficiency in glass-blowing, it being quite unnecessary in an economical point of view, as it is possible to obtain excellent instruments at comparatively moderate prices. Nevertheless, as in a work on Manipulation it would be improper to omit a short description of the method adopted in the construction of these useful adjuncts to the student's labours, the following brief outline will be found to give an idea of the nature of the process.

65. In the first place, we must decide whether to select a tube of perfect equality, or to content ourselves with an imperfect tube, making allowance for the variations in the calibre in a subsequent stage of the proceedings. It has been said by an eminent philosophical instrument maker, that a perfect tube is never to be found; such, however, is not the case, and those whose chief occupation is the construction of thermometers, and who, consequently, have always at hand a very large stock of tubes to select from, are frequently able to cut from a long tube, a portion sufficient for the construction of an instrument so nearly perfect, that no error can be made evident even by the most carefully applied tests.

66. The best method of ascertaining the fitness of a tube for the construction of a thermometer according to the first method, is to draw a small quantity of mercury, say 1 inch, into it and measure it at different intervals; this is easily effected by moving the tube in such a manner as to cause the mercury to pass slowly down; if it measures exactly the same at several points, both at the ends and middle, it is, of course, evident that the bore is equal. The operation of calibrating the tube may be facilitated by the use of the thermometer-gauge; it consists of a syringe, the piston-rod of which is formed from a fine screw, so that by turning the milled head at the top, it may be made to descend, or ascend, in the cylinder, which is filled with mercury. On connecting the instrument by a caoutchouc joint with the

thermometer-tube, so as to be quite air-tight, we have it in our power to inject a small or large portion of mercury at will; and, by a very little management, it may be separated into a column of any length, and be moved with facility to every part of the tube. It is scarcely necessary to caution the operator against handling the tube during this operation in such a manner as to cause the mercury to expand from the warmth communicated by the contact of the fingers.

67. In the next place, we must consider that if it is intended to construct an instrument with a very open scale, or, in other words, one which is to be greatly affected by comparatively small variations of temperature, a different proportion between the dimensions of the tube and the bulb will be necessary, than if the reverse is required. In the first case, we have a very large bulb and an exceedingly small bore, and, in the other, the bulb is made smaller, and a tube is selected of larger calibre. It is advisable to form the bulb into a cylinder instead of a globe, if it be intended to introduce it into retorts. To insert the mercury, the bulb is to be moderately heated to expand the air, and the open end of the tube is plunged under the surface of the metal; as the air cools and contracts, a portion enters the tube and bulb, and is then to be boiled rapidly, the tube being kept hot, and this is continued until the bulb and tube are filled with vapour; upon again plunging the open end into the metal and letting the whole cool, the vapour is condensed, and the instrument becomes filled with the fluid. It must now be considered upon which portion of the tube it is wished that any given point of the scale should fall: supposing, for instance, that it is desired the freezing-point should be about 1 inch from the bulb, and the boiling-point about the same distance from the other end, the instrument is plunged first into melting ice, and if, after it has attained the temperature of the medium, the mercury is found to occupy too high a point upon the scale, a portion is expelled by warming, but if it falls too low, some more is introduced by the same process as before; the operation is then repeated, substituting boiling water for the ice, and the point where the mercury rises to is observed; when

this is done, the flame of the lamp is directed about an inch above the spot to which the mercury rose at 212°; the glass is then drawn out until capillary, and the next point is to expel the air in the tube, that in the bulb having been already got rid of in the first part of the operation. The bulb is to be warmed until the mercurial column ascends, passing through the capillary into the piece of thermometer drawn out; by this procedure the mercury is made to fill the place previously occupied by the air; at this step of the proceedings the flame is directed upon the capillary tube, which is closed and removed.

Before fashioning the end into the knob or ring which is always seen upon the instruments (according as it is to be fixed in a wooden scale, or be graduated upon the stem), it is necessary to examine it carefully to ascertain the entire absence of air from the bulb and tube, which may be done as follows :—invert the instrument so that the bulb is uppermost; if the mercury descends with ease quite to the end we may be sure that air is absent, but it may nevertheless be in the bulb; to ascertain this, we must observe whether the vacuum bubble, which enters the bulb when the instrument is inverted, entirely vanishes from it upon restoring the tube to its proper position; if it does so, we may conclude that, in that respect, the instrument is perfect; if not, the fine point left upon drawing off the capillary-tube must be broken, and the operations previously described repeated, until the result required be obtained.

68. Sometimes a thermometer, when inverted, does not allow the mercury to descend, and inexperienced persons are liable to imagine that air must necessarily be present; but the effect alluded to is frequently caused by the adhesion between the mercury and the glass; if, however, we warm the bulb so as to cause the mercury to ascend in the tube and then invert the instrument, the metal should descend; and if no moderate tapping or swinging will make it do so, we may safely conclude that air forms the impediment. Supposing, however, all these trials to have yielded satisfactory results, we may proceed to lay off the scale, which is usually effected by plunging the instrument first into melting ice,

and then, after the temperature of the bath is attained, marking the position of the mercury upon the tube; we now place it an inch from the bottom of a deep metallic vessel nearly filled with water, and heat until rapid ebullition ensues, care being taken that the barometer is at, or very near, the standard height, otherwise a correction must be made; in this manner another point upon the stem is formed, and from these two points all the others are obtained. Fahrenheit's scale being, if not the most philosophical, at all events the standard generally adopted in England, it is usual to divide the space between the two points mentioned into 180 equal parts or degrees, and, if the calibre of the tube be perfect, the gradations may be continued upwards and downwards as far as may be desired. For all purposes of ordinary research, it may be assumed that the expansion of mercury is equal for equal increments of temperature; we need not therefore make the degrees above $212°$ of a different value to the others*.

69. The directions given for the construction of a thermometer will also enable the student to examine the accuracy of any that he may purchase; it must be remembered, therefore, that the examination resolves itself into the following operations, viz. measuring a column of mercury at different intervals along the tube to ascertain the equality of the bore, ascertaining that the degrees on the scale are equal in value by measurement of the number of degrees included between any given distance with a pair of compasses, and taking the freezing- and boiling-points,— not forgetting that a difference of 1 inch of mercury in the height of the barometer raises or lowers the ebullition point by almost exactly two degrees Fahr.†,—and, finally, testing the instrument as to the presence of air by the methods already given.

70. In chemical investigations, the most generally useful thermometer is one capable of being introduced into the tubulature of a retort, the bulb being, with this intent, made narrow and

* The increasing dilatation of the mercury, as the heat becomes greater, is nearly compensated for by the expansion of the bulb.

† For Table of boiling-points of water at different pressures, see end of the volume.

cylindrical, and the graduations directly engraved on the stem, as
in fig. 57. The first thermometers made on this plan
had, however, the disadvantage of preventing the posi-
tion of the metal being observed by reflected light
without considerable difficulty. It was usual, there-
fore, to keep a piece of paper behind it to facilitate the
reading. Mr. Negretti has, however, entirely obviated
the necessity for this, by having his tube made with a
portion of white enamel down the back, so that the
mercury is always distinctly seen. Those instruments
which consist of two parts, being a thermometer with
a paper scale placed inside a tube, are worse than use-
less; in the first place, although so bulky as to be
impossible to be introduced into the tubulature of a
small retort, they are infinitely more fragile than the
far more slender ones engraved on the tube; in the next
place, the paper scales contract by exposure of the in-
strument to even moderately high temperatures, caus-
ing, of course, considerable error from this alone; and
when, as in some instruments I have seen, the scale is
fixed in its place by sealing-wax, it is of course impos-
sible to use it with any degree of safety.

Fig. 57.

Thermometers attached to wooden or ivory scales are
equally inconvenient with those last described; in most
chemical experiments, especially where accuracy is in-
dispensable, even if the wood is jointed near the bottom,
and has a hinge so placed as to permit it to be folded
back to enable the bulb and part of the stem to be immersed in
fluids, still the wood is liable to contract and warp, owing to
its being exposed to considerable changes of temperature and
variations in moisture.

71. No mercurial thermometer should be used for temperatures
higher than 580° Fahr., above that point there being danger of
the mercury boiling in the tube, as, from being *in vacuo*, the point
of ebullition is lowered considerably.

Care must be taken, where the temperature of a fluid is to

be observed, that sufficient time is allowed for the bulb and the mercury contained in it to acquire the same degree of heat as the medium. And this is especially necessary with gases, where, from their small conducting power, the time required is much greater.

72. In all experiments upon the volume of gases the accurate determination of temperature is of the last importance, from the great degree in which their bulk is influenced by the expansion, the coefficient of expansion of air for each degree Centigrade being 0·00367*.

73. All laboratories where chemical researches are undertaken, should be provided with several thermometers; one or two should have a range from zero to about 580° Fahr.; a very small one should also be at hand, capable of being introduced into a specific gravity bottle, to indicate the temperature of the fluid under examination. The same thermometer, if very accurate, may be used for gas experiments; but it is better to have one with a very large bulb and an exceedingly fine tube, so as to show readily minute differences.

74. It will be quite unnecessary to describe all the varieties of thermometers in use in the various departments of science, the more especially as the investigations in which they are used are more of a physical than chemical nature; there are, however, some, which, from the fact that the chemical characters of substances are sometimes dependent upon their indications, fall to a certain extent within the plan of this work; in the list are found the Differential Thermometer, the Thermo-electric Multiplier, the Self-registering Thermometer, the Air-thermometer, and the Pyrometer.

75. It sometimes happens in physical investigations that it is wished to ascertain whether a given phenomenon is capable of producing heat or cold under circumstances in which the ordinary thermometer is inadmissible; when it is merely desired to know whether a difference of temperature exists or is occasioned by the

* For Table of expansion of gases by heat, see end of volume.

phenomenon under examination, the instrument figured in the margin, and first used by Leslie in his experiments on heat, may be used. It consists of two balls (fig. 58) contain-

Fig. 58.

ing air and sufficient coloured oil of vitriol to fill two of the three limbs of the tube; when in the normal state, the liquid stands at the same height in both of the upright limbs, but when *one* of the bulbs is placed in a position where it is expected to find a disturbance of the thermal equilibrium, any change is instantly indicated by the motion of the fluid; if the temperature falls, the air in the bulb contracts its volume and the liquid rises in the tube; but if, on the other hand, heat is developed, an expansion takes place and the fluid recedes. An arbitrary scale is usually attached to the limb, but the amount of disturbance generally gives a sufficient idea of the degree of heat or cold developed; when, however, a scale is used, it may, if necessary, be converted into one of known value by comparison with a mercurial thermometer.
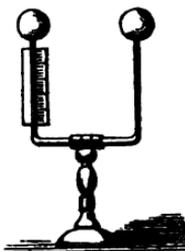
76. The Thermo-electric Multiplier of Melloni is an instrument intended to measure excessively small thermal differences by the amount of electricity developed in a number of bars of antimony and bismuth arranged in a series; the degree of excitement being indicated by the degree of angular motion of the astatic needle of a galvanometer.

77. The Self-registering Thermometer of Negretti and Zambra is an ingenious contrivance intended to facilitate the working out of meteorological observations, and is also used in techno-chemical processes for ascertaining the maximum temperature to which drying closets, &c. have arrived during the night, or any time when actual inspection of an ordinary thermometer placed inside is impossible. It is well known that the old instruments for this purpose contained in the tube, which was bent at right angles at a short distance from the bulb, small rods of steel or enamel, which being propelled forwards, as the mercury or spirit advanced, were left behind as it receded, and consequently indicated the maximum

temperature; but in the instrument now under consideration, the tube, which is bent as in the old ones, has a small piece of glass inserted a short distance from the bulb, which allows the mercury to pass it while expanding; but when contraction takes place, the metal is prevented by the impediment from returning to its normal position.   When it is required to return the mercury to the bulb for the purpose of making a fresh observation, the end furthest from the bend is to be elevated, and the instrument is slightly agitated; by this means the metal repasses the obstruction and indicates the temperature at that time.

78. The Pyrometer of Daniell is an ingenious but comparatively seldom-used instrument, intended to effect the measurement of high temperatures, such as that of furnaces, by the expansion of a bar of platinum; the old plan of Wedgwood, which endeavoured to effect the same object by measuring the contraction that wedge-shaped pieces of clay underwent by exposure to heat, was liable to so many objections, that it became absolutely necessary to devise some plan by which high temperatures could be ascertained with precision; but, while the instrument of Daniell effects the object with greater accuracy than perhaps any other, its use is very limited, it being seldom necessary, in the present state of chemical investigation, to require for guidance anything more than is contained in the expressions dull red, bright red, yellow and white heats.   It is undoubtedly true, that, as the science advances, more attention to the regulation of temperature will be required, as even now there are many instances known to chemists, where the same substances acting on each other at different temperatures produce very different compounds by their mutual reaction; and it is more than probable, that by greater attention to the modulation of temperature, the intensely interesting but highly complex groups of substances produced during the destructive distillation of animal and vegetable matters might be much better understood. As a general rule, it may be asserted that the higher the temperature the simpler the constitution of the substances formed, the more complex groups breaking up under the influence of strong heat into substances whose formulas contain a less number of

atoms, and those arranged in a manner which enables their rela-
tion to each other to be more clearly seen.

79. It fortunately happens that those methods of investigation
in which the exact measure of temperature is necessary, seldom
require a heat sufficiently intense to soften glass; when, therefore,
the limits of the mercurial thermometer are passed, it is possible
to have recourse to the air-thermometer, in which the values
sought are obtained by the expansion of a known volume of air:
this method is used chiefly in ascertaining the specific gravities of
the vapours of the less volatile substances, and from the nature
of the operation and the corrections required (the result of the air-
thermometer being influenced not only by temperature, but also
by the variations in the atmospheric pressure), the process is one
requiring a little care in manipulation.

80. For the more modern and accurate data and researches
upon this subject, chemists are chiefly indebted to the labours of
M. Regnault; and as the process is every day becoming more in-
dispensable, we shall quote the following description of the appa-
ratus and method of procedure*.

81. "The air-thermometer used in these experiments consists
of a simple cylindrical glass reservoir of about 2 centimetres in
diameter and 12 or 15 centimetres in length, and terminating by
a capillary tube, of which the calibre is 1 or 2 millimetres, and
which is bent to a right angle and drawn out at its end.   The
reservoir, a b, is kept in the bath alongside of the balloon in which
the vapour is to be generated.   The first step is to perfectly dry
the reservoir, a b, by creating a vacuum in it several times, and
allowing air to enter which has been dried by passing through a
tube filled with pumice-stone soaked in concentrated sulphuric
acid; after which the bath is heated, and when the temperature

* Regnault, Cours Élémentaire de Chimie, tome quatrième, p. 63. I have,
however, taken the engraving from the plates in the Mémoires de l'Acadé-
mie Royale des Sciences de l'Institut de France, tome xxi., merely alter-
ing the lettering to suit the text. I have also, in a note, given the co-effi-
cients of expansion of glass from a different part of the same work, and
inserted the meaning of the letters used in the formulæ, in order to make
the quotation intelligible. The degrees apply to the centigrade thermometer.

becomes stationary at the point at which the experiment is to be
terminated, the point of the balloon and that of the air-thermo-
meter are closed simultaneously by means of a lamp.

82. "The air-reservoir is then placed on the metallic support
represented in fig. 59, the stem passing through a cork which

Fig. 59.
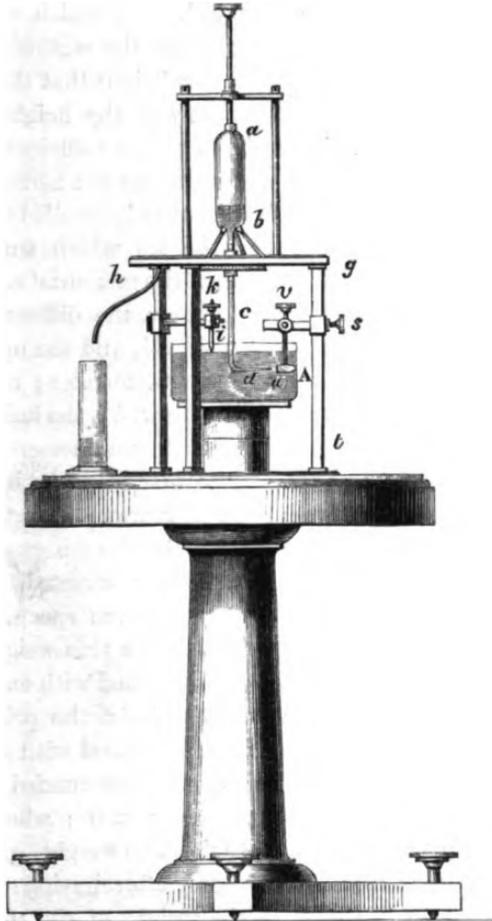
closes a tubulure made in the centre of the disk $g\ h$, while the

curved point, cd, enters a small mercurial bath. The extremity of the point being broken by pincers, the mercury rises in the tube and partly fills the reservoir ab, which is surrounded with pounded ice, in order to reduce the temperature of the air it contains to $0°$, when the open point is closed with a ball of soft wax. In order to perform this operation easily, without changing the level of the mercury in the vessel A, a small iron spoon, u, is used, soldered to an iron rod, uv, which slides along a horizontal bar vs, itself moveable along the vertical foot st; the moveable rod, vs, being fixed at such a height that the bowl of the spoon, filled with soft wax, is exactly at the height and in the direction of the point d. It is therefore sufficient, in order to close the point, to slide the end, uv, along the horizontal rod, vs. The mercury in the vessel, A, is then exactly levelled to the point, i, of a double-pointed screw, ki; the ice which surrounded the reservoir, ab, is removed, and, when the mercurial column attains the temperature of the surrounding air, the difference of height between the mercury in the reservoir, ab, and the upper point, k, is exactly measured by means of a cathetometer; and by adding to this difference the length of the screw, ki, the height, h, of the column of mercury elevated in the air-thermometer is obtained. Let h_o be this height at $0°$, H_o the height of the barometer also at $0°$, when the point, d, is closed with wax; then will $(H_o - h_o)$ represent the elastic force of the air in the reservoir, ab, at the temperature of $0°$. The support is then inverted, the air-thermometer removed, after having detached the spoon, u, and it is weighed with the mercury contained: let this weight be represented by Q. The thermometer is then filled with mercury, which is boiled to drive off the last bubbles of air, the point, cd, being kept during this time in a small capsule filled with mercury.

"When the apparatus is cooled, it is surrounded with melting ice, and completely filled with mercury at $0°$; when it is again weighed, giving now the weight Q'. The weight, q, of the envelope of glass alone being ascertained, after having emptied it of mercury, $(Q' - q)$ is therefore the weight of the mercury at $0°$, and $(Q - q)$ is the weight of the mercury in the thermometer when

it was on the support; $Q'-Q$ therefore represents the weight of the mercury at $0°$, which occupies the same volume as the air remaining in the thermometer when it is at $0°$, and under the pressure (H_o-h_o). If we designate by δ the density of the mercury at $0°$, $\dfrac{Q'-q}{\delta}$ represents the capacity in cubic centimetres of the thermometer, and $\dfrac{Q'-Q}{\delta}$ the volume which the air occupies in this apparatus at the moment of closing the point, d, with wax.

Now the capacity of the thermometer, at the temperature T, being $\dfrac{Q'-q}{\delta}(1+k\mathrm{T})$*, the volume of air $\dfrac{Q'-Q}{\delta}$ at $0°$, and under the pressure (H_o-h_o), therefore occupies, when it is raised to the temperature T and under the pressure H'_o, a volume $\dfrac{Q'-q}{\delta}(1+k\mathrm{T})$. The volume assumed by a volume of air $\dfrac{Q'-Q}{\delta}$ at $0°$ and under the pressure (H_o-h_o), when raised to the temperature T and under the pressure H'_o†, may be calculated, by the known laws of the expansion of air, under changes of temperature and pressure; and is thus found to be

$$\frac{Q'-Q}{\delta}(1+0.00367.\mathrm{T})\frac{H_o-h_o}{H'_o},$$

which leads to the equation

$$\frac{Q'-Q}{\delta}(1+0.00367.\mathrm{T})\frac{H_o-h_o}{H'_o}=\frac{Q'-q}{\delta}(1+k\,\mathrm{T}),$$

whence
$$\frac{1+k\,\mathrm{T}}{1+0.00367.\mathrm{T}}=\frac{Q'-Q}{Q'-q}\cdot\frac{H_o-h_o}{H'_o}.$$

* $k=$coefficient of expansion of glass. The following are the values of k.

Between $0°$ and $100°$	$k=$	0.0000276
,, 150		0.0000284
,, 200		0.0000291
,, 250		0.0000298
,, 300		0.0000306
,, 350		0.0000313

The above values are for the ordinary glass of which the balloons used in Parisian laboratories are made.

† H'_o = height of barometer at time of sealing.

T may be deduced from this equation, but there is no necessity of knowing its value in order to calculate the density of the vapour, which is in fact represented by the expression[*].

$$\frac{P'-P+p}{0\cdot0012932 \cdot V \cdot \dfrac{1+kT}{1+0\cdot00367 \cdot T} \cdot \dfrac{H'_o}{760}}.$$

Substituting for $\dfrac{1+kT}{1+0.00367 \cdot T}$ the value first found, there results for the expression of the density of the vapour,

$$\frac{P'-P+p}{0\cdot0012932 \cdot V \cdot \dfrac{Q'-Q}{Q'} \cdot \dfrac{q}{q} \cdot \dfrac{H_o-h_o}{760}}.\text{,,}$$

[*] P = Weight of balloon and air.
  P' = Weight of balloon and vapour.
  p = Weight of V centimetres of air at t.
  V = Capacity of balloon in centimetres cub.
  T = Temperature of vapour.
  t = Temperature of air.—C. G. W.

SECTION VII.

OPERATIONS PREPARATORY TO WEIGHING.

83. The estimations in chemical research are performed either by weight or measure; and as measures by bulk are founded upon, and referred for verification to standard weights, weighing becomes the chief means of quantitative determination; and as analysis depends for its successful performance upon the accuracy with which we estimate the weights of the substances eliminated by the various chemical methods used, it is essential to the student's progress that he should become perfectly familiar with all the manipulations connected with the use of the balance.

84. The most usual way of preparing substances for the balance-pan, is to convert them into the form of precipitates of known value, i. e. when dry, contain, or are equivalent to, a known amount of the substance to be estimated. But although this last-named method is the most common, it is by no means the only way in which we separate substances from the compounds which contain them; crystallization is not unfrequently as successful a means of separating bodies. In other cases compounds are exposed to temperatures capable of expelling one or more constituents, and leaving a residue of known composition in a state fit for estimation. It is also a frequent occurrence to expose mixtures to an elevated temperature, in a current of some gas which forms a volatile compound with one of its ingredients, which is accordingly expelled, leaving a residue capable of being weighed, as in the separation of antimony from lead. In these cases, and also in all the others which are met with in analytical research, it is of course absolutely essential that the substance to be weighed should exist in a state in which its condition is perfectly known, and more especially its relation to water. Chemists who are inattentive to this are constantly liable to the most serious errors. Even where precipitates will endure heating to redness, they

not unfrequently absorb moisture during cooling; in such instances they should be placed, if in a platinum, silver, or gold crucible, upon a large clean block of iron, which will remove the heat so rapidly by conduction, that if the lid is tolerably tight no appreciable moisture will be absorbed during the refrigeration.   It is imperatively necessary to let the capsule or other vessel in which the ignition was made become quite cold before being placed in the balance-pan, as otherwise errors are occasioned by currents of air, which make the vessel and contents appear lighter than they really are.   Another reason why it is essential to allow vessels to become of the temperature of the atmosphere before weighing is, that they may attain a state of hygrometric repose, otherwise they would keep for several minutes acquiring weight, as a film of moisture gradually deposited on the metal or glass.

85. Wet precipitates, or crystals, require very different treatment, according to their various natures : sometimes it is necessary to weigh substances which are either destroyed or have their constitution altered, by the slightest elevation of temperature ; it is then usual to expose the matter in watch-glasses or capsules to a surface capable of rapidly absorbing moisture, such as oil of vitriol, quicklime, or chloride of calcium.   If placed, under these circumstances, beneath the receiver of an air-pump, the operation is much hastened, but frequently an exposure to a desiccating surface in the manner figured in the margin (fig. 60) for twelve to twenty-four hours is quite sufficient.   The chemist is scarcely ever at a loss for a substance capable of rapidly absorbing moisture; if neither of the substances mentioned above are at hand, which is seldom the case, chloride of zinc, acetate, carbonate or caustic potash may be used.   It must of course be ascertained with certainty that the precipitate or other substance to be weighed is not only in appearance, but in reality, dry ; this may be known by weighing at intervals, until after some hours' exposure it does not decrease in

Fig. 60.

weight. It is extremely convenient in this operation to have two watch-glasses of the same size ground together and provided with a brass clip, as in fig. 61.

During the drying the substance is contained in one of the glasses as in fig. 60, and when it is wished to weigh, the

Fig. 61.

other is placed on as a cover and kept in its place with the clip; it is then balanced in this manner. The weight of the glasses is of course ascertained previously, and may be scratched with a diamond on each of them. Some precautions in regard to the drying of organic preparations will be treated of in the section on the Manipulations in Organic Analysis. The copper hot-air chamber (fig. 52) is very convenient for drying at known temperatures, as the heat is indicated by the thermometer and may be easily regulated.

86. *Ignition of Precipitates.*—In most of the operations in mineral analysis, the precipitates, after being filtered off and washed, are dried, heated to redness, and, when cold, weighed; the operation requires, however, many modifications, according to circumstances. Where the precipitate is not affected by the ashes of the filter, as alumina, silica, carbonate of lime, &c., as soon as it is washed it is to be dried, which may be performed in many ways according to the means at hand; for instance, the aperture in the funnel may be stopped with a cork, and it may be placed in one of the apertures of the steam-bath (figs. 53 or 55), or the funnel may be placed in the hot-air chamber of the furnace, or on the ring of the retort-stand, and the latter may be placed on the plate of the furnace, fig. 1; or, if the paper-filter is sufficiently strong to bear removing from the funnel, it may be placed upon a porous tile, and, when the moisture is sufficiently absorbed, it is to be opened out, and will soon become sufficiently free from moisture to have the exsiccation completed in any of the other methods either already described, or to be pointed out further on. The hot tile is also extremely useful in drying preparations; of

course care must be taken to prevent absorption of any saline matters from the tile itself. Sometimes the filter dried at 212° may be weighed, and the substance collected on it; after washing and subsequent drying, it is to be weighed again, when the increase will indicate the quantity of the precipitate. Before adopting this method, it must be ascertained that the filter contains no soluble matters capable of being removed during the washing, or, if such be the case, the paper should be previously prepared. When the substance is to be heated to redness, it must first be considered whether it is capable of injuring the platinum crucible, and, if so, one of porcelain must be substituted; also, whether the ashes of the filter can do any injury through the carbon they contain. If not, the crucible is to be placed upon a sheet of highly glazed paper, the edges of which are quite smooth, so as to be incapable of retaining any of the powder. The filter is then to have its contents removed, either by shaking or with the aid of a spatula; if any of the substance remains on the latter, it should be wiped with a piece of the filter-paper, which is to be added to the rest; the crucible is now to be placed in a slanting position over the lamp, and, when red-hot, the filter, cut to small pieces with scissors, is to be placed in it, waiting until the flame has disappeared each time before adding more; when the whole of the filter has been added, the lid of the capsule is to be laid in the manner indicated in the engraving, fig. 63. By this means a gentle current of air will be induced in the crucible, too gentle to remove any of the ashes, but sufficient to entirely consume the filter to a white ash in a short time, unless the substance is somewhat soluble in the water used to wash the precipitate, as sometimes happens; when this is so, a little nitric acid may, in many cases, be put into the crucible, when cold, upon the substance, and the heat being again raised to redness, the filter will soon disappear.

Where this is not admissible, from any action taking place between the acid and the assay, the filter may be washed at the last with a rather dilute solution of nitrate of ammonia, which will, to a considerable degree, effect the same thing. It is often more convenient to take the dry filter and its contents, and, after fold-

ing it together, to insert it at once in the crucible, and place the
latter vertically over the flame with the lid on loosely, until no

Fig. 62.   Fig. 63.
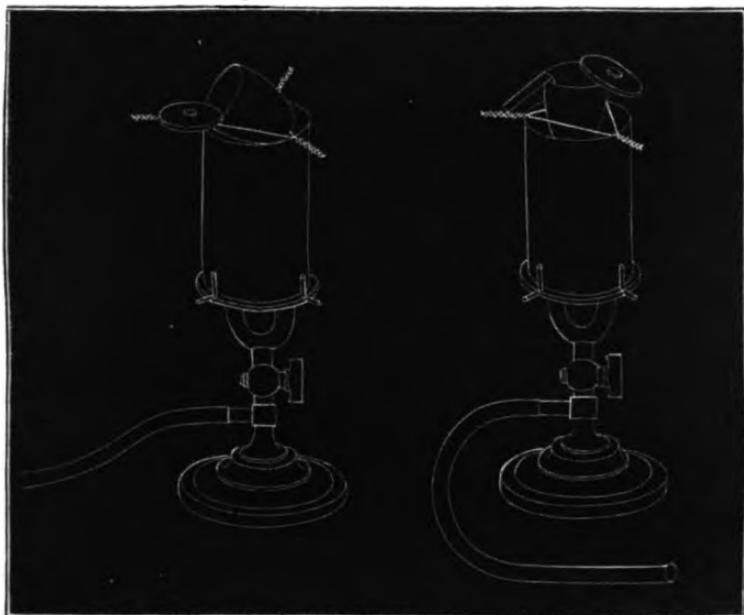
more combustible gases are evolved, when the crucible may be
arranged in the position seen in figs. 62 or 63, preferably the
latter.

87. Where, from the easy alterability of the substances at a
high temperature in presence of carbon, it is impossible to consume
the filter in contact with it, the assay must be carefully removed
from the latter, and be burnt alone, the paper being consumed
upon the lid; and when the black colour has entirely disappeared,
it may be added to the contents of the crucible, except where the
ignited substance is wanted for ulterior examination.   It is sup-
posed that the weight of the crucible has been taken previous to
the ignition, which is by far the best plan; in this case the
weight so obtained has merely to be added to the weight of the

filter-ash, and the sum being deducted from that of the crucible and the ignited matter, we obtain the weight of the latter.

88. It is advisable to use the circular cut filters alluded to at p. 4. By taking a few of these, and burning them in a platinum crucible until all the carbon is oxidized, and dividing the weight of ash by the number of filters used, we obtain a number to be always deducted from the weight of the substance ignited with the filter. It is essential to perform these operations in a place quite protected from air-currents, which would endanger the loss of a portion of the assay; if this should happen, even to the slightest extent, it is imperative to reject the estimation, as it is impossible to know how much has been removed by the accident.

89. It is advisable to make precipitates tolerably dry before igniting them, or a chance is incurred of the substance being partially ejected during the operation, especially if it has a tendency to fly about when heated in a damp state. Where there is any danger of loss from decrepitation the lid may be kept on until it is over.

90. The manner of procedure is liable to so many variations according to circumstances, that it would be impossible to mention all; the operator will, therefore, do well to reflect before he ignites a substance with the habitude of which he is not perfectly familiar. Platinum salts of the volatile organic bases require precautions which may be mentioned, from the frequency with which they occur in some trains of investigation. In the first place, the oily bases form salts with platinum which are liable during ignition to rise like a horn out of the crucible, sometimes to an inch or more in height; care must therefore be taken to heat gently, or a loss of the metal will be incurred. In the next place, the crystals have a peculiar tendency to retain an oily or resinous impurity, which renders it inadmissible to burn them without previously pulverizing, and washing them with alcohol or ether, or a mixture of both, according to their solubility. Previous to washing, the powder generally hangs together as if moist, but afterwards it is as mobile as dry sand. It is necessary also to turn the mass of spongy metal after the ignition, so as to expose the under surface

to the air, when it will be found to glow again from the combustion of the previously unconsumed carbon.

The tendency of silver to form explosive salts with many organic acids, especially those containing nitrogen, must not be lost sight of. The necessity of thoroughly washing precipitates previous to weighing them, and the method of ascertaining the complete removal of the precipitant, will be found in their proper places.

91. *Apparatus to contain substances while being weighed.*— Non-hygroscopic substances may be weighed in small capsules. Where the assay is liable to absorb moisture, a platinum crucible, with a well-fitting cover, is frequently the best instrument. If the substance is excessively deliquescent, it is advisable to add it to a counterpoised vessel of water, and ascertain the increase of weight; the same method, or a modification of it, is sometimes required in weighing substances which emit vapours at ordinary temperatures. Organic substances are generally weighed in small, wide-mouthed, stoppered bottles, or test-tubes with good corks. If in the former, the weight may be scratched on with a diamond; if in the latter, it should be written on the cork.

92. When liquids, such as acid or alkaline solutions, are to be added in known quantities to another until neutrality or some other point is reached, Schuster's alkalimeter (fig. 64) is much used, and is extremely convenient from the facility with which the drops may be regulated by the pressure of the finger upon the tubulure, and thus admitting more or less air. If filters with precipitates upon them have to be weighed after drying at 212°, it is necessary to effect the operation in a closed vessel, in consequence of the rapidity with which dry paper absorbs moisture: in this case the ground watch-glasses previously mentioned are convenient; or a very wide test-tube,

Fig. 64.

fitted with a good cork, may be used. The weight should be ascertained when empty, or, what is perhaps better, counterpoises for all the platinum crucibles, porcelain capsules, and other vessels in which weighings are to be effected, may be constructed from pieces of lead or brass; these being placed in the other pan of the balance, considerably facilitate the estimations.

SECTION VIII.

THE BALANCE.

93. Of all the instruments the chemist possesses, the balance is perhaps the most important, and requires the greatest amount of care in its use. Its very nature renders it fragile and liable to injury from the slightest carelessness or rough usage. Affected easily by acid or corrosive vapours of all kinds, it ought to be kept in a room adjoining the laboratory, and should never be left with the sash open, or without a vessel of some absorbent substance inside the case.

94. It is quite foreign to the purpose of this work to enter upon the mechanical theory of action of the balance; such a knowledge, although extremely useful, is by no means necessary to enable the operator to use the instrument with perfect ease and success; there are, however, a few things connected with the working of the instrument which are absolutely necessary to be known by the student. In the first place, it ought to be constant in its indications, *i. e.* with the full weight it is intended to carry, it should give the same result in several successive weighings; this, which is too often neglected, is, in fact, the best characteristic of a good balance.

It must also be delicate, that is, readily turned by very small weights, and that, equally with empty pans and with the maximum load.

It is also of great importance that it should be rapid in its action, for there are few things more fatiguing than to work at a slow instrument, and, moreover, it causes a very serious loss of time where many estimations have to be effected.

With regard to the adjustments upon which the above qualities depend, the following points are more especially to be observed.

First, the arms must be of equal length, for, if otherwise, equal weights acting upon levers of unequal length will give unequal indications; that which is at the extremity of the longer arm will

E

appear heavier than the other, and although by the method of double weighing (§ 105) this difficulty is overcome, it is essential to avoid the necessity of an operation requiring so much time.

Secondly, the centre of gravity must be below the fulcrum, otherwise, if equal weights be placed in the pans, and the centre of gravity and the fulcrum coincide, the beam will take any position that may be given it, without any tendency in the index to take a central position on the scale. If, however, the fulcrum be below the centre of gravity, the beam will "overset" with any weight, however small. But although it has been said that the centre of gravity should be below the fulcrum, it is essential that it should not be too much so, for the lower the centre of gravity the greater the stability of the balance, or, in other words, the greater the force required to move the beam, and the less delicate the instrument. Most balances have a contrivance for raising or lowering the centre of gravity, according to the circumstances under which they are to be used, as will be described further on.

In the next place, the centre knife-edge on which the beam rests, and the two knife-edges by which the pans are supported, must be parallel to one another, as otherwise considerable irregularities in the working of the instrument become apparent.

The points of suspension and the working edge of the fulcrum must be all in the same plane, for if the fulcrum is situated below the points of suspension, every addition of weight in the pans will have the effect of raising the centre of gravity, until at last the two points becoming coincident, the beam oversets with a small increment of weight. If, conversely, the points of suspension are situated below the fulcrum, all weights added have the property of depressing the centre of gravity, and therefore of increasing its stability, and also the weight required to move the instrument.

95. It will be seen that several of the properties required in a good balance are somewhat incompatible, and the greatest ingenuity and skill is required in so making the final adjustments, that these points to a certain extent neutralize each other.

96. The first persons in England who made any really import-
ant improvements in the balance, so as to render it fit for refined
chemical and physical research, were Robinson and Kater; the
latter gentleman having undertaken the somewhat difficult matter
of adjusting the national standard weights; he engaged Robinson
(whose accurate workmanship was well known) to assist him in
constructing the necessary instruments, and their united labours
succeeded in producing a balance undoubtedly infinitely superior
to any that had been made up to that time; in fact, those who
possess one of Robinson's instruments may be able to dispense
with any other for small weights; but few chemists who have
become accustomed to work with the long-armed balances in
use in modern laboratories, would willingly use one of Robinson's,
especially in organic research, where so much of the glass appa-
ratus is of considerable size, the shortness of the arms of the
latter instrument rendering it extremely inconvenient in such
cases.

The grand feature in Robinson's balance is the long bearing on
which the pans are suspended, instead of the "hook-and-eye"
arrangement adopted in most of the instruments brought over to
this country from the Continent. A little reflection will show any
person, that it is impossible for a hook to take invariably the same
position upon a ring with reference to the centre of motion, so
that the beam is, for all practical purposes, sometimes longer and
sometimes shorter, thereby causing considerable differences in the
indications,—differences which sometimes amount to ·01 of a grain,
and are quite sufficient to render an instrument unfit for delicate
experiments.

97. As an example, we will quote an instance frequently oc-
curring in organic chemistry: where mixtures of organic acids or
alkaloids are under examination, it is usual to convert the former
into silver, and the latter into platinum salts, and by crystalliza-
tion to separate them from impurities; it often happens that
the crops obtained do not exceed 1 or 2 grains in weight, and yet
that the quantity of silver or platinum in the salt has to be esti-
mated with precision: if, now, the balance is liable to a variation

E 2

of ·01 grain, we see that ·5, or 1 per cent. error, is immediately incurred by this means alone; in circumstances like this it is necessary to work upon much larger quantities than if a more perfect instrument were at hand.

The error caused by the hook-ends renders it imperative therefore in refined investigations to use an instrument having long bearings at the extremities of the beam; as by this method of construction a uniform result is invariably obtained.

98. In an active laboratory of research there should be at least three balances: one to carry from $1\frac{1}{2}$ to 2 pounds, and with that load to turn with ·02 of a grain; another for organic and other delicate estimations to carry 1000 grains, and with that load to indicate ·002 of a grain; and a third, for assaying, to work with very small weights, say 30 to 40 grains at the outside, and to turn rapidly and distinctly with ·001 of a grain.

99. The first of these is, perhaps, the most valuable and generally useful instrument. The beam is very long (18 inches), and is divided into ten parts, in order to dispense with the hundredths of a grain weight by using a "rider," which consists of a small weight of the form and size represented in fig. 65; it is constructed of gold- or silver-gilt wire, and weighs 0·1 grain in the pan; and when placed on the beam at the different numbers, it indicates any weight from ·01 to ·09 grain, and renders unnecessary the use of such small and fragile weights as those of that value.

Fig. 65.

A balance of this kind enables us to use weighed instead of measured quantities in the examination of mineral waters, a method decidedly to be preferred where practicable; it, moreover, renders the operator to a great degree independent of the necessity of using vessels of extreme thinness in analytical operations, a moderate weight not affecting the sensibility of the instrument: this property is of great assistance in physico-chemical investigations, where the increase of weight of potash, chloride-of-calcium, and sulphuric-acid tubes, has to be determined with precision.

100. When at rest, the knife-edges are not in contact with the working planes, but by turning the handle in front of the case, from right to left, the supports for the arms descend and leave the points of support on their planes, and in a state of freedom for oscillation.

101. The second balance may have several forms given to it, or rather to its working parts, according as the purchaser is guided by inclination or economy.

The more perfect instruments are made in such a manner that the pans are prevented from oscillating when the beam is at rest; but by turning the milled head, the pans are first released and then the beam. The contrivance, by means of which the eccentrics (which move the supports for the beam and pans) perform their office*, is extremely ingenious and simple; the description of it is, however, foreign to this work, and must be ascertained by inspection. Some balances, on the other hand, are so arranged that the beam itself is raised from the supports, and the pans are not provided with any steadying appliances.

An apparatus for moving the rider without the necessity of opening the case, is also a great assistance in delicate weighings.

102. It will be observed that in chemical balances the index points downwards instead of upwards; and while to the unpractised person this may seem a matter of little importance, it is in fact of the greatest assistance imaginable to the operator, where many and accurate weighings are to be performed. It can scarcely be believed until experienced, how much fatigue is occasioned by the necessity for raising the eyes from the pans to the index, even if we disregard the inconvenience of having the lantern so tall, as must necessarily be the case when so constructed.

103. The next balance which claims our attention is that for assaying purposes. Mr. Oertling has improved it in such a manner as to give increased rapidity of action and constancy of indication; the details of its construction, and the reasons which

* Invented by L. Oertling of Store Street, Bedford Square, London, to whom the author is indebted for the opportunities of minutely inspecting the details of his beautiful instruments, and also for a balance of great precision and delicacy.

led to the peculiarities of the contrivances, will not be dwelt upon; but it is necessary to inform the student of the main features, in order that the great advantages which it possesses may be appreciated.

The old assay balances were constructed with hook-and-eye ends; this arrangement, as we have before said, entirely precluded any constancy in its results; and yet the long bearings or knife-edges at the ends make the beam so heavy as to materially interfere with the delicacy of the instrument. To obviate this, Mr. Oertling has constructed the ends of the best assay balance in such a manner that the support for the pans rests upon two points which work, one in a small cup and the other in a groove; and as the two points lie nearly half an inch from each other, a constancy as great as in instruments with the long bearing, is obtained; by this means the beam may be made of such extreme lightness that great rapidity of action is ensured.

This balance can be made so small as to be carried about in the pocket, and that without losing any of its valuable qualities; and the artist above alluded to has constructed them so small as to go into a case 8 inches long by $2\frac{1}{2}$ high, and 2 inches wide.

104. It is necessary, in weighing, to attend to one or two points which materially assist in ensuring rapidity and accuracy. In the first place, the beams of delicate balances oscillate for a very long time, so that if it were necessary to wait until the index was at rest, weighing accurately would be an exceedingly tedious operation; but a very little consideration will show us that if we simply adjust the weights until the movements of the index on each side the zero of the scale are equal, we shall obtain a result even more accurate than by waiting until it is stationary, because, while oscillating, we are sure that no resistance is offered through the beam "sticking." In the next place, it is essential to try the weights in a regular order; thus it will be seen that in instruments intended for chemical use, they are numbered 1000, 600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1, ·6, ·3, ·2, ·1, ·06, ·03, ·02, ·01. Suppose, therefore, the substance or instrument being weighed requires 1740 grains to counterpoise it, 1000 is tried,—too light;

1600, still too light; 1900, too heavy; 1800, still too heavy;
1700, too light; 1760, too heavy; 1730, too light; 1750, too
heavy; 1740, right.   Now, although this takes some time to de-
scribe, it will be found in practice, that, by adopting this method, a
result is obtained in less than half the time that would be required
by using the weights at random.

105. Weights should never be added or removed while the
beam is oscillating; it should be invariably brought to a state of
rest before making any alteration.

If the beam be a little longer on one side than the other, the
substance on the longer end of the lever appears heavier than the
true weight; but if one pan is invariably used for the weights
and the other for the "substance," the errors, being all of the same
value, do not affect the results of analyses made with it, as the
quantities obtained are not necessarily of one particular standard
so that they are truly proportional.

But if an error of this kind be suspected, it is easy to deter-
mine the fact thus:—place a substance in one pan and accurately
counterpoise it; now change its position from one pan to the
other; if the equilibrium is undisturbed, the arms are of equal
length; but if the reverse happens, and the *absolute* weight is
required, we must adopt the method of double weighing, said
to be invented by Borda, which is thus performed: place any-
thing the weight of which is to be obtained, in one pan,
and counterpoise it; then remove the substance and replace
it by weights; now as things equal to the same are equal
to each other, the weights express the true value of the sub-
stance, for they exercised the same amount of force upon the
beam.

106. For the reasons stated, we should therefore always use the
same pan for the weights; and it will be found by far the more
convenient method to keep the right-hand one for this purpose, as
otherwise the hand has to be used across in adjusting the weights,
and has further to move, a matter of more importance than would
appear to any one inexperienced in these matters.   Each of the
different forms of balance should be provided with levelling screws

and a spirit-level, with which the instrument should be carefully adjusted before use. It not unfrequently happens that what would otherwise be the most convenient position in a laboratory for the balance, is rendered apparently unsuitable, from the fact that, the source of light being behind it, the motions of the index are rendered comparatively indistinct. This may readily be obviated by adjusting a small mirror to such an angle as to throw the light upon the graduated ivory scale.

107. In organic researches, it is necessary to ascertain the increase of weight of tubes which are of a more bulky kind than those in general use in the other branches of the science; the ordinary chloride-of-calcium tubes, and Liebig's potash bulbs will serve as an illustration. As the point sought to be ascertained is

Fig. 67.

Fig. 66.
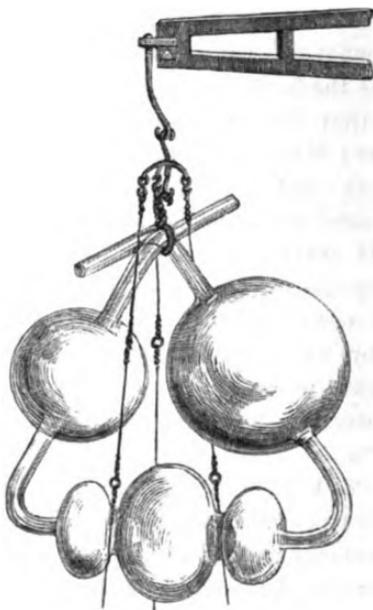
merely the increase of weight before and after certain operations, and as the absolute weight is of no consequence, one of the pans

may be removed, and the chloride-of-calcium or potash tube may be attached by a steel hook immediately to the ring of the wire which is used to support the pans; by this arrangement the tubes appear lighter than they really are, to an extent equal to the weight of the pan, as in fig. 66.   Another method, fig. 67, is still more generally adopted, and is convenient, as it prevents the necessity for removing the pan.   The planes which rest on the knife-edges in balances of the kind represented in the figure, have square apertures or notches which enable them to take the position shown.

It is scarcely necessary to mention, that in performing the weighing it is only requisite to counterpoise the chloride-of-calcium and potash tubes, and the hooks which suspend them; and, after the operation, to weigh again, taking care that the circumstances are exactly similar, that is to say, that the hooks are not changed.   In order to perform this with facility, each chloride-of-calcium tube is provided with a little brass belt and long link, to which the hook may be easily attached.   The potash tube (fig. 67) has an arrangement which is easily seen by reference to the engraving.   It is quite unnecessary to have a pan with a notch cut in it, such as is frequently supplied with the balance for this purpose.

108. Care must of course be taken in using apparatus which occupies so much space, that no part of it touches the beam or lantern of the balance.   There are a few special cases in which precautions are required in weighing; in the first place, it is inadmissible to put any substance or vessel into the balance-pan unless quite cold, as considerable errors become manifest by such a procedure (§ 84).   It has also been said that deliquescent substances are in many cases advantageously weighed by first counterpoising the liquid, or a portion of it, in which they are to be dissolved, and then ascertaining the increase of weight.   If this be impracticable, it is necessary to perform the operation in a well-closed vessel; and if the substance has been recently ignited to expel water or other volatile matters, the platinum crucible in which the ignition was effected should be cooled under circum-

E 5

stances which prevent the possibility of any moisture being ab-
sorbed during that process. The lid of the crucible must fit
accurately, and if it be inconvenient to place it under a bell-glass,
over sulphuric acid, during the refrigeration, it should be cooled
as directed in § 84. If the crucible is of porcelain, it would of
course be fractured by too sudden cooling; the vessel should there-
fore be placed under a dry bell-glass, upon a triangle of thin wire,
so that it is only touched by the metal at very small points; by
this means the danger of fracture is greatly lessened.

109. There are many substances which give off corrosive va-
pours, and if weighed in the balance-case would cause any instru-
ment of ordinary construction great injury; to do away with this
inconvenience, many balances have all the working parts of agate.
This is an excellent contrivance, and perfectly effects the purpose
intended; but it is advisable in such cases to have a good pair of
ordinary scales, and where minute accuracy is not desired, to sub-
stitute them for the delicate balance.

110. In weighing gases, in the operation of taking their den-
sity, it is necessary, from their small weight, to use vessels of
considerable size, which therefore lose in weight an amount equal
to that of their bulk of air. But this loss, being the same in all
the weighings, has no influence upon the result, provided the
temperature and pressure of the atmosphere has not altered during
the experiment. If it has, an error is introduced, the amount of
which it is difficult to calculate; but if we balance the globe in
which the gas is to be weighed by another exactly resembling it,
an accurate result may be obtained, because any change of density
in the air affects the globe containing the gas and its counterpoise
equally. We shall allude to this again further on.

If two vessels of the same capacity cannot be procured, the
smaller must have a closed tube attached to it, the bulk of which,
plus that of the globe to which it is attached, must equal that of
the larger one.

SECTION IX.

SPECIFIC GRAVITY.

111. *Specific Gravity in general.*—The term specific gravity is understood to mean the relative weights of equal masses of matter. It will easily be seen that almost all the various natural and artificial objects which come under our cognizance, have densities peculiar to themselves, *i. e.* equal bulks of them have very different weights; it becomes necessary, therefore, to have some standard which may be taken as unity, and to which the densities of all other bodies may be referred. But it is imperatively necessary that the one adopted should be obtainable with facility in any part of the world; and it must also be capable of easy purification; philosophers have therefore agreed upon water as the body to which all solids and liquids are to be compared, and atmospheric air as the standard for gases. It will be proper to consider these under different heads.

112. Perhaps the first idea which would strike any one who, without previous instruction, commenced an inquiry into the relative weights of equal bulks of various bodies, would be to reduce them to exactly the same size, and then weigh; this procedure would of course immediately eliminate a number expressive of the ratio of the densities; but a little reflection will immediately convince us that it would be impossible to do this in many instances, even if it were the only method of research; the porosity, hardness, and many other peculiarities observed in different kinds of matter, would prove an insurmountable obstacle to such a method; but, fortunately, it is possible to take the specific gravities of solids and liquids in many ways, all equally easy of performance; but the circumstances under which the operation is to be conducted, make one method sometimes more convenient than another.

113. *Specific Gravity of Solids.*—Any solid substance when immersed in water displaces a volume exactly equal to its own bulk; and at the same time loses a portion of its weight corresponding

to that of the volume of water displaced.   The procedure therefore
is as follows :—weigh the substance ac-
curately, then suspend it by a fibre of
silk or a fine hair to the hook beneath
the short pan of the balance, and bring
the latter to an equilibrium ; now take
a glass of pure distilled water, at as
nearly as possible the standard tem-
perature (60° Fahrenheit), and intro-
duce it beneath the substance, so that
the latter may be covered to a moderate
depth ; if any globules of air remain on
it, they are to be removed.   Imme-
diately on the immersion of the sub-
stance in the water, the arm of the
beam to which it was attached rises ;

Fig. 68.

and if we now place weights into the short pan until the equili-
brium is restored, they will express the weight of a volume of water
equal to that of the substance.   For example:—

A globule of gold not hammered, weighing 50·00 grains, lost
by immersion in water exactly 2·59 grains, and

$$\frac{50·00}{2·59}=19·3 \,;$$

the gold was therefore very nearly pure, the specific gravity of
pure gold melted but not hammered being 19·2 ; by hammering,
it may be brought to 19·4, and even to 19·65.

If the substance the density of which is to be taken, is in the
form of grains, a very convenient method is to ascertain the quantity
it displaces when dropped into a bottle full of water the weight of
which is known.   The following account of two experiments will
illustrate the process.   Several globules of gold which had been
purified with some care, and had been slightly hammered, were
weighed, and found to amount to 38·95 grains ; a small flask was
filled with water and weighed, it amounted to 814·20 grains ; the
globules were then dropped in, and of course a quantity equal in
bulk to the gold overflowed ; after carefully wiping the flask and

levelling the convex surface of the water at the mouth, to produce the same conditions as in the first weighing, it was placed in the balance-pan, and required 851·15 grains to equipoise it; but the weight of the bottle full of water without the gold being placed in it (814·20) plus the ascertained weight of the globules (38·95), amounts to 853·15 grains; and 853·15−851·15=2·00, the weight of the water which overflowed, and

$$\frac{38\cdot95}{2\cdot00}=19\cdot475;$$

being nearly the same result as the last, and showing this specimen of gold to be also very pure.

In another experiment, some pieces of metallic cadmium, which had been slightly flattened under the hammer, weighing 59·25 grains, were dropped into a flask full of water, which weighed previously 768·63 grains. On weighing after the introduction of the cadmium, it required 821·1 grains to equipoise it, but the total weight of the flask full of water and the cadmium was 827·88 grains, for 768·63+59·25=827·88, showing 6·78 grains of water to have overflowed on the introduction of the metal, and

$$\frac{59\cdot25}{6\cdot78}=8\cdot739,$$

the generally received specific gravity of cadmium being 8·694. Regnault gives 8·7.

114. There is an instrument which can be easily constructed by any person, and is capable, with care, of rapidly giving tolerable approximations to the density of any substance heavier than, and insoluble in water. It consists of a small test-tube (fig. 69), which has a scale marked on it, commencing about 1 inch from the bottom, indicating grains of water. To use it, the instrument has water put in it until the bottom line of the curve exactly coincides with zero; the substance, the density of which is required, is weighed and dropped in; of course the water then rises in the tube, and, as the value of each division to which the water rises is equal to 1 grain, the weight of a bulk of water equal to the substance is obtained by

inspection. As an example :—17·93 grains of cadmium, which for the purpose of the experiment had been recently melted and made into a rod by casting in a glass tube, were dropped into the tube, which had previously been filled up to the zero of the scale with water; the fluid rose two divisions, indicating that a bulk of water equal to 17·93 grains of cadmium weighed 2 grains, and $\frac{17·93}{2} = 8·965$, the specific gravity required. Again, 26·61 grains on being dropped in raised the water three divisions, and $\frac{26·61}{3} = 8·87$. The density obtained before on the same specimen by a different process was 8·7. It will be seen therefore that the method is capable of yielding approximative results suffi-

Fig. 69.

cient for many purposes; and when the great rapidity with which a result can be obtained is taken into consideration, it may not be going too far to assert that the instrument will, to many persons, more especially travelling mineralogists, be an acquisition. The points requiring care are, in the first place, to prevent bubbles of air from adhering to the specimen; also to allow the sides of the tube to thoroughly drain before ascertaining the zero point of the water, and to take great care in determining the exact\part of the curve to be observed in each experiment. Without these precautions, the results obtained will be very far from the truth.

115. To determine the density of a solid lighter than water, we proceed thus :—Weigh the substance in air, and weigh in

water a piece of lead sufficient to sink it. Attach them and ascertain their weight in water; deduct the number so obtained from the weight of the lead in water, and add to the remainder the weight of the light solid in air; the result is the weight of a bulk of water equal to the light body. For instance, we will suppose a piece of light wood to weigh in air 33·30 grains, the lead in water 60·00, and both in water 23·30. Then, by the rule given, 60·00 − 23·30 = 36·70, to which add 33·30 giving 70·00, and 33·30 divided by 70·00 gives 0·4757 as the density.

Or we may apply the same method as that adopted for ascertaining the density of the globules of gold and cadmium; for by taking a vessel capable of being closed with a stopper or a plate of glass, the weight of which, full of water, is known, and placing the light body in it, a volume of water will be displaced equal to its bulk, from which data the density is easily calculated.

116. If the solid is soluble in water, one of two courses must be adopted: either it may be varnished very thinly, so as to prevent the water from touching it, or its specific gravity may be taken by the first method given, substituting a fluid in which the body is insoluble, and making a correction in consequence of the difference in density of the two liquids. For example, suppose that the substance is soluble in all the liquids within reach except benzole, the density of which is 0·850; a flask is filled to the brim with it, and a flat plate of ground glass laid on the top, to prevent evaporation: the weight is 1087 grains. On introducing the substance, the weight of which is 100 grains, and subsequent wiping, &c. of the flask, the weight is found to be 1100 grains; on deducting this number from the sum of the weights of the flask of benzole and the substance, we obtain 87 grains as the quantity of the hydrocarbon displaced. Now the specific gravity of benzole is to the weight of the bulk of benzole displaced, as the specific gravity of water is to the weight of a bulk of water equal to that of the substance; or

·850 : 87 : 1000 : 102·3, and

102·3 : 1 : 100 :   ·978, the value required.

117. *Specific Gravity of Liquids.*—The density of liquids may

be obtained in several ways. The difficulty which is found in obtaining equal bulks of solids, is not found in this instance; it only being necessary to fill a vessel to a given point with the fluids the density of which is to be compared, and ascertain their weight.

We have said that water is used as a stand-
ard of comparison for liquids and solids, the
usual method being to construct a bottle
capable, when the stopper is put in its place,
of holding exactly 1000 grains of water.
By merely, therefore, counterpoising the
empty bottle, and, after filling with the li-
quid whose specific gravity is to be ascer-
tained, adding weights to restore the equi-
librium, we obtain the result sought without
any calculation. For example:—A bottle
which holds exactly 1000 grains of water

Fig. 70.

is counterpoised, and then filled with pure concentrated oil of vitriol, and the stopper, which is perforated, is then put in its place; the excess escapes by the aperture, and is carefully wiped off; on replacing the bottle, 1845 grains were required to balance it; this number represents the specific gravity sought, which is more correctly written 1·845. If a liquid lighter than water be used, the result is still the specific gravity, but the decimal point is of course placed in front of the number found. For instance, some spirits of wine digested for some time over excess of dry carbonate of potash and slowly distilled, was put, under the circumstances previously mentioned, into the bottle, when 810 grains were required to equipoise it: ·810 is therefore the specific gravity sought.

The bottle with the perforated stopper (fig. 70) has many disadvantages, not the least of which is, that where, as often happens, it becomes desirable to determine the density of a fluid at 32° F. =0° Cent., a continual expansion is taking place during the weighing, unless the operation is performed in an inconveniently cold apartment. If, to avoid this source of error, we make use of a flask with a mark on the neck, and adjust the fluid to it at the

Fig. 71.

freezing-point, it is true that as expansion takes place, the fluid merely rises in the neck, and if the latter be sufficiently capacious and the fluid is not very volatile, the experiment will succeed. But if the fluid evaporates rapidly at moderate temperatures, it is impossible to obtain accurate results. M. Regnault, to avoid this difficulty, uses a flask of the form shown in fig. 71. The fluid is filled to the mark on the neck, and the stopper is inserted in its place. By this means evaporation becomes impossible, and, if expansion takes place during the weighing, the fluid cannot escape in consequence of the enlargement in the neck.
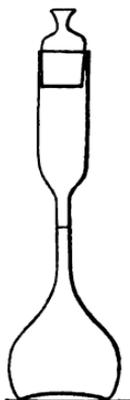
118. It is of the greatest importance, when accuracy is required, that the temperature of the liquid should be at or very near the normal point 60°, otherwise considerable errors will result. It is necessary, therefore, to be careful when taking the densities of recently-made mixtures, the temperature of the ingredients before mixing not necessarily being the same afterwards; in fact, it is very seldom that substances dissolve in water without either elevation or depression of temperature: if fused chloride of zinc is dissolved in water, the temperature rises considerably; when, on the contrary, iodide of potassium or nitrate of ammonia is dissolved, the temperature falls to a great extent; and although few of the salts in use in the laboratory present such distinctly marked phenomena, it becomes essential to be alive to the possibility of alterations of temperature.

Even *liquids*, when mixed, frequently develope heat: every one is familiar with the great heat which ensues when strong sulphuric acid is diluted with water; even a rise is caused, though to a far less extent, when spirit of wine is mixed with water. In the pharmaceutical laboratory it is constantly necessary to add spirit to the concentrated infusions now so much used; if, then, the specific gravity is taken by dipping the hydrometer into the liquid immediately after mixing, a value is obtained which indicates a considerably less density than when the liquid is first

brought to the normal temperature by being allowed to repose for some time: the amount of variation is of course proportional to the increase of temperature.

119. We have alluded above to the hydrometer (fig. 73), which is an instrument in constant use in the laboratory to obtain densities without the necessity of weighing:

Fig. 72.   Fig. 73.

it may be constructed to give results of any degree of accuracy, but this involves the use of several instruments; in general laboratory practice two only are employed: one with a range from the density of pure ether to that of water, and the other from water to oil of vitriol; one of the chief objections to their use, is the quantity of liquid required to fill the glass in which the hydrometer is floated, but, by employing the modification represented in fig. 72, this difficulty is to a great extent removed, a result being obtainable with only an ounce or two of fluid.

It is necessary in some manufacturing processes to determine the specific gravity of liquids with more accuracy than is obtainable by the two instruments alluded to; in these cases recourse is had to a series, six being required to complete the range previously given.

120. Several forms of hydrometers are used in various manufactures and professions, of which it will be necessary to mention little more than the names, as instructions for their use and tables for calculation invariably accompany the instrument when sold; such are the hydrometers of Twaddell, Cartier, Beaumé, and Sykes, the first being much used in the manufacturing districts, and the next two on the Continent; the last is the Excise instrument, and is much more complicated in its construction than the others, being made of metal instead of

glass, and having a set of weights capable of being fixed temporarily in the stem during the operation.

121. There are other instruments formed upon the same principle, and greatly used in various technical operations; brewers, for instance, are in the habit of using one to indicate the pounds of malt per barrel, or the per-centage of sugar; the quality of oil and milk is determined by elæometers and galactometers; physicians frequently have recourse to a little instrument, on the same principle, for estimating the density of urine (fig. 74); in fact there is hardly any limit to the number of hydrometers which may be constructed to suit the special requirements of the various operations of manufacture, and, as a prejudice exists among unscientific persons against the use of instruments indicating directly specific gravities, there appears little hope of a really rational scale being adopted by all classes of manufacturers. The indications of Twaddell's instrument are, however, easily reduced to specific gravities, it merely being necessary to multiply the observed degree by 5, and add 1000 to obtain the number sought. For example, 138° multiplied by 5 gives 690, and on adding 1000, we obtain 1·690, which is the specific gravity corresponding to 138° Twaddell *.

Fig. 74.

The value of alcohol is, it has been said, estimated in England by the hydrometer of Sykes, the degrees of which are both arbitrary and unscientific, the standard being called proof, and the strength of spirit being estimated as under or over proof, the last term being used to indicate spirit of the density ·920 at the temperature 60° Fahr. On the continent four instruments are used for spirits, namely, Beaumé's, Cartier's, Gay-Lussac's, and Tralles'; the latter, generally known as the Prussian scale, has been adopted by the United States.

* For a paper by Dr. Bolley, on the advantages of Twaddell's scale over those of Beaumé and Beck, see Chemical Gazette, January 1, 1855.

122. It has been said that the normal temperature of 60° must in all cases be obtained before attempting to take the density of any liquid; it is, however, possible to have hydrometers made to use at any given temperature; for instance, instruments to be used in the West Indies are adjusted at 84° Fahr.

123. Nicholson's hydrometer is an instrument for taking the specific gravities of either solids or liquids; when used for the latter it acts like that of Fahrenheit, by giving the weight of the volumes displaced by it; it has a mark on the stem, to which it is to be sunk by weights placed in a small cup fixed on the end of the rod which projects above the liquid; the weight of the instrument, plus that placed in the cup, is the measure of the density of the liquid in which it floats.

But the chief convenience of Nicholson's instrument is its adaptability for taking the specific gravities of solid substances; for if, after immersing the instrument in a fluid of known density, preferably water, we place the mineral or other substance in the cup, and then add weights until the mark on the stem coincides with the surface of the water, we have the data for ascertaining the weight in air of the substance; and by removing it from the upper and placing it in the lower cup (which occupies the place generally appropriated to the mercury or shot ballast of ordinary hydrometers), and again immersing the instrument in water and adding weights as before, the weight in water is ascertained, and from the data thus obtained the specific gravity is easily calculated.

124. There is another method of ascertaining the weights of equal volumes which is in some cases preferable to all others; it consists in weighing a heavy substance first in air and then in water, by which the weight of an equal bulk of water is obtained; if the water is now replaced by any other liquid whose density is to be taken, the weight of a volume equal to the water is thus found, being all the data required. This method is particularly applicable where only a very small quantity of liquid is at our disposal; in this latter case it is, of course, essential to work with an accurate balance, in order that the errors of weighing may be too minute to influence the result.

The chemist is generally, however, quite independent of any of the contrivances invented for assisting unscientific persons to obtain the densities of solids or liquids; any vessel capable of being accurately closed may be used for taking the specific gravity of all solids or liquids capable of being introduced; and where the quantity at the operator's disposal is extremely minute, it is only necessary to construct a very small flask or long-necked globule from a piece of quill-tubing, and fill it first with water and then with the other liquid, and weigh under each of those circumstances.

It is frequently required to wash out the specific-gravity bottle, and dry it before making another experiment; in ordinary cases, the instrument need only be rinsed out two or three times with the fluid under examination to render it in a fit state for use; but where this cannot be done, the bottle, after the removal of the liquid previously in it, by solvents if necessary, should be thoroughly washed out with water, and a long glass tube being introduced into it, the bottle is to be turned over a lamp or the plate of the furnace until the water is vaporized; on sucking out air by the tube all the aqueous vapour may be removed. In the case of the small flasks previously alluded to, the neck should not be so small as to prevent the introduction of a very small tube for this purpose. It is sometimes advisable to consider whether it is better to introduce the water or the other fluid first, but of course much must be left to the judgment of the experimenter.

125. The perforated stoppers alluded to previously are not always advantageous, and it is often preferable to employ either a solid stopper or a small flat plate of glass to cover the mouth of the bottle, or else merely to fill a long narrow-necked flask up to a mark on the neck; or a cover may be made to the instrument having a pin or fine wire passing down the neck, and the fluid may be poured in until the point is just reached.

126. A very pretty contrivance is, to have a thermometer so made as to form the stopper of the instrument; the bulb should reach almost to the bottom of the bottle; in this way the bottle

being filled, and the stopper inserted, the whole may be placed
in a warm or cold situation, according to circumstances, until
the mercury marks the proper point; the instrument is then
wiped, if necessary, and put into the balance-pan. Even when
this is not done, a thermometer small enough to be intro-
duced into the bottle should be used; on taking it out, the fluid
sinks, and has to be filled up again: this may generally be done
without much error with a liquid not reduced to the normal
temperature, unless the difference is great; it is better, however,
to use a very small thermometer engraved on the stem, and to
weigh both the water and the liquid in the bottle with the ther-
mometer in it.   A few other precautions to be taken when the
substance is porous or in powder, will be found in the section on
the Air-Pump.

<div style="text-align:center">SPECIFIC GRAVITIES OF VAPOURS AND GASES.</div>

127. *Vapour Densities.*—In modern chemical research it is
by no means uncommon to isolate bodies which form no definite
compounds with other substances; the mere analysis, although it
gives the ratio between the elements present, does not settle the
equivalent of the body.   It is true that the mode of formation,
and the nature of the products of decomposition, frequently give
great probability to one formula, but it is unsafe in the case of
chemically indifferent substances to decide from these data alone.
But if it happens that the compound is volatile without decompo-
sition, at temperatures not too high to be accurately measured by
the air- or mercurial thermometer, we may, by a method of great
simplicity and ease in execution, determine its rational formula.
In effect, most chemists are now agreed that the formula of any
organic compound is that which is represented by four volumes of
vapour.   The equivalent of any organic substance (corresponding
to four vols.), multiplied by ·0346, or half the density of hydrogen,
$H=1$, gives its vapour density.

128. It will, therefore, easily be seen that a knowledge of the
density of the vapour of any substance forms the most severe
check we have on the results of analysis.

But vapour densities may, at times, be made use of in research as a means of ascertaining the nature of substances, where, from the small variation in their per-centage composition, ultimate analysis becomes an unsafe guide. In examining the fluids produced by distillation of the Torbane-hill mineral, I obtained a series of homologous hydrocarbons which only varied in composition as the boiling-point rose, by very small amounts, so small indeed, that, notwithstanding the extreme care with which the analyses were made, it would have been unsafe to draw any conclusion as to the fractions to be selected as expressing the correct boiling-point from them alone; but, on the other hand, the densities of the vapours varied considerably with the different homologues, and by taking advantage of this fact I was enabled with perfect safety to pronounce not only on the formulæ of the substances, but also on their boiling-point.

129. In consequence of the tenuity of gases and vapours, great care is required in the various operations; the balance, air-pump, thermometers, barometer, &c. should be in perfect working order, and no pains should be spared to acquire facility in using them.

Gases are eminently compressible, and greatly affected in volume by comparatively small variations of temperature; the indications of the thermometer and barometer must therefore be carefully registered during the process.

There are two methods by which the densities of vapours are determined; in one, and it is that most commonly employed, the body under examination is introduced into a balloon, the capacity of which in cubic centimetres is afterwards ascertained, and heat sufficient to convert the substance into vapour having been applied, the weight of the known volume is easily found, from which the vapour density may be calculated. In the second method, a known weight of substance is heated beyond its vaporizing point in an apparatus which permits the volume and the circumstances of temperature and pressure to be ascertained with accuracy.

The first method, that of M. Dumas, requires the use of flasks of from 200 to 350 cub. cent., according to the quantity of substance, and the greater or less density of its vapour. Those vapours

which are not much heavier than air, require balloons of con-
siderable size. Fig. 75 shows the shape
usually adopted. It is necessary that

Fig. 75.

they should be of light glass free from
lead, and of a kind that will allow the
point to be readily sealed by a brush of
flame directed on it with the blowpipe.
The flask must be perfectly freed from
aqueous vapour by connecting it with
the air-pump, a long chloride-of-calcium
tube intervening; after covering it with
hot sand and alternately exhausting and admitting air several
times, the balloon will be thoroughly dried.   The tube of the flask
is now (unless it has been done previously) to be drawn out and
cut off with a file, so as to leave an aperture of the size
and shape of the upper part of fig. 76.   The edges are
to be slightly rounded in the lamp-flame, to prevent the
danger of small pieces of glass being broken off.

Fig. 76.

The balloon having been allowed to remain on the
balance-pan until it has ceased to increase in weight
from the deposition of moisture, the exact tare is taken
and the temperature of the balance-case observed.

The flask is then ready to receive the fluid, the density
of which is to be ascertained; but there are a few precau-
tions which ought to be mentioned in this place.   I am accustomed
to make use of a small graduated measure to contain the fluid to
be inserted, in order that if too considerable a volume of residual
air is found at the termination of the experiment, a larger quan-
tity of fluid may be used in the repetition of the operation.   It is
very advisable to use no more than is necessary to expel all the
air, especially with substances which leave a slight residue on
distillation, or which contain a small quantity of a less volatile
substance, as is frequently the case with bodies obtained by frac-
tional distillation.

The amount of fluid which is intended to be used (say 100
grains for a first experiment) having been poured into the measure,

the point of the globe is to be inserted, and the latter being warmed to expel some of the air, the lamp is removed, and, as the balloon cools, the fluid enters.   If the substance the density of which in the state of vapour is to be determined, happens to be in the solid form at ordinary temperatures, it must be fused, and the narrow tube be kept hot during its insertion.

130. It is necessary to consider, before proceeding, what temperature the substance requires for volatilization, and a bath must be selected capable of being heated to at least 100° F. above that point.   The fluids at our disposal which are adapted for heating the balloons are water, neatsfoot oil, melted tallow, solutions of the chlorides of calcium or zinc, melted tin, bismuth, or fusible metal. For temperatures not exceeding 500° F., I find the third substance mentioned above very convenient, if the laboratory is sufficiently large to make the odour of the hot tallow of little moment.

The kind of bath having been selected, the material is to be placed in an iron kettle and heated up to the proper point, the flask properly secured may then be inserted, the aperture being about $\frac{1}{4}$ of an inch above the level of the fluid.

131. There are three methods commonly in use for supporting the globe in the bath.   The first (fig. 77) is by means of an arm of wood which slides on a retort-stand.   It is jointed at a to allow of a motion of the thermometer and flask at various angles.

The balloon is supported by means of a rod, b, sliding through an aperture in the arm; it may be arrested at any height by means of a screw, c.   The thermometer, d, is kept at any required height by the screw, e, which acts on pieces of cork placed at f to prevent fracture arising from too great pressure. The balloon is attached to the rod, b, by means of a wire cage.

Fig. 77.

Another method of supporting the balloon is represented in fig. 78.   It is placed between two
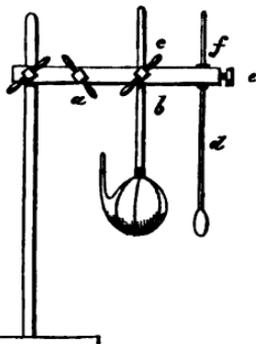
rings, *a b* and *c d*; the latter is moveable up and down, and is fixed on the balloon by means of screws, *g' g*, which press on two corks, *h h*. The screws work in the cross piece, *e f*, which also serves to support a rod, the latter in its turn carrying an arm, *n m*, having two pierced corks attached to the extremities, through which pass the thermometers, TT. The arm, *n m*, is moveable round its centre, so as to allow of various positions being given to the thermometers.
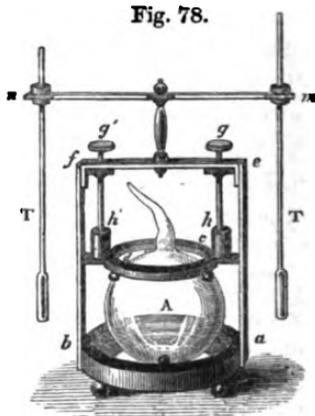
Fig. 78.

132. But the most convenient method of supporting the balloon and thermometer is represented in fig.79, where an iron pot, V, has two rods (*t p* and *t' p'*) attached to its ears by means of screws, *s s'*; on one of these rods slides the bent bar, *c d*; it may be arrested at any height by means of the screw, *r*. Two rings, *e f* and *g h*, move on the bar, *c d*; they are precisely similar to the rings of retort-stands, and may be secured in the desired position by the screws, *i l*. The flask, A, may therefore be steadily held in the bath, and the point, *a*, moved in any direction with ease, a

Fig. 79.

very necessary thing in many cases. The rod, *t' p'*, supports an arm, *r' K*, having a pierced cork at its extremity, serving to hold the air-thermometer, B, or a mercurial one, according as the temperature to which the bath is to be raised is more or less elevated.

The iron kettle may be placed on an iron triangle over a charcoal fire, or the lower part (fig. 11) of a Luhme's furnace. I prefer, however, a powerful double ring gas-burner enclosed in a case

of sheet iron, the latter serving as a gas-furnace and support for the kettle.

133. The balloon and its contents being attached to the support, is to be depressed into the bath, and the contents, if valuable, distilled into a tube. For the latter purpose, the neck of the balloon must of course be directed downwards. As soon as the substance ceases to distil, the neck is placed in an upright position, and the balloon is depressed in the bath until only a $\frac{1}{4}$ or $\frac{1}{2}$ an inch of the neck remains above the level of the fluid. The evolution of vapour again commences, and as soon as it almost ceases, the furnace-doors are closed, or the gas slightly lowered so as to render the temperature of the bath steady for a few minutes. During this time, care must be taken to chase away, with a red-hot coal, any fluid which may condense in the neck of the balloon. As soon as it is found, by applying a cold substance to the aperture, that no more vapour is being expelled, and the temperature is stationary, a good blowpipe-flame is directed on the point until it is quite closed; the temperature is then carefully observed, and the balloon removed; it is now placed for a few minutes point downwards, so as to permit the fluid to run into the neck: by this means it is immediately seen whether the sealing has been perfectly accomplished, as, if not, a stream of air-bubbles will be found to enter through the fluid. The balloon is to be carefully cleaned, and when no longer perceptibly warm, is placed on the balance-pan and allowed to remain for twenty minutes; it is then weighed.

134. The next part of the process is to break off the point of the flask under mercury; to effect this, the globe is held in the hand, its point being depressed considerably below the surface of the metal; a file-mark is then made on the neck by another person, and the point snapped off. The mercury now rushes in with violence, and, together with the condensed fluid, generally fills the flask to within 2 or 3 centimetres of its capacity. The balloon is now placed on a ring with its point upwards, and the condensed fluid is removed by means of a pipette with a long and thin point, and transferred to a small measure. The mercury is then poured into an accurately graduated bell-jar, and its bulk,

as thus ascertained, plus that of the condensed fluid, represents the volume of the vapour. The globe is then filled with water, which is to be measured in the same manner as the mercury. The bulk of the water gives the capacity of the flask, and the difference between the bulk of the mercury, plus the condensed fluid and the bulk of the water, expresses the amount of residual air. To expel the water from the flask without breaking the neck, more than is necessary, is effected by means of a small curved tube, *b*, fig. 80, the point of which enters the neck of the inverted flask; on blowing air in at *a*, the fluid escapes into the graduated jar, *c*. The superior density of the mercury renders it unnecessary to use this expedient in ascertaining the bulk of the vapour.

Fig. 80.

The measurement by means of water may be dispensed with, by having a vertical burette with compression stopcock accurately divided, and capable of indicating $\frac{1}{4}$ centimetres; it is filled to the normal point with mercury and, previous to removing the condensed fluid, the metal is to be allowed to run into the globe until the liquid arrives at the orifice; the quantity of mercury required to do this gives at once the volume of the residual air. I found this method to cause great saving of time, where many vapour densities had to be taken in succession.

135. The following very simple and (for most chemical purposes) sufficiently accurate formula [*], will give the density of a vapour, from an experiment conducted as above, in a minute or two; and will, even where it is intended subsequently to recalculate the experiment with all the corrections, be found useful to determine whether an experiment has been successful.

D = the required density of the vapour;

P = difference in weight between globe and air and globe and vapour;

* J. Müller, Annalen der Chemie und Pharmacie, xxviii. 162, and Liebig's Handbook of Organic Analysis, p. 114.

V = capacity of balloon in cubic centimetres;

v = residual air;

n_t = weight of one cub. cent. of air, at temperature at which the globe filled with air was weighed;

$n_{t'}$ = weight of one cub. cent. of air, at temperature of sealing the globe; we have therefore

$$D = \frac{P + V n_t}{(V - v)\, n_{t'}}$$

The values of n_t and $n_{t'}$ may be obtained without calculation by means of Table XVII., remembering that the latter is calculated for the Centigrade scale; and that if, therefore, the temperature was observed by a Fahrenheit thermometer, the degrees must be reduced to Centigrade by means of Table I.

136. If baths of fusible metal are to be employed, the following formulæ will be found useful.

FUSIBLE METAL.

Melting-point 200°.	Melting-point 208°·4.
1 part lead.	5 parts lead.
1 part tin.	3 parts tin.
2 parts bismuth.	8 parts bismuth.

It is very advantageous, in determining the vapour densities of bodies not previously examined, to make the experiment at gradually increasing thermometric intervals, for some bodies only obey the laws of permanent gases when heated very considerably above their boiling-points; for example, acetic acid (monohydrated), with a boiling-point of 240° at the normal pressure, gives the following densities at different temperatures:—

257°	3·180	338°	2·460	464°	2·090
266	3·105	356	2·438	518	2·088
284	2·907	374	2·378	590	2·085
302	2·727	392	2·248	608	2·083
320	2·604	428	2·132	637	2·083

It is sometimes the case that the vapour densities of bodies have to be determined whose boiling-points lie near that at which they begin to decompose; it is then very desirable to make the experiment under a pressure so much diminished that the substance will distil considerably below the temperature at which it undergoes change. For this purpose, M. Regnault proposes the

following arrangement:—A capillary tube, $a\,b$, fig. 81, ending in
an enlarged portion, $c\,d$, is attached to the balloon

with the aid of the blowpipe; the balloon being im-
mersed in the bath, it is, by |means of the tube
cd, made to communicate with a large bottle placed
in a water-bath, kept at a constant temperature,
not greatly differing from that of the atmosphere.

A second tubulature in the bottle communicates with a mercurial
manometer, which
constantly shows the
internal pressure,
and also with an air-
pump, by means of
which the air in the
bottle and balloon is
reduced to the re-
quired degree of elas-
ticity. The experi-
ment is then con-
ducted in the same
manner as usual, it
being only necessary
to substitute in the
formula the elastic
force of the air ob-
served on the mano-
meter for the ba-
rometric pressure*.

Fig. 82.

137. It now remains
to describe the second
process (devised by
M. Gay-Lussac) for determining the volume occupied by a given
weight of substance at a known temperature and pressure.
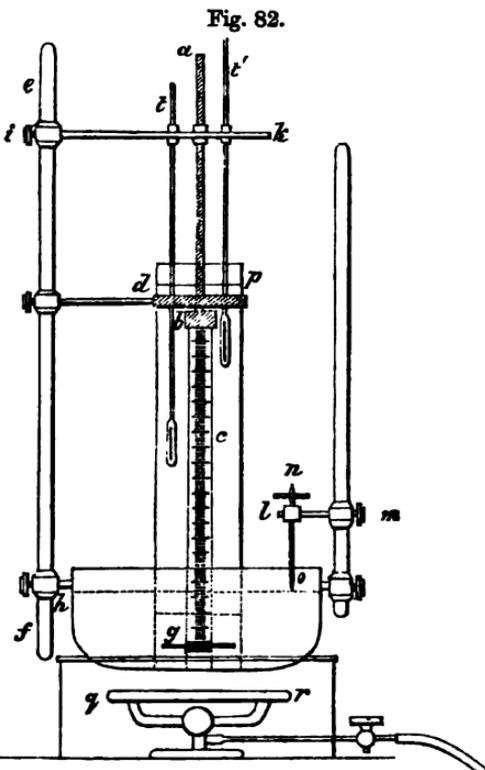
* Where extreme accuracy is desired, or where the above modification
becomes necessary, the reader is referred to M. Regnault's work, which con-
tains a very convenient formula, including all the corrections.

For this purpose, a glass jar, c, fig. 82, divided into cubic centimetres, is perfectly dried, and, after filling with mercury, is inverted in a pot of the same metal; a little very thin globe containing the fluid is then passed up under the mercury, so as to rise to the top of the bell-glass, c. A glass cylinder, open at both ends, is then lowered over the bell-jar, the latter being kept in the axis of the cylinder by means of three projections affixed to a small ring, g, sliding stiffly over the bell-jar. The cylinder is held steady by the ring, d, attached to a vertical rod, e f, passing through a nut, h, which is screwed to the iron pot. The vertical rod carries another arm, i k, having three apertures, one of them serving to admit the end of a rod, a b, the lower end of which carries a cap, b, which, by slipping over the top of the jar of mercury, assists, in conjunction with the three projections previously mentioned, in keeping it vertical and in the axis of the cylinder. Two other apertures in the arm serve to hold pierced corks through which pass the thermometers t t'. Another arm, l m, on the other side of the pot, is for the purpose of supporting a double-pointed screw, n o, the use of which will be mentioned presently. The cylinder is to be filled for an inch or two above the mercury jar with some fluid capable of supporting, without blackening, a temperature considerably above the boiling-point of the substance the vapour-density of which is to be determined. Water and neatsfoot oil will suffice for most purposes. The line, d p, shows the height of the fluid.

The gaslight, q r, being lit, the fluid gradually rises in temperature, and, before long, the globe will have broken by the expansion of the included fluid, its vapour gradually depressing the mercury in the bell-jar. If water is used (and the process is better adapted to fluids the boiling-point of which is below 212° than to those which exceed it), the heat is to be permitted to rise until it boils; the volume of the vapour, the height of the barometer, and the exact temperature are then to be noted.

It is evident that the external pressure is balanced partly by the vapour and partly by the column of mercury which rises in the jar above the level of the mercury in the pot. To ascertain the height of the latter, we note the division on the bell-glass to

which the inner level of the metal corresponds; the screw, $n\,o$, is then carefully turned until its lower end just touches the surface of the mercury. The water is then siphoned off, the interior being dried by filtering-paper; by this operation the metal will have receded from the screw, and more is to be added, until it again exactly touches its point. The mercury is now on the same level on both sides of the cylinder, and it is to be observed to what division on the bell-glass this level reaches. The distance between the two points thus observed on the jar is the correct height of the column of mercury, which, being reduced to 32°, is to be deducted from the height of the barometer (also reduced to 32°), in order to obtain the true pressure to which the vapour was subjected.

Having thus ascertained the volume which a known weight of substance occupies at a given temperature and pressure, we have merely to compare these data with the weight of the same volume of air at the same temperature and pressure.

The weight, W, of a known volume, V, of air at a given temperature, T, and pressure, P, may be obtained by means of the following formula:—

$$W = 0.0012932 \text{ grm. V.} \; \frac{1}{1 + 0.00367\,T} \cdot \frac{P}{760}.$$

By using a gas-flame, as represented in fig. 82, instead of the furnace usually directed, much assistance is gained in regulating the heat; for where the density is to be taken at comparatively low temperatures, it is otherwise difficult to make the thermometer immersed in the cylinder of water indicate the same temperature for even a few minutes.

I have contrived an entirely different apparatus for determining the densities of vapours, by measuring the volume of their vapour under known circumstances of temperature and pressure. It possesses some advantages over that described, inasmuch as it permits the pressure to be increased or diminished at pleasure; and enables us therefore to determine whether the vapour departs from the law of Mariotte at increased pressures. Another advantage is, that the heat is derived from steam thrown into the cylinder of water which serves to heat the bell-glass containing

the vapour; we are not therefore incommoded by the heat of the apparatus, while reading off the volumes: the quantity of mercury required is also very much less. The results will be given in the Appendix.

138. *Densities of Gases.*—There are several modes of determining the densities of bodies which are gaseous at ordinary temperatures. We shall confine ourselves to those which have been found in practice to yield the best results. The first of these is that of M. Regnault, and is detailed in his magnificent work on the laws of, and data for the steam-engine *. The annexed account, although condensed, will enable any person to use the method.

In order to lessen the influence of small but unavoidable errors of weighing, &c., large balloons, capable of containing 10 litres, are used. The balance also is large, but of great delicacy; for when charged with one kilogramme in each pan, it permits with certainty an appreciation of half a milligramme.

It is evident that the apparent weight of the balloons will be less than the real weight by an amount equal to the weight of a bulk of air of the same volume as the exterior bulk of the balloon; but if the density of the air remains invariable between the weighings, no error need be feared on that score; however, this is seldom the case. The temperature, humidity, and atmospheric pressure change so much, that great errors may be introduced, unless some method of obviating them is made use of. With this intention, the balloon in which the gas is weighed is counterpoised, not entirely by weights, but chiefly by another balloon of the same kind of glass, and of the same bulk. To do this, it is necessary to determine the volume of air displaced by the balloon in which the gas is to be weighed, and which we will call *a*. It is to be filled with water, and then weighed in water of the same tem-

---

* " Relation des expériences entreprises par ordre de Monsieur le Ministre des travaux publics, et sur la proposition de la commission centrale des machines à vapeur, pour déterminer les principales lois et les données numériques qui entrent dans le calcul des Machines à Vapeur. Par M. V. Regnault," Mémoires de l'Académie Royale des Sciences de l'Institut de France.

perature. The apparent weight of the balloon in water is so small, that this may be effected on the balance to be used for the densities. The balloon is now to be removed and weighed, after wiping, but still filled with water, on a strong balance capable of indicating one decigramme. The difference in the two weighings is equal to the weight of water displaced by the external volume of the balloon. Another balloon, b, fig. 83, of nearly the same capacity as a, but, preferably, a little smaller than that of the first and its stopcock, and made of the same kind of glass, is taken, and has

Fig. 83.
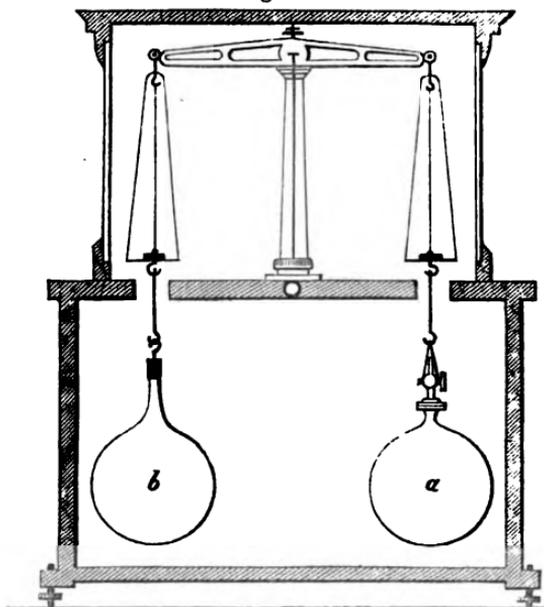
cemented to it a brass mounting, terminating in a hook, to enable it to be suspended from the balance-pan. If the united weight of the water displaced by the balloon, b, and its mounting is less by n grammes than the weight of the water displaced by the balloon, a, we must attach to b a glass tube closed at each end, and having an exterior bulk = n cent. cub. of water*.

* Because 1 cent. cub. of water weighs 1 gramme.

The engraving, fig. 83, shows the method of suspending the balloons beneath the scale-pans of the balance, in a chamber closed with glass doors to prevent currents of air.

The flask, *a*, has a stopcock attached to it, which allows it to be connected either with a three-way tube communicating with

Fig. 84.
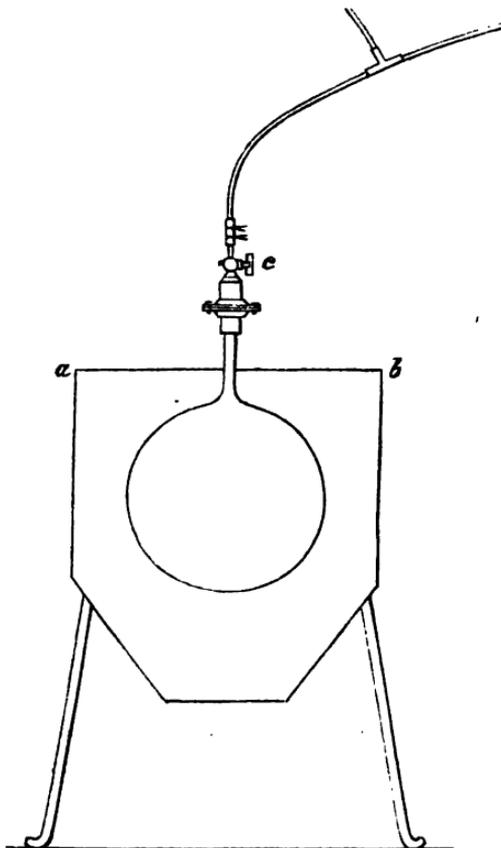
the gas-holder*, or with the air-pump.   The air having been removed as completely as possible, the gas is allowed to enter,

* Of course the gas must be absolutely pure and perfectly dry.

but, as a small amount of air still remains, the operation is to be repeated twice. Previous to the third

Fig. 85.

time of filling the globe, it is, after as complete exhaustion as possible, to be placed in a case, *a b*, fig. 84, and covered with melting ice; the cock being opened, the globe is allowed to fill with gas, and when full, a momentary communication is made with the atmosphere to equalize the pressure; the cock, *c*, is closed, the globe removed, wiped with a damp cloth to prevent electrical excitation, which might cause serious errors in the weighing, and suspended on the balance. It is not weighed until two hours have elapsed, so as to permit the temperature to become the same as that of the balance-case, and thus obviate currents of air, and also that its surface may be covered with the normal amount of humidity. After careful weighing, the balloon is placed anew in the case, *a b*, fig. 84, surrounded with ice, and the gas removed by the pump. It is necessary now to ascertain both the atmospheric pressure and the elastic force of the gas remaining in the balloon; for this purpose, an instrument called a barometric manometer is made use of. It consists of two tubes, A B and C D, fig. 85, attached to a support, which is secured perpendicularly to a wall. The tube, A B, is a barometer of 20 mm. interior diameter; the metal in the tube having been carefully boiled, it is inverted in a cistern of dry mercury. This cistern is a box divided
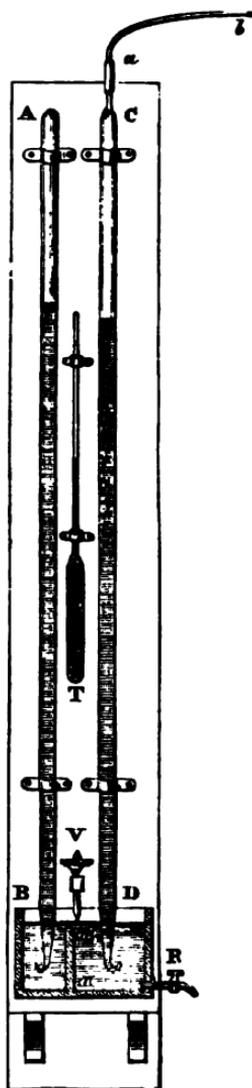
into two parts, the smaller of which serves for the cistern of the barometer. Into the second compartment is plunged the tube, C D, which has the same diameter as A B. C D is capable, by means of a leaden tube, $a\,b$, of being placed in communication with the balloon.

When it is intended to ascertain the atmospheric pressure by means of this instrument, mercury is poured into the cistern until it rises above the level of the division, $m\,n$. The double-pointed screw, V, is then adjusted until its lower end just touches the surface of the mercury. If, now, we measure, by means of a cathetometer, the difference of level between the surface of the mercury in the barometer and the upper point of the screw, and add to this the length of the screw previously ascertained, we have the height of a column of mercury exactly balancing the atmospheric pressure. The tube, C D, of the manometric apparatus, is, as we have said, to be placed in communication with the air-pump and the balloon, by means of the three-way tube and the leaden pipe $a\,b$. The gas having been removed, the cock communicating with the air-pump is closed, and the difference of level between the two columns of mercury in the tubes, A B and C D, is measured by a cathetometer; this difference is the measure of the elastic force of the gas remaining in the balloon. A thermometer, T, indicates the temperature at the time of the experiment.

The division, $m\,n$, in the cistern is necessary, in order to prevent air reaching the barometer in consequence of the great oscillations in the level of the mercury during experiments. The balloon, thus again exhausted, and having the elasticity of its residual gas known, is to be closed, removed, wiped and weighed as before.

The difference, $P-p$, between the two weighings represents the weight of the gas, which at $0°$ Cent.$=32°$ F. fills the balloon under a pressure equal to the barometric pressure, H, observed at the moment of closing the cock, diminished by the elastic force, h, of the gas remaining in the balloon after making the exhaustion. The weight of the gas at $0°$ Cent. and under the normal pressure of 760 mm. (29·922 inches), is obtained by the formula

$$(P-p)\,\frac{760}{H-h}.$$

139. A convenient method of taking the densities of gases is that described by Dr. Frankland in his researches on the isolation of the organic radicals. The same, or nearly the same, process was also used by Dr. Kolbe in his experiments on the electrolysis of organic compounds, the only difference being, that in the latter case the gasometer used (that described below) was one of more general applicability than that used by the former chemist. The following is the method of performing the operation :—The gas evolved in

Fig. 86.
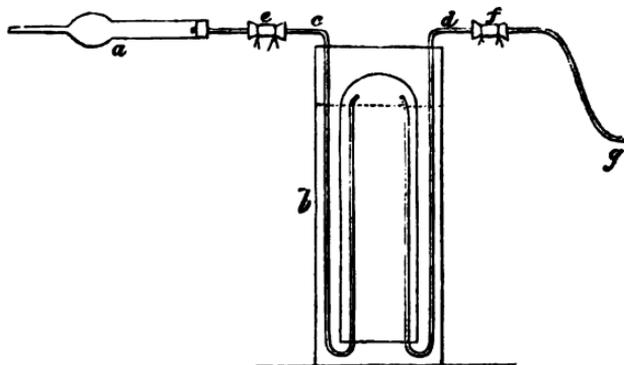
an experiment arrives through a chloride-of-calcium tube, *a*, by which it is dried; it then passes into the gas-holder, *b*, which consists of a cylinder of glass 3 inches in diameter and 11 inches in height, containing an inverted bell-jar, open at the lower extremity, and enclosing one vertical branch of each of the two U-shaped tubes, *c* and *d*. The bell-glass is fixed by a holder in its lowest position, and the apparatus filled with mercury to such an extent that the two tubes, *c* and *d*, through which the air contained in the bell-jar is expelled, rise only a few lines above its surface. Each of the caoutchouc connectors, *e* and *f*, has a piece of glass rod inside, small enough to allow of the passage of the gas under ordinary circumstances, but enabling the apertures to be securely closed by means of a silk ligature. The tube, *d*, communicates with the delivery-tube, *g*, which is so placed that its extremity may readily be dipped beneath the surface of mercury in a trough.

The gas is to be passed through the system of tubes and away by g, until all the air in the apparatus is expelled; the valve, f, being then tied, the gas accumulates in the inverted bell-jar, which is allowed to rise to a proportionate degree by means of the holder previously mentioned. When a sufficient quantity of gas is collected, the valve, e, is tied, and f being opened, the bell-jar is depressed and the gas is collected by the aperture, g. The density is taken in a light flask, capable of containing upwards of 200 cub. cent., and having a millimeter scale etched upon its neck. A few pieces of fused potash having been introduced into this flask (if the gas has been collected over water, in which case the drying tube, a, is unnecessary), and fixed to the glass by being first moistened with water and then gently heated, it is to be filled with mercury, and inverted in a vessel containing the same metal. The aperture, g, is placed under the neck of the flask and introduced within it, so that the orifice is above the level of the external mercury. The gas is allowed to enter until the internal and external mercury stand at the same level. A thermometer being now brought into the vicinity of the apparatus, the whole is allowed to remain for several hours in a room of constant temperature until the moist gas is dried by the potash. The thermometer, barometer, and height of the internal column of mercury above that in the outer vessel, are then read off by means of a telescope placed at the distance of a few feet, and the flask, after being securely stopped, without bringing the hand in contact with it, is to be weighed, afterwards filled with dry air, and lastly with mercury, the weight being taken in each case. If the apparatus for holding the gas has been filled with water, including the ingress and egress tubes, as is sometimes convenient, then the orifice, g, being inserted below the mercury of the trough, the water which escapes is to be removed from the surface of the metal by blotting-paper before inserting the exit-pipe into the neck of the flask.

SECTION X.

SOLUTION.

140. It is well known that one of the greatest obstacles to the free exertion of chemical affinity is the attraction of aggregation, the force, namely, by means of which the particles of bodies are held together; pulverization to a great extent obviates this source of sluggish action; but solution, by separating the particles to considerable distances, and by conferring mobility upon them, enables bodies which have a tendency to react upon each other, to do so, and that under the most favourable circumstances, for allowing a free exercise of their mutual action.

Moreover, by solution we are frequently enabled to separate substances of unequal solubility from each other; sometimes the separation is perfect, while at others the operation has to be repeated many times to ensure a complete division.

141. Water is by far the most widely employed and generally convenient solvent, but there is scarcely any liquid procurable with moderate ease, that may not be used with advantage under certain circumstances. It becomes therefore an extremely important matter that the chemist should so familiarize himself with the deportment of substances towards solvents generally, that he may in most instances be able with certainty to pronounce upon the best menstruum to be employed in any case which may come under his observation.

Among the fluids in ordinary use in research, the following may be mentioned; they are placed nearly in the order of their frequency of application:—Water, acids, alcohol, ether, alkaline solutions, wood-spirit or methylic alcohol, benzole, chloroform, and turpentine.

142. A few instances of the circumstances in which each of these liquids are applied will be of service to the beginner, and are properly prefaced by a glance at the general properties of solvents.

No fluid should be applied at random in endeavouring to bring a solid body into solution, but in every case it should be carefully considered what the object is that has to be attained; whether, for instance, it is desired merely to dissolve, or to have a chemical action exerted, and if the latter, of what kind. If the substance be a salt, water will generally effect our purpose; a little may be introduced in the state of powder or small fragments into any of the vessels mentioned below, and, water being added, the vessel must be agitated; if the substance disappears, the question is answered; if otherwise, the mixture is to be boiled, and, if still ineffectual, one or more of the solvents to be mentioned must be tried, carefully considering the chemical action which it is capable of exerting.

143. The acids most generally in use are the hydrochloric, nitric, sulphuric, acetic, and hydrofluoric; the first of these is the most resorted to in inorganic chemistry, as its compounds with metals are pretty generally soluble; and, moreover, its chemical effects are more limited than those of the nitric or the sulphuric. It is particularly valuable in analysis, from the fact of its forming an insoluble chloride with silver; if, therefore, we precipitate the chlorine of a metallic chloride by nitrate of silver, we at once, by ascertaining the amount of the latter, get a clue to the formula of the salt under examination. Chlorine, moreover, forms an insoluble protosalt with mercury, and a difficultly soluble one with lead; most other chlorides dissolve with comparative ease in water, and many are extremely deliquescent. On the other hand, we are acquainted with many examples in organic chemistry, of salts which are regarded in the light of bi-hydrochlorates and are yet almost insoluble. We may adduce in this manner, the bi-hydrochlorates of the chloro-compounds of some alkaloids and the bi-hydrochlorate of platino-pyridine.

144. In organic chemistry hydrochloric acid has many uses, as, for example, in extracting alkalies from plants, and condensing ammonia and other volatile bases in processes undertaken with a view to their purification or estimation: the chlorides of all the volatile bases, except ammonia, are exceedingly soluble

in alcohol; we thus have a valuable method of separation; and it is singular that the presence of the chloride of a volatile base diminishes the solubility of sal-ammoniac in alcohol, and thus greatly increases the accuracy of the result.

145. Nitric acid has many, and in fact, almost an equal number of uses, but of a different kind; before using it, we must remember its peculiar tendency to part with oxygen to the metals or other substances dissolved in it; in many instances this property may be turned to valuable account, but in others the reverse happens. Tin and antimony are converted into insoluble peroxides by its action, and are sometimes by this means separated from other metals which form soluble salts with it. Iron, or its proto-compounds, are quickly converted, especially on boiling, into salts of peroxide; copper, silver, and a few other metals, are more readily dissolved in nitric than any other acid.

It must not be forgotten, that nitric, and indeed most acids, act in very different ways, as they are more or less diluted; for instance, nitric acid has much less oxidizing action when very weak and at low temperatures, than when stronger and at higher temperatures; very weak nitric acid acts on excess of metallic iron with formation of protonitrate; but if the solution be even moderately heated, yellow fumes are evolved, and a pernitrate is the result. Again, if to a mixture of the oxides of cerium and lantanium which has been ignited, an acid solution containing 99 parts water and 1 part nitric acid be added, the oxide of lantanium is dissolved, to the almost complete exclusion of the cerium.

146. Sulphuric acid, in its concentrated form, has comparatively few uses as a mere solvent, but in a diluted state it acts upon some oxides and metals with ease; it is characterized by the insolubility of its compounds with lead, baryta, strontia, and lime; the three first being almost entirely insoluble in water, and the latter equally so in spirits of wine.

147. Hydrofluoric acid is extremely limited in its application, being seldom used except for the purpose of separating silica from compounds, from which it is with difficulty removed by other

means; hydrofluosilic acid being volatile, it may be expelled at a moderate heat.

148. Alcohol is much employed in organic chemistry as a solvent for alkaloids and numerous other bodies; one of its uses has already been alluded to under hydrochloric acid; it is also a solvent for some resins, and in fact, its uses in the organic are almost as manifold as that of water in the inorganic branches of the science. It is frequently necessary to subject organic bodies, generally mixtures from which it is wished to extract certain soluble constituents, to the action of alcohol or ether for a very long time, in order to thoroughly exhaust them.

149. Ether is chiefly used for dissolving resins and resinous matters, also as a solvent for fatty acids and many other substances.

150. Alkaline solutions are seldom used as solvents in inorganic chemistry; alumina, glucina, and uranium are, perhaps, the most commonly occurring instances; but in the organic branch many crystalline substances are separated from resinous impurities by means of them.

151. Wood-spirit is sometimes employed for the same purposes as ether, but its uses are more limited; it forms a good menstruum for shell-lac when required in the fluid state for cement. Its properties as a solvent are perhaps less known than those of alcohol and ether, and it is probable that they may be very much extended; methylated spirit, however, may be used with as good results as pure alcohol for almost every purpose requiring a spirituous menstruum.

152. Benzole, or the lighter portion of coal naphtha, boiling at 176° Fahr., is becoming much used as a solvent for alkaloids, especially for quinine, as in the processes of Herring and others; it may also be used for the preparation of cantharidine, strychnine, and many other organic bodies.

153. Chloroform is sometimes, but rarely employed; a solution of gutta percha in it is used as a species of collodion, and amber dissolved in it forms a beautiful varnish for photographic purposes. It also dissolves camphor and other resinous matters.

154. Turpentine holding camphor in solution is used as an assistant in glass-cutting with files, and other operations which will be mentioned in their proper places; it moreover dissolves caoutchouc, resin, and many other substances.

155. *Apparatus for Solution.*—The apparatus for containing substances while exposed to the action of solvents, is generally of the simplest character, consisting of test-tubes, retorts, flasks, basins, and porcelain and platinum capsules. They will be noticed in the order in which they have been named.

156. Test-tubes are of almost universal application in chemistry; they are thin cylinders of glass with rounded bottoms; the most convenient forms are those in figs. 87, 88, and 89, where they are depicted half the real size.

157. Where substances are to be dissolved in acids, and much vapour is evolved in the operation, it is essential, if exactitude is required in the experiment, to prevent the loss of particles mechanically removed with the escaping steam. This may be effected by placing the flask in a sloping direction; or, if the matter is carried over partly chemically and partly mechanically, as is the case with osmium during the solution of the ore of platinum in aqua regia, it is better to use a retort and receiver, as in fig. 90.

Fig. 87.

Fig. 88.   Fig. 89.
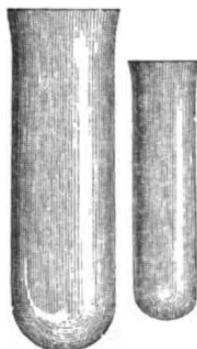
The forms of flasks which may be used for solutions are very various, and depend, to a great extent, upon the fancy of the operator. It is advisable to have them, when required exclusively for solution or precipitation, of the shape shown at fig. 94, which, it will be seen, has no shoulder or projecting parts where any solid matter can lodge, so as to be with dif-

ficulty removed. They may be held during the operation upon any of the supports mentioned in the section upon that subject. It is better to have them with flat bottoms. The flasks, figs. 91 and 92, are extremely useful for various analytical purposes during solution, filtration, digestion, or precipitation; but other forms are required in various other processes, and

Fig. 90.

will be described in their proper places.

The porcelain vessel, fig. 93, is very convenient, from the ease with which it can be cleaned out, and the porcelain capsules (figs.
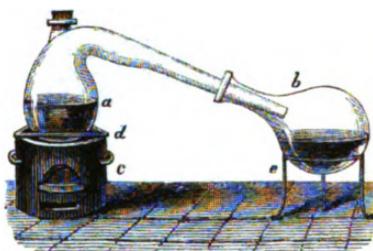
Fig. 91.   Fig. 92.   Fig. 93.   Fig. 94.

Fig. 95.

Fig. 96.

95 and 96), from the facility with which they are handled when hot. Beakers (figs. 97 and 98) are vessels of perhaps more extended use than any others in the laboratory; there is scarcely an operation in which they are not more or less required. From their thinness, they admirably withstand sudden changes of temperature; and their form particularly adapts them for precipitations, from the extreme ease with which every particle may be removed. They are generally sold in nests, and the laboratory should be well stocked with them.

158. Several glass rods, formed from what is known in the glass-houses as "cane" by cutting off lengths with a file, as

described under glass-cutting, and rounded by fusion at the ends,

Fig. 97.   Fig. 98.
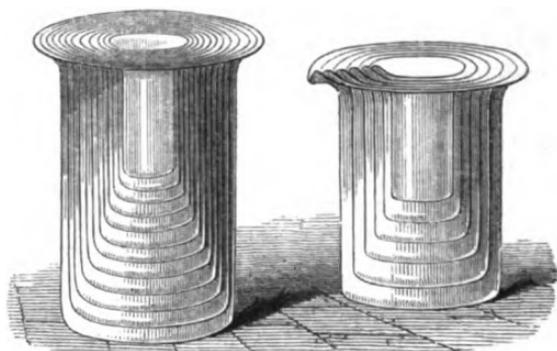
must be provided as an adjunct to the other apparatus for solution.

159. It should be remembered that great advantage is derived from a minute state of division, when it is desired to bring refractory substances into solution; as an instance of this, may be cited the fact, that if a little flint-glass be very finely powdered, and, after moistening, be laid on reddened litmus paper, the latter will be restored to its original blue by the alkali dissolved out of the glass by the water*.

160. It is of great importance, when a flask containing a solid matter and a fluid is to be heated, that the temperature is not raised too rapidly, as it is liable to endanger its safety; and the moisture which almost invariably condenses on the bottom should be removed with a cloth. Flasks, and other glass or porcelain vessels, when hot, must not be placed to cool on rapidly conducting surfaces, as such a proceeding is almost sure to cause its fracture. A very convenient stand for this purpose may be easily constructed, by winding list round tin or copper rings. A cold liquid should not be added to another when boiling; if unavoidable, it must be poured in by small portions, and over different parts of the surface of the hot fluid.

* See also Pelouze on the action of water on glass, Chem. Gaz., Sept. 15, 1856, and Comptes Rendus, July 21, 1856, p. 117.

161. Many substances during solution emit corrosive and offensive fumes; such cases may be met by placing the vessel emitting them under a hood or chimney, or in the close closet; or if none of these appliances are at hand, a tube may generally be adapted to the apparatus which will convey the vapour out of the window.

The arrangements for forming solutions of gases in water belong to the section on Gas Manipulation, and will be described in that portion of the work.

There are several operations in organic chemistry in which the object is to extract the soluble parts of plants. Sometimes this may be done by mere *infusion,* which consists in pouring a hot liquid upon the substance whose valuable parts are to be extracted. *Decoction* consists in boiling the material to be exhausted, for a considerable time; it is chiefly resorted to in manufacturing processes.

162. *Percolation* is frequently had recourse to in research, to extract the soluble constituents of vegetable substances. On the small scale, the apparatus, fig. 99, may be made use of; the lower end of the long tube at *e* is closed with a cork cut in notches, so as to allow the passage of the fluid; the vessel is then filled with broken glass to *a*, and moderately fine quartz sand to *b*; the substance to be exhausted is placed above this, and the solvent carefully poured on so as to avoid disturbing it; if properly done, the menstruum will slowly drop into the vessel, *c*; but even then the powder or other matter to be exhausted remains saturated with the liquid, and the latter has absorbed all the virtues of the material. We have now to displace this portion absorbed, by adding more of the liquid, equal in quantity to that remaining among the powder, in the same way that the first was introduced; the fresh liquid displaces the saturated portion,

Fig. 99.
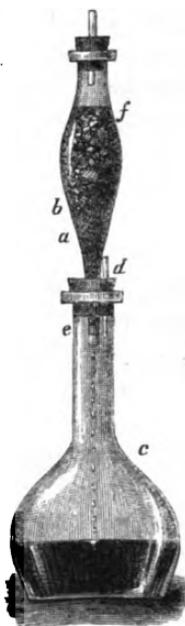
which then drops into the lower vessel, and is ready for examination. If spirit is employed, the greater part may be recovered by distillation. The tube, *d*, is to allow the air to escape as the fluid drops into the lower vessel: it is advisable, where spirit is used in this process, to adapt a tube with a small aperture to the upper opening of the vessel, *e f*, so as to allow enough air to enter to permit the descent of the menstruum, without at the same time permitting the spirituous portion of the solvent to escape.

163. M. Payen has contrived an apparatus for extracting the soluble constituents of organic bodies by continuous distillation. It is represented in fig. 100, where *a* is a two-necked flask, the longer of the two orifices being fitted with a tube, *b*, intended to contain the organic matters to be exhausted; they are packed with equal care to those intended for the ordinary process. The flask, which contains alcohol or ether, is heated by the water-bath, *e*, the temperature of which is regulated by means of the thermometer, *i*, supported by a cork attached to a rod sliding on the vertical bar, *f f*, which in its turn is supported by passing through an aperture capable of being tightened with a screw. The vapour of the alcohol passes by the tube, *c c*, into *b*, where being condensed among the animal or vegetable matter, it falls back into the flask, to be again raised as before. The three-bulbed apparatus, *d*, acts as a safety-tube, and also serves to condense any of the spirituous vapour which might otherwise be lost. The digesting vessel, *b*, is supported by the clamp, *h h*, which slides on the rod, *f f*. The gas-burner, *k*, enables the temperature of the bath to be regu-

Fig. 100.
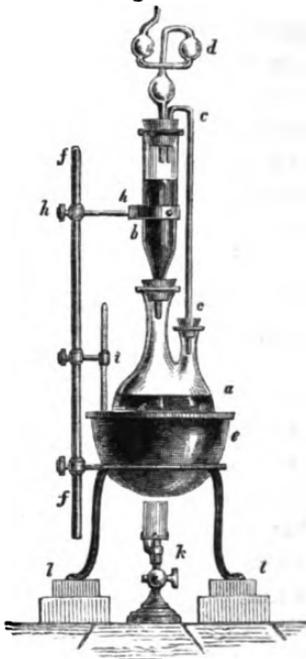
lated with more nicety than could be done with a spirit-lamp. The tripod is supported over the gas by the blocks of wood, *l l*.

164. In making solutions in analyses, it is constantly necessary to pour from one vessel to another, without spilling any of the liquid; and it is usual to have lips or spouts to vessels to facilitate the operation; but in most cases it is quite impossible, in spite of this arrangement, to prevent a small portion of the fluid from running down the outside of the spout, and consequently we are liable to a loss from this means sufficient to render an analysis worthless. In fact, when the vessels used have a flange (as in beakers, for instance), it becomes not only unnecessary, but a disadvantage, to have spouts; and with test-tubes and flasks, they are a great inconvenience. It is usual amongst chemists to prevent any source of error arising in this way, by first *slightly* greasing the lip of the vessel, and then pouring down a rod in the manner represented in the engraving, fig. 101; it is possible thus to avoid even the slightest loss, and the student should omit no opportunity of acquiring dexterity in operations of this kind.

Fig. 101.

It is advisable not only to apply a little grease to the lip of the vessel, but also to wet the rod with the liquid to be transferred, and, after placing it against the edge, to slowly raise the vessel until the fluid meets the glass rod; it will then run down it with perfect regularity, and may be directed even into the neck of a small flask as conveniently as by the use of a funnel.

165. Where basins are used for purposes requiring heat, the bottoms should be extremely thin, to enable them to bear rapid transitions of temperature; flasks also should have the bottoms thin; but as they are frequently used for gas manipulation and distillation, the necks should be somewhat stouter.

G

It is important to observe, that when a flask is to be placed upon a hot sand-bath, the bottom should be quite dry, as otherwise the water being converted rapidly into steam, scatters the sand about, and in all cases there is danger of fracture to the vessel if the precaution is neglected.

Much care is required in introducing weighed quantities of pulverulent substances into flasks where accuracy is desired; if, for instance, a piece of rough paper is used, or even if it be polished and yet not perfectly dry, the powder is liable to adhere, and thereby involve a loss; moreover, if the edge is not cut, irregularities will mechanically retain a portion of the material. Let it be supposed that a soluble substance is to be introduced from the platinum crucible, in which it was heated to redness and weighed, into a flask, as in the analysis of soda ash, by the methods of Fresenius and Will or Parnell; a flask must be selected the neck of which is not too narrow, and the contents of the crucible being dropped carefully into it, the washing-bottle (§ 200) may be used to rinse the crucible out. If, on the contrary, the substance is insoluble, and yet it is essential to transfer it into another vessel previous to its being dissolved, it may, as far as possible, be removed by dropping it from one vessel to the other, and the particles adhering to the first must be washed out by directing a stream of water upon it. The washing-bottle by which this is performed will be described in its place, at p. 142.

166. In operations connected with solution, it is necessary to be made acquainted with some circumstances which modify the solubility of substances in water; for instance, lime, which is only slightly soluble in pure water, dissolves abundantly in a moderately strong syrup, and the alkaline reaction of the lime is not in the slightest degree affected. This property may be made available in the solution of several analytical problems; a liquid of the kind is used by M. Peligot in his process for estimating nitrogen.

It is not uncommon in organic investigations to find crystals deposited, which on examination prove to be merely sulphate of lime, the solubility of which is, under certain circumstances,

greatly increased by the presence of organic matter. The student will also find in his Manuals of analysis how greatly the action of reagents is modified by this cause; one instance among many is the difficulty of precipitating oxide of copper by potassa in a solution containing sugar or other vegetable or animal substances.

In organic chemistry it is a common process to separate one substance, or group of substances, from complex mixtures by taking advantage of the solubility of one of them in some menstruum to the exclusion of the others; thus, the acids of coal oil may be separated by agitation with a strong solution of caustic alkali, and the bases from the same source may equally well be removed by agitation with acids.

One group of hydrocarbons may sometimes be separated from others by treating the mixture carefully with fuming nitric acid: the benzole and $C^n H^n$ series dissolve, and fluids which I have ascertained to possess the composition and other properties of some of the organic radicals are left unacted on[*].

[*] Proceedings of the Royal Society, May 22, 1856, and January 22, 1857.

SECTION XI.

PRECIPITATION.

167. Precipitation is one of the most valuable processes for separating substances from each other, and is perhaps the most frequently used operation in research. It depends upon the conversion of substances from a soluble to an insoluble state, with reference to the menstruum employed. When a substance in solution has a reagent added to it which contains a body capable of forming with it a comparatively insoluble compound, the latter falls to the bottom of the liquid with different degrees of readiness, depending upon its state of density, aggregation, or insolubility, and is then said to be precipitated. It sometimes happens, although the matter previously in solution becomes insoluble and separates, that, from its want of density, it floats or remains suspended; nevertheless, by a convenient expression, it is generally said to be precipitated.

The instance last alluded to, where a substance is added capable of forming an insoluble compound with the matter which it is wished to separate, is by far the most common kind of precipitation, but there are numerous other cases arising from very different circumstances. A change of temperature of the solvent will frequently induce precipitation, but then the matter separating in the solid state frequently assumes a regular form, and is said to crystallize, the term precipitation being more frequently used to designate an amorphous condition. As an instance of the effect of temperature upon precipitation, may be cited the case of an admixture of a soluble salt of lime with a very dilute solution of a soluble sulphate; no precipitation takes place in the cold, but, on boiling, the sulphate of lime assumes the crystalline form and precipitates. Titanic acid is sometimes separated in the insoluble state by the mere boiling for a considerable period of the solution containing it.

168. Precipitation is also frequently effected by converting

substances from one state to another, by passing a gas, generally carbonic acid, sulphuretted hydrogen or chlorine, into a solution containing them. Alteration of the nature or proportions of the solvent present will also effect precipitation: if excess of nitric acid be added to a moderately strong solution of nitrate of baryta, the salt is precipitated, being comparatively insoluble in nitric acid; it is highly desirable to be quite familiar with cases of this kind, persons often concluding that nitric acid contains sulphuric acid from the fact, that, on adding strong solution of nitrate of baryta to the undiluted acid, they have found a white powder fall. The precipitation of alcoholic solutions of the resins and of camphor by the addition of water is also a somewhat similar case.

169. It will be seen, from what has been said, that precipitation is one of the best and most generally applicable means of separation of bodies, and that it is essential for the student to acquire a good general knowledge of the nature of precipitates, and of the methods of separating substances by this means as a step towards their estimation. A careful operator will always consider, before adding a precipitant, the order of sequence, and the substance best adapted for the purpose. If, for example, it be desired to ascertain the presence of sulphuric and hydrochloric acids in the same portion of a solution, some judgment is required; for, if chloride of barium be added to demonstrate the presence of the sulphuric acid, it becomes impossible to test the same portion of liquid for hydrochloric acid, as chlorine has been introduced in combination with the baryta; but if nitrate of baryta be added, and the precipitated sulphate be filtered off, it is possible to detect the chlorine in the filtrate by nitrate of silver.

It will be seen to be imperative that a pure salt be used in testing, for if the nitrate of baryta used is contaminated by the presence of chlorine, of course a source of error is at once introduced. Fortunately, however, nitrate of baryta is more easily freed from chlorine than most other salts.

170. Sometimes it is desirable to remove one substance from a solution without introducing any other matter into the resulting

product, as in precipitating the sulphuric acid from the sulphates of potash or soda in the process for preparing the pure caustic alkalies; this may be done by adding caustic baryta somewhat in excess to the solution until the whole of the sulphuric acid is rendered insoluble as sulphate of baryta, the small excess of baryta being easily removed, for as the liquid is boiled down, it attracts carbonic acid from the air and becomes insoluble.

171. Where exact precipitation is required, as so frequently happens in analytical operations, the precipitant must be added by degrees, it being generally advisable to agitate the liquid the whole time, in order to facilitate subsidence; this may be done by stirring with a glass rod. When the solution to which the precipitant has been added is dilute, it is generally easy to ascertain the completion of the process, because the precipitate falling leaves a portion of the liquid clear, so that the action is easily controlled; but where strong solutions are used, the fluid frequently becomes nearly solid (this is well seen by adding ammonia to acid solutions of cinchonine, quinine, or peroxide of iron); here it is advisable to dilute the whole of the solution with water, but if this is inadmissible, a little of the mass may be stirred up in a small glass with a little water, and, after filtration, be tested. It is requisite in cases of this kind to thoroughly stir the thick mass before any is removed to be tested, as otherwise it is impossible to make sure that the precipitant has been perfectly incorporated with the solution to be precipitated.

172. It is frequently extremely advantageous to add a considerable excess of the precipitant if rapid subsidence is desired; an excess of acid also is sometimes used for this purpose with great success; and further, it often happens that a precipitate which otherwise requires a long time to settle, does so rapidly on the application of heat. In some instances, as that of the precipitation of sulphuric acid by nitrate of baryta or chloride of barium, it is proper to add the precipitant in excess to a hot solution, and then boil for a short time; by this means rapid subsidence is effected, and error arising from the tendency of the precipitate to pass through the filter is obviated. As in all laboratories a vessel is

kept to receive the silver solutions which are constantly accumulating, it is of no importance, in an economical point of view, that an excess of nitrate of silver be employed in precipitating hydrobromic or hydrochloric acids. It is desirable always to have an excess of hydrochloric acid in the silver-washing recipient, so that it is merely necessary to pour off the liquid and throw it away when the vessel becomes filled, as the whole of the metal will be found at the bottom as chloride.

173. It is by no means indifferent whether, as a general rule, precipitants are added to hot or to cold solutions, for the condition of the resulting product is often materially influenced by this cause alone; if, for instance, hot liquids be used in precipitating iodide of lead or biniodide of mercury, the whole of the salt is not deposited immediately, but on cooling a considerable quantity of crystals fall, and from their extreme beauty, this process is often adopted purposely.

In organic chemistry it is frequently inadmissible to heat solutions previous to precipitation, as this method of procedure would often decompose substances of no great stability. Solutions of the platinum salts of organic bases undergo remarkable alterations by even short exposure to temperatures at or even below 212° Fahr.

In analytical investigations it is very common to wish to ascertain by precipitation whether a substance suspected to be present be really so or not, and cases of this kind are so numerous, that it is difficult to propose a general rule which shall be applicable at all times; there are, nevertheless, a few points worthy of being remembered. If the precipitate looked for be coloured, the cylinder containing the solution to which the precipitant has been added may be placed upon a sheet of white paper, when, if any perceptible quantity be present, it will become evident, after a short time, on looking down the vessel, so as to observe through a considerable thickness of fluid. If precipitation is not immediate, stirring will not unfrequently determine its formation; if this be unsuccessful, heat may be applied; if this does not effect the purpose, it is seldom that any other operation will enable us to obtain the indi-

cation sought, unless, as sometimes happens, the solutions were too dilute; by evaporation of a considerable portion of liquid to a small bulk this difficulty may of course be overcome, and this is the method adopted in the analysis of mineral waters, where, from the extreme dilution of the solutions, almost the only matters capable of ready precipitation are the sulphuric and hydrochloric acids.

. 174. It sometimes occurs that the addition of alcohol will cause a precipitation, and this method is often used for the separation of sulphate of lime, as such, from solutions.

Potash, soda, and ammonia are constantly in request for precipitating metallic oxides, but there are also numerous *salts* which are separated from solutions containing them by those reagents, and it is of much importance to be aware of this in order to avoid serious error. If either of the alkalies alluded to be added to solutions of alumina or peroxide of iron containing phosphoric acid, the whole of the latter is also removed as phosphate of iron or alumina. Phosphate of lime is also precipitated by them. A series of reactions, arising from the singular manner in which phosphoric acid tends to follow metallic oxides while being precipitated, led one of the most illustrious of modern chemists into the error of raising the subphosphate of yttria to the dignity of a new metallic oxide.

. 175. Metallic oxides, when precipitated by alkalies, frequently carry down with them a considerable portion of the precipitant, which it is often very difficult, and sometimes impossible, to remove perfectly by washing; this makes ammonia extremely valuable as a precipitant of such substances, from the facility with which it is removed by ignition.

176. It has been said that agitation frequently assists in determining the subsidence of a precipitate; this must not be lost sight of in performing the assay of silver by the volumetric method; in this process the solution of silver is contained in a stoppered flask, and if, after each addition of the standard solution of chloride of sodium, the flask be violently agitated, the chloride of silver settles with remarkable rapidity. Sometimes the precipitate adheres to the vessel only in the places where the glass rod

has touched; this peculiarity has not, it is believed, as yet met
with a really satisfactory explanation.

177. Where metallic oxides are to be precipitated by sulphu-
retted hydrogen, it not unfrequently happens that if present in
very minute quantity, the only effect of the gas is to create a slight
change of colour, best seen by looking down the test-glass.

One of the uses of precipitation arises from the facility with
which it enables us to obtain organic acids in a state of purity
from their compounds with lead, silver, baryta, or lime; the acid
having been precipitated in combination with either of these oxides,
or obtained in that state by some other means, it is possible in
each case to remove the base by selection of the proper precipi-
tant, and a careful performance of the operation.   When acids are
obtained in combination with lead, the latter is generally removed
by sulphuretted hydrogen gas; silver may be separated by the
cautious addition of hydrochloric acid; baryta by a dilute solution
of sulphuric acid, and lime by oxalic or sulphuric acids: in the latter
case, it is generally necessary to add excess of alcohol to determine
the complete separation of the sulphate of lime.

178. Certain salts of acids are sometimes met with in nature:
the dark brown semi-crystalline deposit from the concentrated
decoction of cinchona bark consists chiefly of kinate of lime, which
was contained in the bark; and after purification of the salt, the
earth may be removed in the manner above indicated, and the
kinic acid obtained pure and white by crystallization and treatment
with animal charcoal.

In quantitative estimations, it must not be forgotten that the
stirring-rods almost invariably remove some of the precipitate;
this portion should be recovered by the use of the washing-bottle.

179. The student cannot be sufficiently careful to render him-
self familiar with the habitudes of substances, in order that he
may be enabled successfully to modify his processes according to
the peculiarities of the materials which may come under his notice.
It is generally necessary to neutralize acid, and sometimes even
alkaline solutions, before adding precipitants; this must not be
lost sight of in practice.

It very commonly occurs that the electro-chemical relations of metals may be made available for their separation and examination; in fact, one of the prettiest applications of science to the arts is the electrotype, by which it is possible to obtain fac-similes in copper, gold or silver, of almost any object capable of being copied in wax or plaster. If a plate of copper be immersed in an acid solution of silver, the whole of the latter metal is deposited in a state of purity in the form of a powder; and the method affords an easy, and frequently extremely convenient, method of obtaining the metal in a state fit for conversion into nitrate or other salts of silver. If a solution of cadmium be placed in a platinum crucible with a piece of zinc immersed in the fluid, the whole of the former metal is deposited on the platinum, and after washing, which may be performed without fear of removing the coating, the pure cadmium may be dissolved in nitric acid.

180. When chloride or bromide of silver is fused in porcelain capsules in the process for estimating hydrochloric or hydrobromic acids, it becomes so strongly attached that it is generally unsafe to attempt its removal by mechanical means; but if a piece of zinc be placed in the capsule touching the fused mass, and a little hydrochloric acid added, it may, after a few minutes, be removed with facility.

There are some few cases where, although a precipitant has been added in excess, the action, nevertheless, is incomplete, a certain portion of the metal, &c. remaining in solution; it is then sometimes admissible to finish the precipitation with another reagent; this procedure is frequently applied to zinc in analysis, and sometimes even in manufacturing operations; if, for example, the solution procured by digesting excess of zinc with iodine and water, in the process for making iodide of ammonium (a salt once much used in photography), has excess of carbonate and some caustic ammonia added, the greater portion of the metal present will be removed as a bulky white precipitate of carbonate of zinc; but a somewhat considerable amount still remains in solution, and must be precipitated by sulphide of ammonium, the latter also removing any

iron which may have been present in the zinc and not precipitated by the mixture of carbonate and caustic ammonia.

181. Substances may often exist in solution, yet not in the condition in which they afford characteristic reactions; when this occurs, it becomes necessary so to modify their state that they may with proper reagents afford the reactions required; for instance, if iron is present in the state of protoxide, it is generally essential to peroxidize it before adding the usual precipitants to it, unless, of course, it is intended to throw it down as protoxide or proto-sulphuret. When calomel is to be examined in the humid way, and it is desired to form the very characteristic scarlet iodide of mercury, it may be boiled with nitric acid and evaporated gently to dryness, after which treatment it can be precipitated as perio-dide by the careful addition of iodide of potassium.

It is necessary to be on our guard against the many circum-stances which modify and sometimes prevent the action of pre-cipitants; organic matters especially have a retarding influence upon precipitation: it has been said before that a very small quantity of sugar or other organic matter prevents the complete precipitation of oxide of copper by potash, even after protracted boiling. Moderately acid solutions of antimony are precipitated by water, but if tartaric acid be added, it enables us to dilute the solution to any extent that may be required; this peculiarity may be made valuable use of in the analysis of minerals and alloys containing that metal, the more especially since organic matters have no power to prevent the precipitation of antimony by sul-phuretted hydrogen.

182. Gases, particularly hydrosulphuric acid, are greatly used as precipitants in both organic and inorganic research; it becomes important therefore that the student should acquire familiarity with the methods of using them: the details of the processes will be found in the chapter on Gas Manipulation, but as there are several points which more particularly belong to this section, they will be pointed out.

Gases should never be passed directly from the generating vessel into the solution to be acted on, as it is invariably found

that they carry over mechanically a portion of the acid, &c. into the fluid under examination, thereby involving a source of error. The methods of preventing this are numerous, and will be pointed out in their proper place.

Gases are not only used with the intention of causing precipitation, but sometimes also to modify the state in which a substance exists in solution, so that it may afterwards be separated from others, which, although existing in the same fluid, are either not at all, or much less acted on by the same reagent; for example, in Rose's excellent method of separating cobalt and nickel, chlorine is passed into the hydrochloric solution until the cobalt is peroxidized, while the nickel remains unaltered, after which carbonate of baryta is added until the cobalt is precipitated, the nickel remaining in solution.

The action of sulphuretted hydrogen upon metallic solutions has been so well studied, that it has become one of the most valuable methods of qualitative, and in some cases quantitative separation. Its action is different accòrding as the solutions exposed to it are acid or alkaline; the nature of the compounds formed, and the subdivision of the metals, &c. into groups by the action of hydrosulphuric acid, sulphide of ammonium, &c., belong to manuals of analysis, and will not therefore be dwelt upon here; but it may, notwithstanding, be mentioned, that some clue to the nature of the precipitate is frequently to be obtained by observing the colours of the precipitates. When, after the passage of hydrosulphuric acid gas through a metallic solution, a white precipitate is obtained, which proves to be quite volatile, it consists entirely of sulphur, and is generally due to the presence of peroxide of iron, which is reduced to the state of protoxide by the hydrogen of the gas, the sulphur being at the same time precipitated. We shall allude to this again in another part of the work.

If the precipitate is yellow, we may look for cadmium, persalts of tin, arsenic, or antimony; a black one, on the other hand, may be occasioned by the presence of copper, lead, protosalts of tin, gold, bismuth, platinum, palladium, and several others of the same group. Zinc is precipitated from neutral solutions as a white or

pinkish sulphide; it is also thrown down from its solution in acetic, but not hydrochloric acid.

When a nitric solution of vanadiate of lead is precipitated by sulphuretted hydrogen a peculiar blue tint is produced, the vanadic acid being at the same time reduced to a lower state of oxidation.

183. It is very often necessary to pass a stream of carbonic acid through solutions containing free lime, in order to remove the latter as carbonate; in this case it is imperative to heat the solution after the passage of the gas and before filtering, in order to expel excess of the gas, which might have redissolved any of the lime as bicarbonate; as an example may be mentioned the solution formed by neutralizing with lime the acid liquor produced by distillation of sugar or starch with peroxide of manganese and sulphuric acid in the preparation of formic acid; the filtered liquid is found to contain excess of lime; on passing carbonic acid through, the free lime is thrown down, and, if continued long enough, is partly redissolved; on heating the solution to boiling for a short time, however, the carbonate of lime is all removed on filtration, and the solution contains no lime save what is in combination.

Lime is much used as a precipitant of iron, more especially on the large scale and in technical operations, but it is essential that for this purpose the metal should be in the state of peroxide; and there are several other precautions which are necessary to success, all of which, perhaps, are required in producing the commercial white fused chloride of zinc, much used in medicine. In giving the details of the operation, it is to be understood that the same process, or a modification of it, will be necessary in almost every case where a substance containing protoxide of iron is to be freed from it by lime, and it is of course for this purpose that the method is introduced. Commercial metallic zinc is to be dissolved in hydrochloric acid, a considerable excess of zinc being present; the whole is digested for a day or two, by which means the lead, copper and some other metallic impurities are thrown down and removed. The liquid is filtered and concentrated by heat,

while boiling nitric acid is added in small quantity until the iron is converted into peroxide; the whole is then boiled to dryness and fused; the cake is, when cast out to cool, of a red colour, and is to be dissolved in cold water; the liquid becomes heated during the process of solution, and must therefore be allowed to repose until quite cold: if, now, the moderately diluted fluid has a little cream of lime, or, preferably, an ounce to the gallon of prepared chalk added, and the whole be well mixed, and after about ten hours filtered, the liquid which comes through will be perfectly colourless and not contain a trace of iron. When fused, the salt, if the previous directions have been carried out, will be of the purest white. The same procedure with regard to the nitric acid and subsequent operations may be employed in preparing white fused chloride of calcium, and in many other operations.

184. Precipitation, when the result of a somewhat sluggish chemical decomposition, may be facilitated by exposure of the reacting materials to a very gentle heat. To illustrate this, the precipitation of gold by protosulphate of iron or oxalic acid, may be mentioned; moreover, nitrobenzole, when being acted on by alcoholic solution of sulphide of ammonium, should be placed in a moderately warm situation. This is an instructive example, because the amount of sulphur is an index to the quantity of aniline produced, and the reaction may be viewed as the type of many others, where, the substance sought being in a fluid state, the amount formed during the operation may be estimated by the quantity of precipitate. This process is, however, not the best means of obtaining aniline from nitrobenzole, protacetate of iron being far more effectual.

185. In organic chemistry, perhaps more care is required in the choice of precipitants, and in the method of adding them, than in the inorganic department of the science; and this is caused partly by the easy decomposability of organic substances generally, and partly by the fact, that when the precipitate is obtained, the liquid frequently has to be examined for other complex substances, which would be more difficult of separation after the addition of an unnecessarily large quantity of the precipitating reagent.

Sometimes much advantage may be gained, where two precipitants at the first glance appear equally eligible, by a careful selection; narcotine is equally well precipitated by ammonia and potash, but if the latter be used, the resins present are retained in solution, and the narcotine is obtained pure and white with much greater ease than it would otherwise have been. In the preparation of picric acid, the same precaution may be taken, but greater care is required to prevent solution of the salt, which takes place where too great an excess is used.

186. In laboratories where a valuable substance, not absolutely insoluble, is frequently being precipitated, it is sometimes advisable to preserve the mother-liquids, and at a convenient time to concentrate them, and recover by proper methods the portion dissolved.

It is sometimes found that where two substances exist in solution, each capable of forming an insoluble salt with some reagent, that nevertheless by a careful addition of the latter, the whole of one of the two ingredients in the solution may be thrown down in the first portions of the precipitate, that subsequently obtained containing the other material; this method of research, which is termed fractional precipitation, is probably capable of being much extended. A mixture of fatty acids may be separated by adding solution of nitrate of silver in small portions to a solution of the soda or ammonia salts, and filtering after each addition. The first precipitates, of course, contain those acids forming the most insoluble salts with silver.

187. The apparatus used for precipitation is almost the same as for solution: Phillips's jar, fig. 102, is employed for the collection of precipitates, and, from the conical form, allows them to subside rapidly, but the beakers, figs. 97 and 98, are equally or better adapted for the purpose; and in fact the beaker is in most cases preferable, not only from the extreme convenience of its shape, but also from the facility which it affords for heating the liquid before or after precipitation.

The test-glass, fig. 104, is the most convenient shape I have seen; it may be made about one and a half times the size of the

engraving, unless required longer for demonstration. The tall glass, fig. 103, is well adapted for lecture experiments, if made of

Fig. 102.

Fig. 103.

Fig. 104.

a considerable size. They are sometimes made of the same shape as that represented in fig. 103, but blown at the lamp and exceedingly thin, and thus resemble a test-tube on a foot; they are very convenient in many experiments of a delicate character.

Flasks of the form and size of the porcelain digester, fig. 94, page 117, are admirably adapted for the precipitations in quantitative analysis, where only small quantities are worked upon; their shape renders them extremely easy to cleanse, as it is possible to insert the finger against any part.

188. In precipitations on the more minute scale, as in microchemical experiments, test-tubes may sometimes be employed; but they are far from convenient in quantitative experiments, unless made short and wide.

Porcelain vessels from their opacity are objectionable in precipitations, and are therefore seldom employed.

The washing of precipitates is an operation which is so much more conveniently discussed under the head of Filtration, that it has been placed in the next section.

SECTION XII.

FILTRATION AND WASHING OF PRECIPITATES.

189. In analytical operations, it almost always happens that filtration immediately follows the formation of a precipitate, its object being to collect the substance together, to enable all soluble matters to be removed by washing; but sometimes it is considered preferable to wash the precipitate by the process called decantation, which consists in adding a considerable quantity of water to it in some convenient vessel (preferably a tall and narrow one), and, after thorough incorporation of the washing-fluid and the precipitate by stirring, it is allowed to settle until the whole of the solid matter has been deposited; the fluid is then poured off, and the operation repeated until the precipitate is sufficiently washed, the latter point being ascertained in all cases by testing. When the washing is completed, the precipitate is freed from water as much as possible by a siphon, or careful pouring off, and the rest is removed by a pipette, or fold of bibulous paper, after which the precipitate may generally be placed in a warm place to dry. It is convenient to transfer the wet precipitate to a capsule or evaporating basin, in which to complete the removal of the water and subsequent desiccation, as the capsule or dish may, without fear of injury, be placed upon a sand-bath to dry.

Fig. 105.

190. Where the water cannot well be poured off from a precipitate without danger of disturbing it, it is advisable to use a siphon to remove the liquid, as in fig. 105. The leg in the liquid has the end turned up, so that the precipitate is not disturbed by the current.

Methods of constructing very convenient siphons for this

and other purposes will be found in the section on Glass-working.

191. Filtration is, in fact, a species of sifting, being a process by means of which we separate more dense and coarse from finer and more subtile particles, by the use of a medium capable of letting the latter pass through its pores while the former is retained. It will easily be seen, therefore, that many substances are capable of performing a function of this kind under certain circumstances; and in practice several varieties of filters are employed, according to the numerous cases which have to be met: paper, calico, flannel, sand, glass, asbestos, tow, and many other media may be resorted to with advantage in chemical processes, where a solid is to be separated from a liquid; at present we shall only have to deal, at any length, with paper, that being almost exclusively used in experiments of research.

It is of the greatest importance to the chemist that his filter-papers should be of unexceptionable quality, yet, until within the last few years, it was a matter of extreme difficulty to obtain a paper even tolerably well adapted for the purpose; now, however, such an advance has been made in this respect, that excellent paper may be easily procured, already cut to the most convenient shape.

192. There are several properties which ought to be possessed by a good filtering-paper; in the first place, it ought to filter rapidly, and yet it should be sufficiently close in its texture to retain the finest powders; it must not become too rotten when wet, or it is liable to break by even the most careful pouring of a solution into it. It is highly desirable that it should contain no soluble salts, or several sources of error are introduced into experiments. It is, moreover, especially necessary that, if any soluble matters *are* present, they should not consist of sulphates or chlorides.

193. It is proper to caution the student against the fallacy of supposing, that because filters are of the same size they must necessarily be of the same weight. It has been recommended to collect precipitates upon a double filter, and when the washing is

completed, to dry the precipitate upon both filters, and in weigh-
ing to place the second filter upon the opposite scale of the ba-
lance as a counterpoise, the increase of weight of the one filter
being supposed to. indicate the weight of the precipitate; but
this procedure involves more than one source of error: it is, how-
ever, merely necessary to instance one, which is, that the texture
of paper is so irregular, that even when cut by an arming-press,
as is generally the case with the circular filters found in com-
merce, it is extremely rare to find two of the same, or even of a
tolerable approximation to the same weight.

194. By far the most convenient shape for a filter is that of a
circle, as it then folds without any projecting parts, and exactly fits
the funnels, provided they are constructed with the proper angle.

They should not, when burnt, yield more than $\frac{1}{400}$ to $\frac{1}{500}$ of
their weight in ashes; and it is a good plan to burn a dozen of
each of the sizes in use in the laboratory separately, and ascer-
tain the weight of the ash; this amount, divided by 12, will give
the average weight of the ash of one filter, which is therefore a
constant quantity to be deducted from the weight of precipitates
ignited with filters.

195. When it is desired to collect a precipitate upon a weighed
filter, with the intention of ascertaining the weight of the former
by the increase of the latter, it is important to ascertain whether
the filtering-paper contains any soluble matters, as if so, the paper
loses during washing, and thus vitiates the result unless precaution
is taken to prevent it, by washing the filters intended to be used
for some time with hot water; when, after being dried, they may
be employed for the purpose alluded to, without much fear of
error.

196. There are two methods of folding filters in use in the
laboratory: the first is by far the more useful and convenient,
and is performed with ease and rapidity; the second is, on the
contrary, seldom used, and whenever necessary, may probably
with much advantage have a calico-bag filter substituted for it.

If a square piece of paper be folded in half, diagonally, and
then into quarters, it will form a triangular figure like that in

fig. 106, and if the corners are cut off in the direction of the curved line, a circle will be formed on opening out, the mode of

Fig. 106.
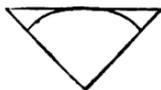
Fig. 107.
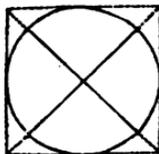
Fig. 108.

formation of which is seen by fig. 107, where the dotted lines represent the parts removed; upon opening the folded paper, so that three thicknesses come on one side and one on the other, a filter is obtained, as shown in fig. 108, which merely requires to be placed in a funnel supported by a retort-stand, or other convenient instrument, and is then, after being wetted, ready for the reception of the liquid to be filtered.

197. The ribbed filter, as it is called, was in considerable use among the older chemists and pharmaceutists, but is now very little resorted to, from its requiring some time to construct, and when made, being far from convenient, especially where the solid product of a filtration is the part required for use. It is obtained by taking a piece of paper, and after doubling it, folding it into halves, quarters and eighths, as in fig. 109, where it is seen that the creases are all on one side of the paper; the foldings are now repeated on the other

Fig. 109.

side, each crease coming between the previous ones, and projecting in the reverse direction; if the paper be now opened out and then depressed in the centre, a filter resembling fig. 110 will be obtained, and after cutting off the spires, may be dropped into a funnel, and the liquid to be filtered poured in. The intention of having the ribs, is to afford passages for the air and liquid between the paper and the funnel, so as to allow of rapid filtration; the whole arrangement is seen from fig. 111, where a funnel con-

Fig. 110.

taining one of these filters is supported by a piece of wood perforated in the centre and placed over a beaker.   In quantitative experiments the plain filter, single or double, is invariably used, the ribs and creases of the other rendering it almost impossible to remove a precipitate thoroughly from its surface. Where large numbers of filters are used, it is economical to purchase the paper in sheets, and cut it into circles for use in the laboratory, instead of buying the circular filters ready made. For this purpose an apparatus of great simplicity and convenience has been contrived by Mr. Stevenson, a philoso-

Fig. 111.

phical instrument maker of Edinburgh.   It consists of several discs of metal of the sizes of the filter to be cut; to the centre of each is capable of being attached a moveable rotating arm, carrying a knife which, by means of a very simple arrangement, may be adjusted to any size of filter.   With a little practice, filters may be cut with great perfection by it.

198. When a filter and its contents, or a filter alone, have to be weighed after drying, it is necessary to do so in such a manner that they shall not be in contact with the air, for dry paper is so excessively hygroscopic that, under the circumstances mentioned, the filter would greatly increase in weight, even during the short time required for it to be on the pan of the balance. A very good method of weighing filters is between two watch-glasses ground at the surface and held together by a clip, fig. 61.   In some cases a wide test-tube, like that represented in fig. 88, but fitted with a cork, may be used, or even a platinum crucible with a close-fitting lid is available under certain circumstances.

199. In most filtrations it is necessary to support the filtering-paper in a funnel; and the latter must invariably be of glass for all purposes connected with research.   Funnels should be made to an angle of 60°, in order that the circular filters may accurately fit.   It is, moreover, desirable for them to be ground on the top, to enable a glass plate to be used as a cover when required, either for the purpose of preventing the access of dust,

evaporation of spirit, or the absorption of carbonic acid in the filtration of alkaline solutions.

Filter-stands, retort-stands, perforated boards, &c., will be described in a section appropriated to Supports for Apparatus.

200. *Performance of the Operation.*—When a liquid is ready for filtration, and the funnel, supported by a retort-stand, or in some other convenient manner, has a filter placed in it, the latter is to be wetted by a little water, and the fluid and the precipitate are then carefully transferred to it, either by pouring down a rod (§ 164) or otherwise, and any particles of precipitate adhering to the vessel are to be washed into the filter by a stream from the washing-bottle, fig. 112. This instrument, the contrivance of Leopold Gmelin, has now become indispensable in all laboratories; its construction is extremely simple: a flask of any convenient size has two tubes adapted to it air-tight, and bent as shown in the figure; one of these reaches to the bottom of the flask, the other merely enters it; the vessel is filled with water, and when required to be used, the mouth is applied to the tube on the right-hand, and air being forced into the flask, the water issues in a jet from the left-hand tube, which ends in a fine orifice. It is convenient to have a small piece of vulcanized india-rubber tubing fastened to the end where the mouth is applied, as by its means much facility is gained in moving the bottle in various directions, the pressure not being required to be kept up all the time by the mouth, it being sufficient to blow into the flask; and then closing the caoutchouc tube by the teeth, a stream of water will issue for some seconds, while the bottle may be moved in every direction.

Fig. 112.

201. Before Gmelin's washing-bottle was introduced, the apparatus employed by Berzelius for effecting the same object was in general use; it consisted of a flask having a tube with a fine orifice adapted to it. On blowing into the tube and closing the aperture dexterously with the tongue while inverting it, a fine

and powerful stream of water can be directed on a precipitate in a manner admirably adapted for stirring it up thoroughly, and washing away any soluble matters.

Several washing-bottles are required in a laboratory, even if only one person is at work; one for cold and another for hot distilled water; the latter must have some arrangement for enabling it to be handled with ease when containing boiling water: a wire handle is very easy of construction. Bottles are also required for alcohol and ether; and in investigations where a number of precipitates or other substances have to be washed with any particular fluid, it is desirable to have a washing-bottle filled with it at hand.

202. It is proper in almost every case, especially if the operator has not considerable experience in analytical chemistry, to test the washing-water at certain intervals as it passes through, to ascertain when the operation is completed. Of course the test will vary in almost every case, and must be selected accordingly. The filtering-paper should never rise above the edge of the funnel; and even if, from inadvertence, such should be the case, especial care must be taken that the liquid is not permitted to rise above the level of the funnel; if, however, the operation in hand be an analysis, it is better that the paper should be thrown away and a fresh one taken.

Fig. 113.

203. It so frequently happens that precipitates require prolonged washing, that many expedients have at different times been adopted to render the procedure independent of the presence of the chemist. The most simple method of effecting this is to invert a flask of distilled water over the funnel containing the precipitate to be washed, as in

fig. 113, in such a manner that the neck of the flask is below the water; in this position no water escapes from the flask until the liquid in the funnel falls below the neck; when this takes place, a bubble of air enters and an equivalent bulk of water escapes, and the washing proceeds slowly in this manner, until the whole of the liquid has passed through the precipitate.

204. Another method is by the use of a peculiar modification of the siphon, said to have been first adopted by Gay-Lussac; it is constructed as follows:—A bottle of convenient size is taken, and fitted with tubes in the manner represented by fig. 114, where it is seen that $a\,b$ is merely a straight tube open at both ends, passing tight through a cork, which is perforated to allow the passage of the even-legged siphon, $c\,d\,e\,f$, the legs of which descend a little below the bottom of $a\,b$; the end, f, of the siphon is intended to be placed in the funnel, which is so arranged that when fullest the water should rise to the same height as a.

It will be observed that the effective difference of the length of the limbs of the siphon is equal to the space between c and a; when the liquid rises to a the flow ceases; but directly it falls below, the funnel becomes replenished, and by this means a constant level is obtained. The arrangement is exceedingly useful where a fluid is required to be boiled for a long time, and it is desired to prevent loss by evaporation; as, for example,

Fig. 114.

in the water-baths employed to keep pressure-tubes at 212° for many hours.
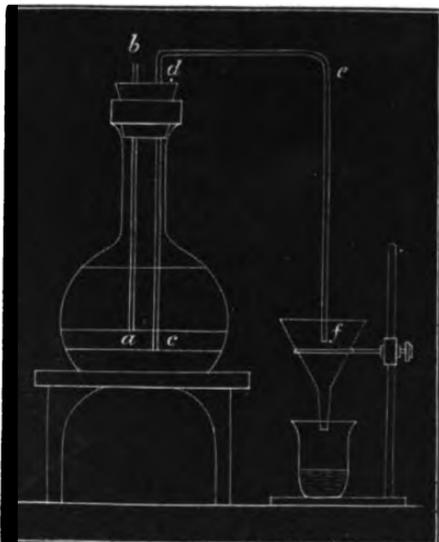
Nothing but its extreme fragility prevents the washing-tube of Berzelius from being much used in cases of protracted washing of precipitates. It is represented in fig. 115. It is fixed by a

Fig. 115.
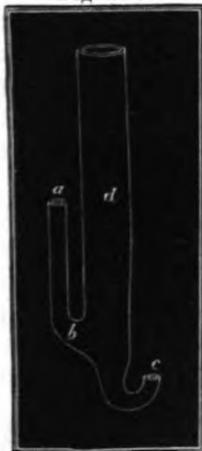
Fig. 116.
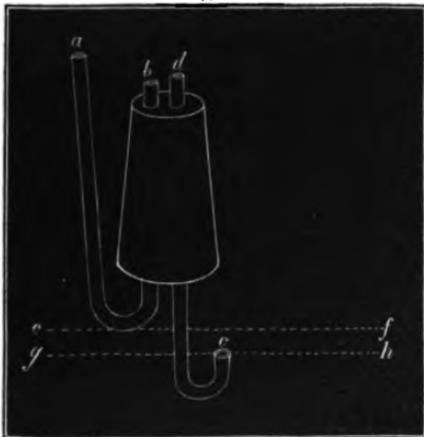
perforated cork into a flask supported as in fig. 117. The mode of action is somewhat peculiar: when inverted in a funnel, the point, c, is placed below the level of the liquid, and in consequence of its smallness, it exerts a somewhat retarding effect upon the egress of the water, so that when inverted in the air, only a very small quantity escapes; but when the point is immersed, the resistance is removed and air enters by a as the water escapes by c, and by this means a constant level is preserved. By arranging tubes in a cork in the manner shown in fig. 116, the same end may be attained, and the chief

Fig. 117.

objection to the beautiful contrivance of Berzelius, viz. its fragility, is at once removed.

H
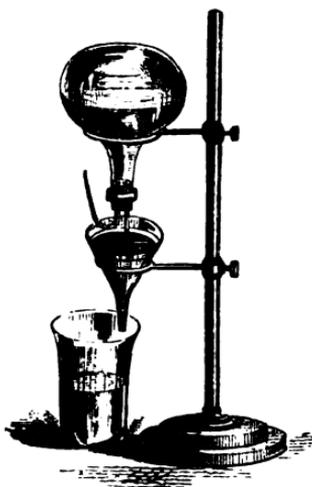
205. It should be observed that the downward tendency of the fluid in the last arrangement, equal to the column of water between $e f$ and $g h$, is less than the resistance to the passage of air through the water in the tube, $a b$, which resistance is owing to its capillarity, and therefore, when the bottle is inverted, no liquid escapes after the first few drops; but this resistance is destroyed by even the small force exercised by the contact of the water in the funnel with that in the tube, c; and if the funnel be filled until the water just rises to the height $g h$, the water will flow out as it sinks in the funnel and maintain a constant level. The conducting power of a piece of wet paper or a finger applied to c, is sufficient to cause the water to flow. On constructing this arrangement, care must be taken to copy exactly the relative lengths and positions of the tubes. Another and very elegant method of obtaining continuous filtration, is that seen in fig. 118. An ordinary glass siphon, with suction-tube, has, previous to bending, another tube of larger calibre placed outside it; during the bending the two become attached, but nevertheless sufficient space remains between them for air to pass. The whole arrangement is fixed by a cork into a flask. On sucking, the water flows, air passing between the two tubes to supply the place of the water removed, but as soon as the water rises in the funnel

Fig. 118.
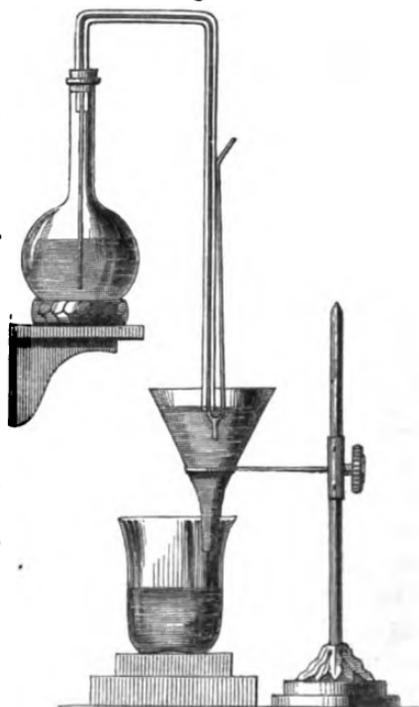
sufficiently high fo close the opening of the wider tube, the air no longer is able to enter the flask and the flow ceases. As the water passing through the precipitate falls in the funnel below the opening of the wide tube, the flow again proceeds, and so on, until the whole of the water in the flask has been expended.

206. The following method of securing continuous filtration, is mentioned by Dr. R. D. Thomson as the contrivance of his pupil, Mr. Eustace C. Summers, and is probably convenient where extremely troublesome precipitates are being washed, or it is necessary for the operator to be absent from the laboratory for considerable intervals; under any other circumstances it would, from the space required for its use, cause more trouble than would be repaid by its superior effectiveness. Into the lower aperture of one of the stone bottles so much used as as-pirators, a piece of tube is fitted by a cork passing at an angle in the same way that the opening is made in a gasometer to pass in the tube evolving gas. A glass tube, smaller than the one last mentioned, is bent into a siphon, the shorter leg of which is inserted inside the first glass tube; the longer leg dips into the funnel containing the precipitate; by this arrangement the water in the reservoir escapes by the siphon, air entering between the two tubes to supply its place; but when the liquid in the funnel rises so as to close the aperture of the siphon, the further egress of the water is prevented until the dropping of the water from the funnel has lowered the surface sufficiently to permit a further escape.

207. Where, as frequently happens, a liquid is being filtered, which, from its weight, corrosiveness, or other reasons, it is feared, will break the filter-paper, it is necessary to use a double one, which is merely one common filter placed inside the other in opposite directions, so that the triple side of one filter is placed against the single one of the other; by this means the filter be-comes so much strengthened as to bear very considerable pressure without fracture, especially if the aperture of the funnel is not too large, a fault at all times to be avoided.

208. It is requisite, when making or folding filters, to carefully

H 2

insure against the presence of moisture on the hands, as in that case it is almost a matter of certainty that a hole will be found in the paper on pouring the solution into it.

Circular filters are so extremely convenient, that where they are not to be procured it is advisable to have some tin quadrants adapted to the size of the funnels, so that when a square piece of paper is folded into a filter it may be placed against the metal and the corners be removed, the piece of tin serving as a guide to the scissors.

209. When a filter has been wetted and is ready to have the solution poured into it, care must be taken that the fluid is not allowed to descend from too great a height, as not only does such a proceeding cause a risk of loss by splashing, but it endangers the safety of the filter, the mechanical force of a fall of water of a few inches being quite sufficient to break many of the less tough kinds of paper when wet.

210. It frequently happens when a precipitate is poured, together with its solution, into a filter, that the fluid runs turbid at first; it must then be returned to the funnel until it comes through perfectly brilliant, and this must never be judged of by the appearance of the liquid as it runs from the funnel, but by letting some run into a glass or test-tube, and holding it between the eye and the light.

211. Filtration is not merely applicable to the separation of solid from fluid particles, but also at times to the removal of one fluid from another; but this is only practicable where they are not miscible; if, for instance, a mixture of oil and water be poured into a thoroughly wet filter, the water will pass through to the exclusion of the oil. This mode of procedure is useful in researches on oily bases, as, where they have in the crude state been dissolved in an acid, any non-basic oil separates and rises to the surface, and if the two are thrown upon a wet filter, the acid solution of the bases passes through, leaving the other matter behind.

212. *Calico Filters.*—This description of filter is much used in manufacturing operations, and also in laboratories of research where large quantities are being worked upon. They are particularly useful where infusions or decoctions have to be filtered

from feculent matters.   The best material for their construction, as far as my experience goes, is what is termed "yard-wide unbleached calico."

If large quantities of precipitates have to be filtered, or where careful collection is desirable, a very convenient and useful strainer is formed by stretching a piece of calico over a square wooden frame, fastening it on by means of a few tacks.   A filter of this description affords peculiar facilities for the collection of every particle of the precipitate, whereas conical bags are somewhat troublesome to thoroughly empty without waste.

Flannel bags, from their great strength, are sometimes useful, but only in coarse operations: they are inadmissible for liquids containing free alkali.

213. Sand, glass and asbestos are adapted for concentrated acids and strong alkaline solutions; although not often used, they are sometimes extremely convenient in cases which otherwise would cause considerable difficulty.   Sand and glass filters are constructed in the same manner, and therefore one description will serve for both.   The throat of the funnel is first to be obstructed with rather large pieces of the substance used; on this are strewed smaller pieces, then coarse powder, and finally, fine powder.   Care must be taken not to disturb the arrangement of the powders when pouring the liquid in, and it is generally necessary to pour it back two or three times before it becomes bright.

214. Asbestos filters are made by merely obstructing the throat of a funnel with clean asbestos, *lightly* packed, otherwise the liquid will pass with difficulty.   In making filters with sand, glass or broken flint, it is sometimes convenient to use a little asbestos at first, instead of the larger pieces of the material. It is of importance to ascertain that the sand, &c. does not contain any substance capable of being acted on by the fluid filtering; and it is proper for this reason to wash it with hydrochloric acid, and afterwards to remove the latter by repeated edulcoration with water until the washings no longer precipitate nitrate of silver.

215. Tow is a rough medium of filtration, and is only applied

in the coarsest operations, such as the removal of mechanical impurities from oils, infusions, &c., and is seldom or never used in experiments of research, especially where any delicacy of manipulation is necessary.

216. In the filtration of viscid fluids on the large scale, it is necessary to use pressure to force them through the pores of the medium, as, from their sluggish motion, they would, without this assistance, pass through so slowly, that in many cases the prolonged exposure to the air would cause injury, if not decomposition.

The pressure is obtained in several ways; of these, two are most generally adopted, namely, atmospheric pressure obtained by the use of an air-pump, and the pressure of a column of fluid: these methods are seldom or never resorted to except in manufacturing laboratories.

Fig. 119.

217. It is a very common occurrence that a hot fluid containing a considerable quantity of matter dissolved, and which is deposited on cooling, has to be filtered; it is then required to keep the funnel, &c. hot during the whole time of filtration; this may be accomplished very conveniently by Plantamour's ebulli-

Fig. 120.

tion funnel, shown in figs. 119 and 120, the latter being the one more generally used.

It will be seen, that in the first instrument a chamber contain-

ing water has an opening which enables a funnel containing the fluid to be filtered at the high temperature to pass through, the fluid in the vessel being maintained in ebullition by means of a lamp placed beneath a projecting portion of the apparatus. The second is simply a double funnel, the interior of which contains water capable of being kept boiling by a portion projecting over a lamp-flame in the same manner as the first. These two instruments, or one of them, should find a place in every well-appointed laboratory. Where access is unattainable to an ebullition funnel, the apparatus for filtration must be placed within the hot-air closet, or, if very small, in the square water-bath, fig. 52.
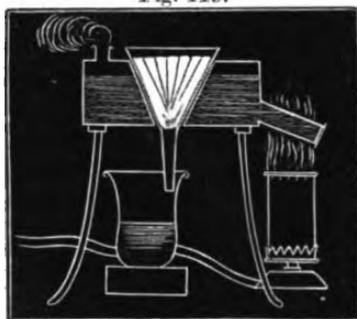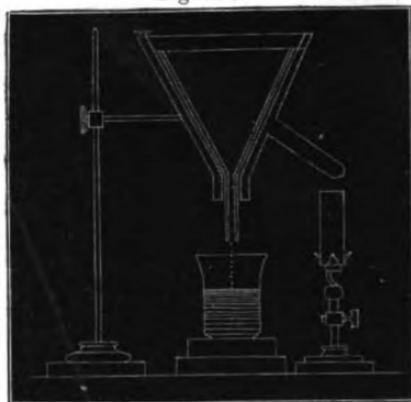
218. Where volatile fluids have to be filtered, the funnel used should have its upper surface ground, and a glass plate (also ground) may be placed over it to prevent evaporation as far as possible.

Platinum salts of organic bases, no matter how finely crystallized, must, before burning to ascertain the quantity of platinum, or organic analysis, be finely pulverized; they are then generally found to be rather adhesive, and the particles to have a tendency to hang together; but if washed upon a filter with a mixture of alcohol and ether, the impurity causing this adhesion is removed, and when dry the powder of the platinum salt is found to be extremely mobile, and generally, on combustion, gives a nearer result than if the process is omitted[*].

219. When the quantity of fluid to be filtered is extremely small, it is necessary to use proportionably small filters, and these are sometimes supported over a beaker or other convenient vessel by the porcelain three-legged instrument, fig. 121. In all quantitative operations the point of the funnel should touch the edge of the beaker or other vessel into which the filtrate is to

Fig. 121.
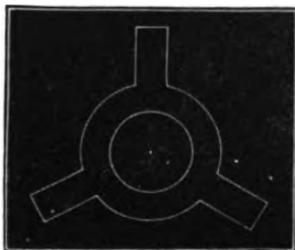
* Phil. Mag. October, 1854.

fall, in order to prevent the drops from striking the fluid with
sufficient force to cause splashing.

220. It is sometimes required to filter caus-
tic alkalies out of contact of the air of the
laboratory in order to prevent absorption of
carbonic acid, and this is easily managed by
an arrangement either the same as, or on the
principle of fig. 122, where, for every drop of
liquid which falls, a corresponding portion of
air is expelled from the lower and passes into
the upper vessel, and so enables the filtration
to proceed.   The neck of the upper bottle is
slightly choked by linen, asbestos, or some
other convenient substance, care always being
taken to select one unacted on by the fluid
filtering.

Fig. 122.

SECTION XIII.

SUPPORTS FOR APPARATUS.

221. Almost all arrangements of apparatus involve the neces-
sity of supports of some kind to keep the various parts in their
proper places, or to prevent their disarrangement by slight con-
cussions, or even the shaking unavoidable at times during expe-
riments.

It frequently happens that the illustrations in chemical works
either do not show the method of supporting the apparatus in
the positions represented, or, which is more objectionable, give
supports which appear intended merely to have a picturesque
effect, and do not really afford a true idea of the practical methods
adopted in laboratories to effect the required end.

The various supports required differ more in size and appear-
ance than in principle, and but little ingenuity has been expended
by chemists upon them, yet there are few subjects that would
better repay the time and trouble employed than the invention
of some really good, cheap, and strong supports, adapted for
the complicated and fragile systems of apparatus which are
frequently unavoidable in the present state of chemistry, and
will probably become still more in requisition until the science
has become so improved as to enable us to procure combinations
and decompositions by simple and direct methods.

222. Few things have a more beautiful appearance than a
complex system of chemical apparatus well put together; and,
moreover, success in very many instances is due to the skill
with which this is effected. And when it is known that much
depends upon a judicious selection of supports, it will be seen
that any instructions calculated to guide the student or operator
in his choice will not be an unprofitable subject to which to de-
vote a few pages.

223. *Supports for filtration.*—These are of the simplest kind,
such as the filtering-stand (fig. 123), which should find its place

H 5

in every laboratory. Care must be taken in deciding upon the

Fig. 123.
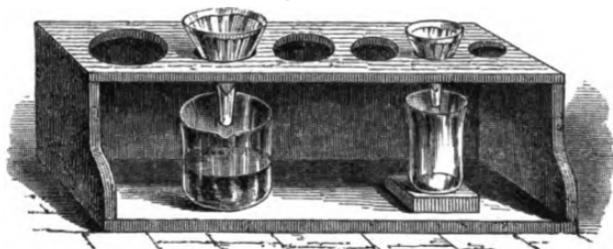
proper place for this useful article. It should be in a spot free from dust, sufficiently near the operator's place for working, and yet not so close as to occupy otherwise valuable space. It should be strictly kept for the purpose intended, and ought never to be made use of as a depository for flasks and retorts, as its peculiar shape is liable to cause this to take place: those instruments must have a place specially appropriated to them. The mode of using the filtering-stand is evident from inspection of the figure, and need not therefore be described. A few blocks of wood of different thicknesses form a useful adjunct to it, and should therefore be provided.

Fig. 124.

224. Retort-stands are extremely useful for this purpose, but it is scarcely judicious to appropriate them to it, as they are required for so many other operations; but the small wooden filter-stands (fig. 124) made upon the same principle, are cheap, and should be provided in quantity; the laboratory should possess a considerable number of them.

225. The porcelain and glass filter-holders (fig. 121) are some-

times extremely convenient, and when supported on the ring of a retort-stand, care should be taken that the point of the filter touches the edge of the glass or basin, in order to ensure the running of the fluid into them without splashing.

226. *Supports for pulverization.*—These are few, and consist chiefly of a large wooden block intended to support the iron mortar, and an equally large one of a different shape for the anvil.

227. *Supports for thermometers.*—Most chemical thermometers have a ring formed at the top, intended to facilitate suspension in liquids, but they (the rings) are seldom used, it being more convenient in general to support them by means of a perforated cork fitting into one of the rings of a retort-stand. I am in the habit of using the apparatus, fig. 125, for sup-

Fig. 125.

porting thermometers in baths or other situations where they may be required. I construct the screws with the aid of a screw-cutter*; it consists of a wooden arm, *a b c*, intended to support two thermometers.   The aperture at *a* serves to allow of the instrument being attached to a retort-stand, the screw, *d*, enabling the operator to fix it at any height. The apertures, *b* and *c*, contain perforated corks, through which pass the thermometers; they may be secured in any required position by means of the screws, *e* and *f*.
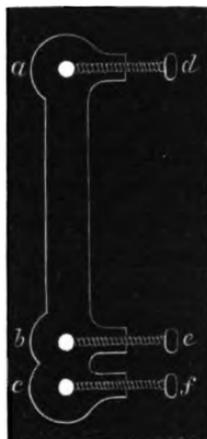
228. The wire triangle, fig. 126, is easily made, and is much used to support platinum and porcelain crucibles, it being generally laid on the ring of a retort-stand, or immediately on the chimney of the lamp.

229. When it is wished to cool a platinum crucible rapidly, it is best effected by placing it upon the anvil or any other large clean iron surface (§§ 84 and 108); it need scarcely be said that

---

* This instrument will be described in the section on Miscellaneous Operations.

hot porcelain or clay crucibles would be fractured by cooling them in the same manner. Clay crucibles may very conveniently be supported on the table, by interposing pieces of brick between them and the wood.

Fig. 126.

230. A retort-stand is also a convenient support for hot crucibles, or a piece of coarse wire trellis lying on the top of a glass or other convenient vessel may be used.

231. *Supports for evaporation.*—The appliances for this purpose are very similar to those used in distillation, &c., but vary in some cases. Few supports are more convenient than the sand- or water-bath during evaporation, and the methods of supporting these have already been described in treating of the instruments themselves. The tripod-stands, (§ 236) and especially the lamp-furnaces, figs. 28, 29 and 127, are greatly used in evaporations on the small scale.

Fig. 127.

232. *Supports for ebullition, distillation and sublimation.*—So many different kinds of supports are used in various ways during the performance of these operations, that the instruments themselves will be described, and the application of them must be left to the judgment of the operator.

The table-support, fig. 128, is an exceedingly valuable piece of apparatus, and is applicable in a very great number of operations: *a* is a flat table fixed on a rod, *b*; it slides up and down a hollow

support, *c*, and is capable of being arrested at any height by the screw, *d*. This portion of the apparatus is much used for supporting lamps at different heights during distillations, and many other processes. The part *f* is a support for flasks and dishes, which rest upon the three pegs; it is likewise fixable at any height in the tube, *c*, as is also the crook, *e*, which is of great service in supporting necks of retorts and long tubes in distillations and reduction operations, as in fig. 129. Sefström's holder is convenient in distillation, especially for heavy retorts, and to hold a Liebig's condenser, for which its considerable strength renders it particularly applicable. It is seen performing this office in fig. 130.

Fig. 128.

Fig. 129.
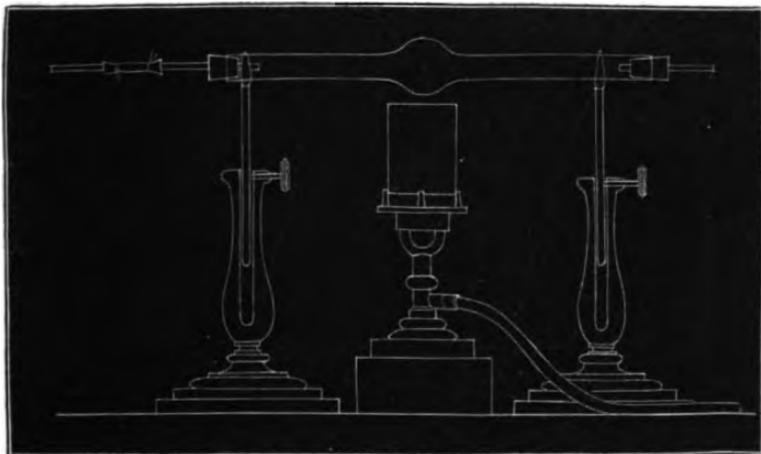
It will be unnecessary to dwell upon the method of its con-

struction, as it is rather troublesome to make, and can be easily procured from the dealers in chemical instruments.

Fig. 130.
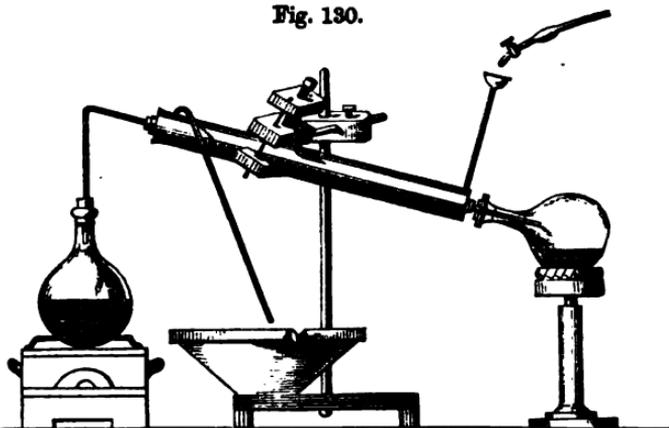
233. A still more generally useful instrument is the wooden

Fig. 131.

vice, fig. 131: *a* is a rod turned to fit the hole, *k*, of the block, *i*, fig. 132, which moves up and down the rod, *f*, and is fixable at any point by means of the screw, *g*. The vice is jointed at *b*, and is opened or shut by the motion of the screw, *c*, which, strictly, is only capable of shutting it; but a spring, *e*, forces it open when the screw is turned in the proper direction. The part *d* is made slightly arched, to enable the vice to grip round substances, as the necks of retorts, test-tubes, &c.
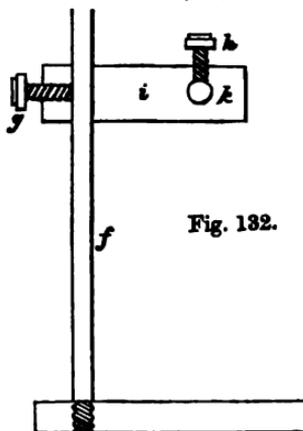
Fig. 132.

The instrument is particularly applicable to the support of small retorts during distillations, and in fact is constantly useful where vessels have to be supported at varying heights.

234. A retort-stand fit for many purposes is easily made out of a few pieces of wood and wire. The common form, however, is that shown in fig. 133. The rod, d, should be tolerably stout, and fit into a heavy loaded foot, f.
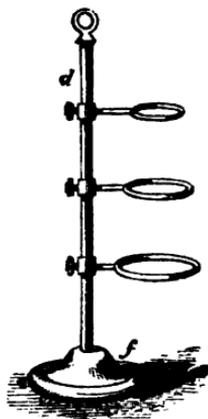
Fig. 133.   Fig. 134.
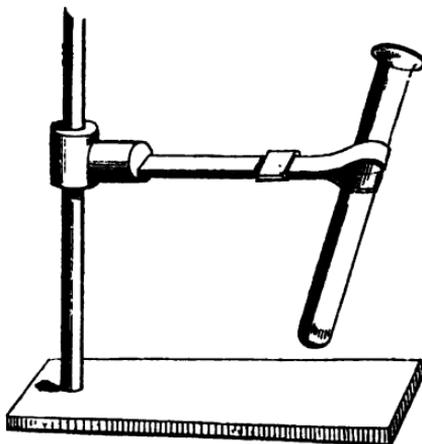
Distillatory apparatus, constructed of test-tubes, may very conveniently be supported by means of the tin test-tube holder, fig. 134. There it is seen that steadiness is obtained by means of the friction of a perforated cork enclosed in a tin cylinder, and sliding upon the rod; while the support for the tube is made to grip by slipping the piece of tin along the clasp. This is a cheap and useful piece of apparatus, and may be constructed with ease out of pieces of tin and a few corks.

235. A superior kind of retort-stand is often used, the rings of which are moveable and capable of being fixed by dropping into square sockets in the parts which slide upon the rod; it is advisable to have several pieces of apparatus so made as to be capable of dropping into the sockets, such as a screw clamp (fig. 131), a Plantamour's ebullition funnel, and a crucible jacket.

236. Flasks are conveniently supported, while fluids are boiled in them, by means of a tripod, as in fig. 135.

237. Mr. Griffin, to whom the chemical public is indebted

for the introduction, from the Continent, of an immense number-
ber of instruments, until then al-
most unknown in England, has
described a vertical clamp well
adapted for the support of small tube
retorts, and several other pieces of
apparatus.

Fig. 135.

238. I have often made vertical
supports of the form of fig. 136, with
the aid of the tools described in the
section upon Miscellaneous Opera-
tions.   Two slips of wood, preferably
of a hard and springy kind, are
screwed to a small block, *c*, which
keeps them apart, and thus forms
the spring.   A screw, *d e*, is made
upon a rod (by means of a screw-
cutter); it is fixed at *d* by means
of a pin, and passes loosely through the other slip.   A female
screw is cut in a block of wood, *e*,
which has two projecting pieces
to assist in turning it.   On screw-
ing up the block, *e*, against the
slip, *b*, the two are brought into
contact.   The instrument to be sup-
ported is held between two pieces of
cork glued on at *a* and *b*.   The whole
is then cemented into a mortise in
the foot, *f*, which is loaded with lead.

Fig. 136.

Lamp-furnaces are also very con-
venient for supporting retorts, &c.
in small distillations: they have
already been described (§§ 42 and 231).

239. *Supports for burettes.*—These valuable instruments are
supported in a vertical position, by means of a socket made in a
block of wood.   Binks' alkalimeter, which is far better and less
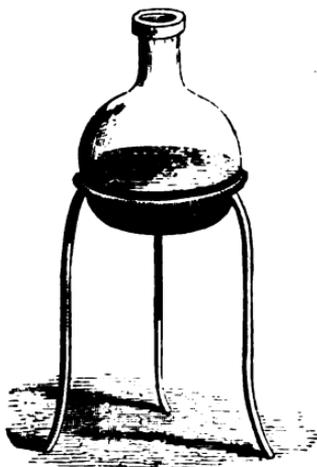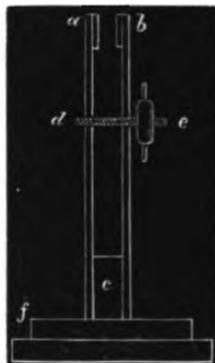
fragile than Guy-Lussac's, is, from its simple form, capable of being supported by a circular tube of wood with a foot.

240. *Supports for gas apparatus.*—The apparatus used in manipulations connected with gases, is generally somewhat more complex than the other kinds; and not unfrequently several supports of different kinds are required in one arrangement, as in fig. 137, in which the operation of collecting a gas over mercury

Fig. 137.
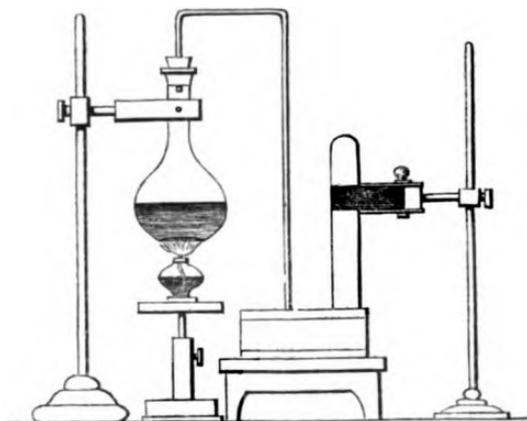
is represented, and where, from the weight of metal, it is necessary to have the supports of considerable strength. The gas jar

Fig. 138.
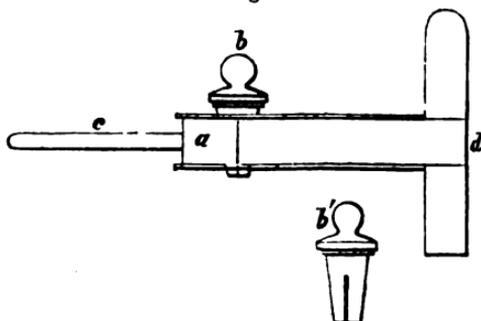
is held by one of Gahn's cylinder-holders, an excellent contrivance, the structure of which is seen by reference to fig. 138.

A block of wood, *a*, having a rod, *c*, to enable it to slide in a
hole formed in a block, as at *k*, fig. 132, has a slit cut in it to
enable a broad silk ribbon, *d*, to pass through, which is then
fastened by one end to a slit in the conical plug, *b*, which is re-
presented again at *b'*, to show the position of the slit; the other
end of the ribbon passes round the end of the block, and is fast-
ened to the other side. The manner in which this is done is
observable from fig. 139, where it is seen from above. By twist-

Fig. 139.

ing the plug, the ribbon is tightened round the cylinder, and the
conical form of the plug enables it to be fixed by a slight pressure
downwards after the ribbon is tightened.

241. The flask in fig. 137 is secured by a clip, and the lamp is
seen to be supported by the table, fig. 128.

The rod on which the Gahn's holder is fixed, is sometimes
clamped to the edge of the mercurial or pneumatic trough.

242. In gas experiments, as in many others, wooden blocks
are often of great service for raising and lowering apparatus to
different heights; they should be about 4 or 5 inches square,
and may vary from half an inch to 2 inches in thickness.

243. U-shaped chloride-of-calcium tubes are generally tied by
string to a wooden support, but preferable methods will be found
in the Appendix.

244. The U-shaped desiccating tubes, with a conducting tube
at bottom, much used lately for drying gases, by passing them
over fragments of pumice moistened with sulphuric acid, are con-
veniently supported against a board by means of wires passing
through the wood and round the tube, a piece of vulcanized
caoutchouc intervening.

245. The apparatus used in experiments on the solution of
bodies requires no special supports, the appliances already men-
tioned being capable of meeting all ordinary cases.

246. An exceedingly useful support for U-tubes, and many other kinds of apparatus, is represented in fig. 140.   It merely consists of a frame-work of wood, to which the U-tubes are suspended by strings attached to nails or pegs.

Fig. 140.
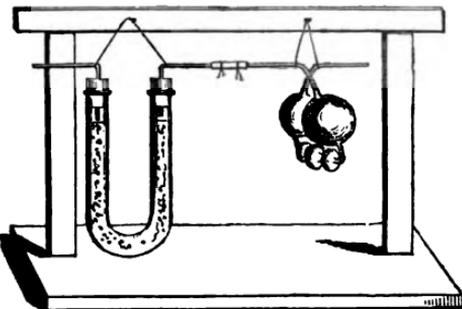
247. *Support for thermometer and vapour-flask.*— In taking the densities of vapours, I have sometimes constructed the arm for supporting the thermometer and vapour-flask (see § 131) of the form of fig. 141.   No difficulty will be found in making it. It is represented turned sideways, to show the position of the screws, &c.   It is jointed at *a*, to allow of its being raised or depressed

Fig. 141.
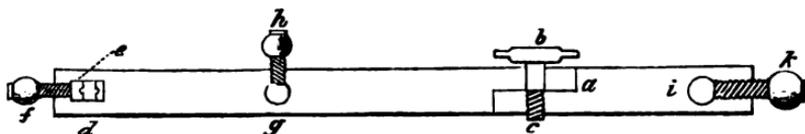
to any angle, and may be fixed tight in its position by the screw, *b c*, which passes smoothly through at the upper side, and has the screw cut upon its lower portion.   A square hole is mortised at *d*, containing two pieces of cork, one of which, *e*, is moveable, and serves, by turning the screw, *f*, to fix the thermometer.   The rod supporting the cage which holds the vapour-flask passes through the aperture, *g*, and is held in the desired position by means of the screw, *h*.   The hole, *i*, enables the arm to slide upon a retort-stand, and it may be arrested by the screw, *k*, at the proper height.

SECTION XIV.

DISINTEGRATION, &c.

248. It has already been observed that the attraction of aggregation is one of the greatest obstacles to chemical action, and that the further the particles of bodies are separated from each other, the more freely and easily are they attacked by chemical reagents; it will be seen, therefore, that any means enabling the chemist to effect the disintegration of bodies, should be thoroughly familiar to him.

There are many methods by which solid bodies may be reduced to powder, but only a limited number of them are capable of being used in researches; this arises from the fact that there are but few processes possessing the necessary but somewhat incompatible qualifications of not only pulverizing substances, but at the same time preserving their purity. The ordinary operations of grinding by means of stones, slabs and mullers, mills, &c., will not be noticed in this work, as they are almost solely applicable to manufacturing and technical pursuits; it is true that there are occasions on which the scientific chemist is obliged to avail himself of their assistance, but such are of comparatively rare occurrence.

249. The manner of proceeding to reduce a substance to a fine state of division necessarily depends upon its physical characters; for example, a piece of chalk and an ingot of silver require very different kinds of procedure, the first being easily brought to almost any degree of fineness by mere trituration, the second being only procurable in a pulverulent form by precipitation or filing.

250. The instruments most commonly used by the chemist for the purpose are the pestle and mortar, and these are necessarily made of many different forms and varieties of material, to suit the particular cases which present themselves. Porcelain, glass, agate, porphyry, marble, granite, iron, steel, brass and bell-metal all being in use for various purposes, but only four of them are

employed in the laboratory, namely, porcelain, agate, steel, and iron. Under the head of porcelain is of course included the extremely valuable Wedgwood-ware mortars so much in use. It is considered unnecessary to enter into a description of the best shape adapted for a mortar, because those last alluded to are generally, perhaps always, made upon an unexceptionable model, and the other varieties of form in use in the laboratory are all appropriate in certain processes. In the operation of pulverization, as in most others, much time and trouble may be saved by a systematic method of procedure, and an equally great loss incurred by careless manipulation. Some substances, such for instance as sugar, when touched by the pestle, fall immediately into small fragments, and are easily reduced into fine powder by a grinding motion; others, like sulphuret of iron, require a great deal of pounding, and some care is necessary to prevent dispersion of the fragments; this may be prevented by striking with the pestle straight down, carefully avoiding lateral blows, it being these which chiefly cause the particles to fly about. After the substance has become tolerably reduced, it is better to substitute a movement between that of a blow and a grind for the directly downward motion of the pestle; this is effected by grasping the handle firmly in the hand, the striking portion of the pestle pointing somewhat inwards, and then striking downwards, drawing the pestle towards the operator's body; when by this means a certain degree of fineness has been obtained, it is advisable to entirely substitute trituration for blows, the pestle travelling in turn over the whole of the lower portion of the inside of the mortar. Where the matter adheres to the inside, it must be scraped down towards the centre with a spatula. It is necessary to have only a moderate quantity in the mortar at once, as, otherwise, the fragments are protected by each other from the action of the pestle. If the contact of organic matter is unimportant, it is convenient, and assists the operation, to sift the matter as fast as it is pounded, and return the fragments which are too large to pass through the sieve into the mortar to be repulverized.

A good method of sifting small quantities of matter where sieves would be inapplicable, is to put the powder into a piece of muslin of the proper fineness, and gathering up the ends, to strike the end of the pestle gently with the bag thus formed, over a sheet of paper, of course avoiding a draught, if the powder, from its small density, is liable to be blown away.

251. It is always best to have the pestle formed out of one piece of porcelain, instead of the old plan of cementing a wooden handle into a Wedgwood foot. If the pestle is used for pulverizing oxide of copper or chromate of lead this is indispensable, as it is sometimes difficult to prevent fragments of the cement being projected into the mortar.

252. It is important to ascertain the soundness of the material of which the mortars are made before using them, as a bad one is worse than useless, and sometimes gives rise to serious errors. One of the worst faults is porosity; if sulphuric acid be put into a mortar and left for some hours, it ought to be immediately and thoroughly removed by merely rinsing with cold water; if, moreover, any colouring matter be left in it for twenty-four hours, the same ought in general to be the case. Some unglazed mortars, however, although in other respects excellent, have a tendency to slightly retain colouring matters with great obstinacy, while acids or other fluids do not appear to be absorbed. It is essential that the mortars should be sufficiently hard to allow of substances of considerable hardness being pulverized without injury. It is sometimes found that the pestles and mortars, although purchased together, are not of the same degree of hardness, very hard mortars being sometimes accompanied by worthless pestles, and *vice versâ*; where this is the case, it is better to throw away the imperfect instrument than to run the risk of causing the failure of an experiment by retaining it in the laboratory.

253. When a good instrument has been procured, every care ought to be taken to preserve it. Sudden changes of temperature are to be avoided; many mortars have been destroyed through careless persons mixing sulphuric acid and water in them, or plunging them into boiling water for the purpose of cleansing.

Impurities may be removed from mortars by rubbing in them a little sand saturated with a strong acid or alkali, as the case may be; it is seldom that any dirt is found to resist the action of nitric or sulphuric acids or caustic potash. With the same view, namely, to prevent destruction of a good mortar, care should be taken to prevent unnecessarily hard blows being used in pulverizing; moreover, where it is essential to warm the mortar, as is the case in the comminution of very deliquescent substances, it ought to be done very gradually (such as by letting it remain for some hours in the warm closet) before attempting to make it hot.

254. The operator cannot be too strongly cautioned against pulverizing a chemical mixture with the properties of which he is unacquainted; this especially applies to anything in which chlorate of potash enters as an ingredient, several fearful accidents having occurred in this manner.

255. It has been said that some kinds of unglazed mortars retain colouring matters with obstinacy; it must not be inferred therefore that glazed mortars are the best; on the contrary, and even where the glaze exists, it is only for a short time, as the attrition from use soon removes it, and, in fact, a glaze is an obstacle to the use of a mortar, its polish enabling the substance to slide over its surface without meeting with the proper degree of attrition.

256. It often happens, especially in the preparation of refractory silicates for analysis, that substances are to be reduced to an extreme state of division; it is then generally best to commence by reducing the mineral to coarse fragments, by first heating it to redness and then quenching it in water; this fills the mineral with innumerable fissures, which greatly assist the further progress of the disintegration. It must not however be assumed that this is invariably a correct mode of operating, because there are instances where such a procedure would destroy the possibility of obtaining an accurate result.

257. A very good general method of reducing hard substances into moderate-sized fragments, either after heating to redness and

then quenching or otherwise, is to wrap the mass in a few folds of paper, and holding it with the forefinger and thumb of one hand on the anvil, to give it a few smart blows with a hammer more or less heavy, according to the hardness of the substance. Some bodies, as the phosphuret of rhodium, are very difficult to reduce to fragments even by this method, and are perhaps best broken in the diamond mortar to be described presently. After breaking the mineral to moderate-sized fragments, it may generally be reduced to a coarse powder in an ordinary Wedgwood or Meissen porcelain mortar, and be finished by long trituration in the one of agate.

258. These last-named instruments are absolutely indispensable in the laboratory. The demand for them having greatly increased during the last few years, they may be procured at very low prices, and are therefore within the reach of almost all who study the science to any extent. They are only available for trituration, having generally more or less fissures, which weaken them so much as to cause them to fly to pieces with a smart blow. They are, however, excessively hard, and consisting almost entirely of silica, the nature of any matter introduced may be known and estimated accordingly. The pestles are generally inconveniently short, and therefore should fit into a handle, or the whole arrangement may be made as in fig. 142, where the mortar is fixed and the handle is attached to a tube, which, from the mode of supporting it, allows of a considerable amount of motion, and at the same time greatly facilitates the working of the instrument. It will be seen that the agate mortar from its shape is also singularly well adapted for the pulverization of small quantities of valuable substances for analysis, and should therefore find a place among the apparatus for organic as well as inorganic analysis ; it is also cleaned with extreme facility, partly

Fig. 142.
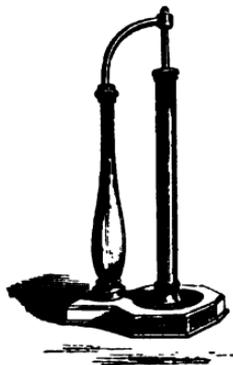
in consequence of its shape, and partly from the perfect absence
of porosity, that is at least in good specimens, for some agate
mortars contain flaws upon the basin; these should be rejected.
In examining them they should be held against the light, when
many imperfections which would otherwise pass unnoticed will
become visible; care must, however, be taken not to mistake the
lines and streaks (almost always to be found in agate) for flaws.

259. One of the great uses of an agate mortar is in qualitative
blowpipe analyses, for procuring the metallic globules formed by
exposure of oxides with carbonate of soda, &c. to the reducing
flame; the charcoal, after the blowpipe process is ended, is cut
out at the spot where the action took place, and is ground in the
agate mortar, after which the powder is carefully washed away,
and the grinding and washing continued, sometimes alternately
and sometimes together, until nothing remains in the mortar but
the reduced metallic globules, which may generally be recognized
by their physical characters, or, if not, by a few simple tests.
The reason why only an agate mortar is properly applicable in
this process, is, because the rough surface of an ordinary mortar
would almost infallibly destroy the globules. A porcelain capsule
and the polished end of a porcelain pestle may sometimes be
substituted for the agate, where the latter is not to be procured.
Great care must be taken in this process to avoid too powerful a
stream of water, which would wash away the globules with the
charcoal. Several other precautions are also to be taken at times,
which belong to analytical treatises, and cannot therefore be
entered upon here.

260. An iron mortar is useful for many purposes, and should
therefore find a place in the laboratory. It is well adapted for
pounding the hard masses of fused chromate of lead and sulphuret
of iron, the former used in organic and the latter chiefly in in-
organic analysis. It is constantly used, moreover, for pounding
marble and several other hard substances.

261. The student should endeavour to familiarize himself with
the physical and chemical characters of substances, in order to
be able to perform with facility any operations of solution or dis-

I

integration that may be required, it being well known that different bodies require very different methods of reducing them to powder; for example, camphor is a somewhat troublesome substance to reduce to fine powder *per se*, but if it be moistened with alcohol, it is readily obtained in the required state. Chloride of ammonium is extremely tough if struck at right angles to the grain, but if the blows are given in the direction of the fibres it yields readily.

262. Metallic gold may be obtained in powder by several chemical and mechanical methods: in the first place, it may be precipitated by a solution of protosulphate of iron or by oxalic acid, or it may be ground with honey to a paste, and the honey may afterwards be removed by water. Tin and lead may conveniently be pulverized by melting them and pouring into a wooden box, which is to be vigorously agitated as rapidly as possible after the introduction of the fluid metal.

Fig. 143.

263. Before levigating hard minerals, it is usual to reduce them to a certain degree of fineness in the diamond mortar (fig. 143), consisting of three pieces, *a*, *b*, and *c*; the pestle, *c*, fits into *b* very accurately, so that no particles can be lost by dispersion, and *b* in its turn fits into *a*, which serves as a foot and steadies the whole. When the mineral is inserted into the cavity of *b*, the pestle is put into its place and struck smartly with a hammer, until it is found that the mineral has yielded, which it invariably does if the hammer is wielded properly. Although the instrument is constructed of the finest and hardest steel, it is generally found that more or less has been abraded, and this must either be allowed for or removed, according to circumstances; generally the latter, it being usual to digest the assay in weak hydrochloric acid to remove the steel.
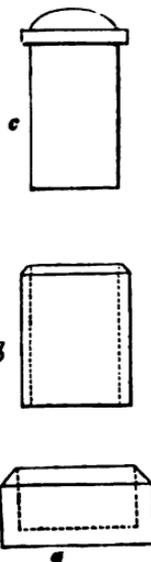
SECTION XV.

CRUCIBLES AND OPERATIONS AT HIGH TEMPERATURES.

264. Crucibles are generally used for experiments which require very high temperatures, and are made of many different materials, according to the purposes for which they are intended. Those of clay are commonly used in laboratories, and are convenient if the operations are not of great delicacy, and the material to be heated is not liable to injury from the contact of the matter of which the vessel is composed. For the fusion and reduction of metals, and the preparation of many chemical compounds, they are invaluable, and it becomes important therefore to be acquainted with the characters of the various kinds in general use, in order to enable us to make a selection of the best adapted for any operation which may present itself.

265. *Cornish crucibles* are very refractory, and if treated well, may be used for the same kind of operation several times in succession without cracking, especially if they are recharged before cooling; they are well adapted for the fusion of alloys, melting and reduction of gold and silver, fusion of chromate of lead, ignition of oxide of copper, &c.; and, moreover, they have the convenience of covers, which is not the case with Hessian crucibles, which in many respects have much resemblance in properties; the latter, however, are triangular, while the Cornish are round.

266. Ordinary English crucibles may be obtained of several shapes and sizes, according to the purpose for which they are to be used; figs. 144, 145, and 146 give an idea of their general appearance. It will be seen that they are made both triangular and round, besides the egg-shaped vessel, fig. 147, generally known as a " skittle-pot."

For ordinary fusions the triangular crucible is convenient, and affords considerable facilities for pouring the melted metal from the angles into small moulds or other positions. They all

have covers. The skittle-pots are particularly convenient in

Fig. 146.

Fig. 144.
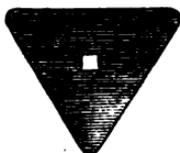
Fig. 145.
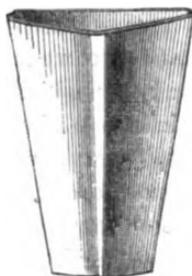
Fig. 147.
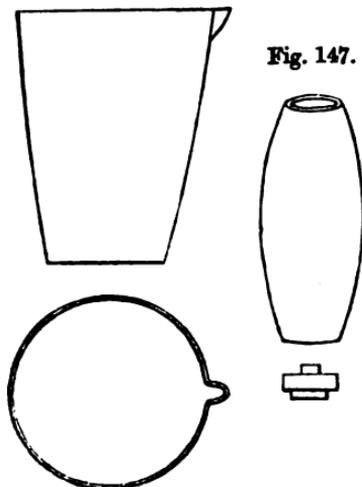
some operations, from the facility with which reduced and melted globules descend and form a button at the bottom; they are, moreover, useful for charring animal and vegetable substances without access of air, and in some metallic fusions. It must not, however, be forgotten that most kinds of English crucibles, except the Cornish and London, are not only fusible at very high temperatures, but are peculiarly liable to crack if suddenly heated or cooled, and should therefore be warmed through before being placed in the furnace; and when the operation for which they have been used is concluded, they should, immediately after the contents are poured out, be placed among the hot ashes to cool slowly. It is seldom, however, that they can be used twice, unless it is for the same operation; and when this is the case, it is usually necessary to recharge them before the temperature has much fallen, and even then they often crack in the fire on the second heating; I have on occasions, however, fused some hundred-weights of chloride of calcium with only a few large crucibles, by taking the precaution not only to refill them before the tem-

perature had much fallen, but also to warm the charge before inserting it.

267. *Hessian crucibles.*—These are sold in nests, and in material have much resemblance to the Cornish; they are, however, triangular, and are more neatly made. They withstand a very high temperature, and if warmed before insertion in the fire, are not very liable to crack*; they have the inconvenience of not being provided with covers; this may be obviated by using an English cover, or by inverting one of the same kind a size smaller inside the larger one.

268. *Blue pots.*—These crucibles, which resemble fig. 146 in appearance, are made from a mixture of plumbago and clay, and are admirably adapted for many metallurgical and technical operations, but their composition renders their use in chemical experiments very limited; this is unfortunate, as they are not only capable of resisting very high temperatures, but are also less liable to crack than most others. They are much softer than ordinary crucibles, and may easily be sawn and drilled so as to make small chauffers and furnaces, which are extremely neat in appearance, and retain heat a long time, but are much less convenient than the small iron furnace, fig. 19, in practice, from the fact that after being used a few times they invariably crack, and then require to be bound round with wire to enable them to be used; they may be obtained of all sizes, from an ounce to 2 or 3 gallons capacity.

269. *Porcelain crucibles.*—These beautiful vessels are now made in Germany and France of the most exquisitely white thin and hard porcelain; they are to be procured of all shapes and sizes, and have become absolutely indispensable in the laboratory. They do not crack when heated, and are but little acted on by

---

* Mitchell, 'Manual of Practical Assaying,' states that "the Hessian pots are worst of all; they do not stand the least change of temperature without certain fracture, so that they require to be very carefully used." This does not accord with my experience, for I have used the same Hessian crucible for igniting oxide of copper to distinct redness (preparatory to use in organic analysis) a dozen or more times in succession without a crack occurring, and without taking any special precautions.

even the most energetic chemical reagents; they therefore communicate no impurity to the substances which are being examined in them. For some operations they supersede platinum, particularly in the ignition of precipitates of the more reducible metals, which would infallibly destroy a platinum crucible. Their beautiful whiteness frequently makes them eligible instead of test-glasses, the action of coloured reagents being very often equally well observed in them as by ordinary transmitted light. They do not retain colouring-matters, and are not porous. Their covers are also excellently adapted for many cases of testing.

270. The crucible of the shape represented in the margin may be procured of any size, from a few drops capacity to about half a pint, and is very well adapted for the ignition of precipitates in analysis, especially where the use of a platinum vessel is inadmissible.

Fig. 148.

271. The capsule, fig. 149, is also adapted for ignitions and fusions, but is more appropriate to evaporations and crystallizations on the small scale, especially those in organic research.

Fig. 149.
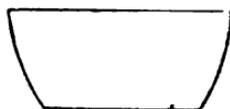
272. The porcelain digester, as it is termed (fig. 150), would more properly have been described in the section on Solution. It is an admirably useful vessel in many experiments, but is not, I think, a very general favourite. I know of no vessel better adapted for slow evaporations and other operations on the sand-bath; and I have had some glass ones made, which are excellent for many purposes, and are particularly convenient from the facility with which they may be cleaned.

Fig. 150.
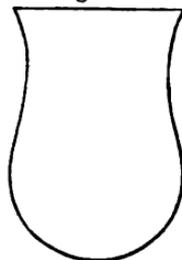
273. Small porcelain capsules of the shapes seen in figs. 151, 152 and 153, but of larger size, may be obtained of extreme thinness

and lightness, and are better for the ignition of chloride, bromide, &c. of silver than any other vessels with which I am acquainted.

Fig. 151.   Fig. 152.

Fig. 153.

I have often had them in almost every-day use for months for the ignition of silver and platinum salts, &c., and have found them neither vary in weight nor crack. Those which are unglazed on the bottom part of the outside, may very conveniently have their weights marked upon them with a black-lead pencil, which will remain legible for some little time; and ink, although destroyed by the heat, leaves a red mark, caused by the iron in it, which may be read even after several ignitions.

It must be remembered that porcelain capsules, from their small conducting power, require a more powerful heat to raise their contents to the same temperature than vessels of platinum.

274. *Platinum crucibles.*—Perhaps no single invention has more contributed to the development of accurate analysis than the discovery of the method of constructing platinum vessels; their uses are almost infinite, and the platinum crucible has become one of the most indispensable of all the analyst's instruments. They are chiefly employed in the ignition of precipitates for analysis, and in the fusion of silicates with carbonated alkalies to render them soluble, a preliminary step to their analysis. The shapes of the vessels that may be used for these purposes are numerous, but the most ordinary form of the platinum crucible is that represented in fig. 154. The lids of some are, however, constructed in such a manner that they may, when separated from the crucible, be used as a capsule for ignitions and evaporations of various kinds, as in fig. 155.

Fig. 154.

275. Spoons made of the same form as those alluded to in the section on Blowpipe Apparatus, but much larger, are also very valuable for many operations. Platinum

capsules, of the form of figs. 156 and 157, are also extremely con-
venient.   Platinum crucibles are absolutely
unacted on by carbonated alkalies at a high
temperature, but this is not the case when
caustic alkalies are substituted: the vessel is
then liable to be seriously damaged.

276. In the ignition of platinum salts of or-
ganic bases, in order to establish their atomic
weights, &c., it is advisable to employ porcelain capsules, for by

Fig. 155.
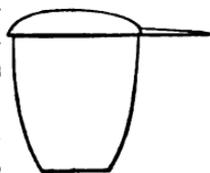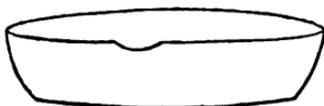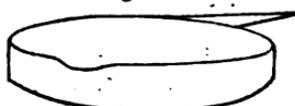
their use it is possible to obtain results of equal precision, without
injury to the valuable platinum crucible; for when this operation
is performed in it, the spongy platinum formed adheres with
tenacity, and cannot be entirely removed.   It is also of great im-
portance to observe that no metallic oxides of easy reduction are
to be heated with filters, or in any other manner that can possibly
introduce free carbon, as the metal will unite with the platinum
at a high temperature, and the capsule will probably be rendered
useless.

277. It is convenient to have counterpoises made of lead or
other metal for all the platinum vessels, so that the increase may
at once give the weight of the precipitate without calculation.
See also *ante*, pp. 71 and 72.

Platinum capsules, &c. may be heated in many ways, which
will be seen by inspection of the articles on Lamps and Fur-
naces, where the methods best adapted for the purpose are
detailed.

278. When used in furnaces, they must be protected by being
placed within another crucible of clay, as otherwise they would
be infallibly destroyed by the slag, and also by the vapours
containing sulphur, which invariably exist in furnaces.   It

has been said that crucibles, &c. are never to be weighed in a
heated state, but it frequently happens that a substance is to
be estimated which rapidly increases in weight even in a covered
crucible, for their lids seldom fit very accurately after they have
been much used. In these cases it is usual to place the hot
crucible or a wire triangle over a vessel of sulphuric acid under a
bell-jar, which mode of proceeding effectually prevents all access
of moisture, and also retards the cooling; but where it is desired
to proceed rapidly, any delay like this is a source of some annoy-
ance; I have therefore been in the habit of placing the hot cru-
cible upon a clean steel anvil which, from its size and conducting
power, renders it perfectly cold in a space of time so short
that few substances would absorb moisture during the operation;
where, however, this is not practicable the first method must
be adopted (§ 84.)

Where silicates have been fused in platinum vessels with car-
bonated alkalies, it is usual to extract their contents with hydro-
chloric acid, in order to bring them into a state fit for analysis;
but it must be remembered that if the silicate contained cer-
tain peroxides, chlorine will be liberated during the solution of
the fused mass in the acid, which will act upon the crucible, and
not only injure it, but introduce platinum into the analysis.
Under such circumstances, the crucible must be boiled with water
until the contents are sufficiently softened to allow of removal,
and when the whole has been removed, and transferred to a
beaker, hydrochloric acid may be poured on and digested with it
until the required result is obtained.

It must not be forgotten that when an acid is added to the
contents of the crucible after a fusion with alkaline carbonates,
a violent effervescence will take place unless it is added by small
portions, and even then danger is incurred of loss of substance.
During the effervescence, it is proper therefore to place a cap-
sule over the beaker, which will prevent the escape of the par-
ticles of liquid thrown up, as they will strike upon the convex
surface, and trickling down, will fall back; after the effervescence
has ceased, however, the bottom of the capsule must be washed

I 5

by a stream of water from the washing-bottle (§ 200), the liquid being allowed to drop into the beaker with the rest.

279. Gold crucibles are exceedingly valuable in many operations, from the admirable way in which they bear the action of alkalies; but they are comparatively fusible, and from their value, of course require proportionate care.

280. Silver crucibles are much used for fusions with caustic alkalies, as they are far less acted on by them than platinum; but it must be remembered that they are dissolved by nitric acid, even when very dilute, are very fusible, and in general are more easily destroyed than platinum or gold crucibles.

281. Iron crucibles are sometimes to be obtained, and for some purposes are extremely convenient; but their use is limited, and they do not therefore demand any special notice. The same observation applies to those made of copper; it may, however, be remarked, that if Wöhler's new process for preparing pure potash from the nitrate, is found practically convenient, it will cause them to be more extensively employed than they have been hitherto.

282. *General remarks on crucible operations.*—Crucibles at high temperatures are handled by means of tongs of various shapes and sizes, according to the weight and nature of the vessels to be lifted. When large and heavy, they are to be lifted out of the fire with strong ring-tongs. The latter are almost indispensable in these operations, because if straight ones were used they would break a piece out of the edge, and perhaps be the cause of serious accidents.

283. Small platinum and porcelain crucibles are handled by means of the tongs represented in the figs. 158 and 159.

It is very important to see that the anvil or other place upon which the platinum crucible is placed to cool, is free from dirt or fragments of readily fusible metals; as, if the former adhered to the crucible, an error would be introduced into the weighings, and if the latter, the vessel would stand a great chance of being destroyed.

284. Most persons commencing experiments at high temperatures, raise the heat too much; it is well, therefore, for the

student to make himself familiar with the nature of the various
terms used to express roughly the intensities of the tempera-

Fig. 158.
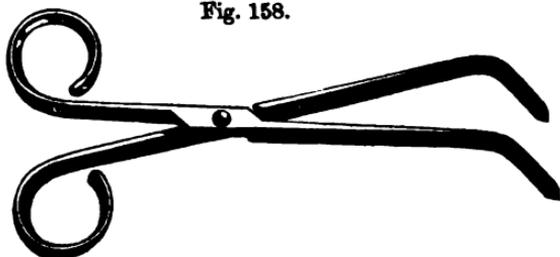
Fig. 159.
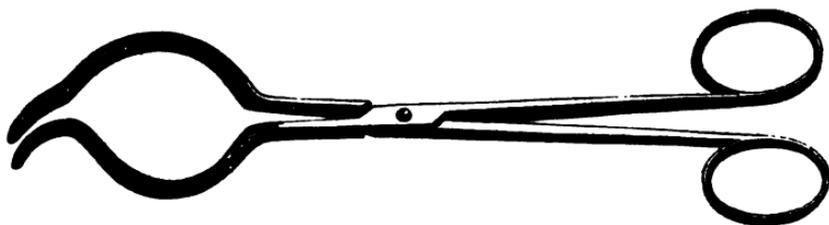
tures of furnaces.   The expressions alluded to are generally
known as dull red, cherry-red, yellow, bright yellow, white,
and blue heat*; these distinctions are generally sufficient to
enable the experimenter to apply the proper degree to his cru-
cible in the present state of the science.   Undoubtedly the time
is approaching when terms so loose as these will be quite inade-
quate to express the gradations of temperature adapted to re-
fined processes, but for the present they suffice, it being a very
rare occurrence to resort to the indications of the pyrometer,
except for the purpose of ascertaining the fusing-points of metals
and other substances which require a very high temperature for
fusion.

285. Charcoal crucibles were much in vogue amongst the older
chemists for experiments of reduction; they fell, however, into
disuse, until the employment of them was revived by M. Deville.

* This term, *blue* heat, is employed by M. Sainte-Claire Deville as indi-
cative of the highest temperature obtainable in furnaces; it was also used
long ago by Faraday.

Two ways of making them are adopted : the first and more ancient, consists in taking a piece of fine hard charcoal and modelling it to fit the inside of a clay crucible ; a hole is then bored in the charcoal sufficiently large to contain the subject of experiment, and a stopper is made to fit it ; this is also cut out of another piece of charcoal.   When used, the substance is placed in the aperture, and the stopper inserted ; the whole is then placed inside the clay crucible, and the latter has a cover luted to it, a small hole being left for escape of gas.   The next method is much simpler, and is perhaps more generally useful : a quantity of charcoal is powdered to a moderate degree of fineness, and after being moistened with weak glue or gum-water, is pressed into a crucible of refractory clay ; a hole is then made in the charcoal paste by pressing in it the small end of a pestle ; it is dried at a very gentle heat, and is then ready for use*.

It is well known that in ordinary furnaces the maximum heat is an inch or two above the bars ; it is usual therefore to support the crucible to be heated, upon some substance equally able to stand the temperature to be employed.   A portion of an old crucible, or a fragment of brick, is generally used.   The fire must be built round the crucible with great care, so that when it falls, as the combustion proceeds, the position of the vessel may not be altered, or its safety, and that of its contents, endangered.   It is not always convenient to warm the crucible previous to the operation in a separate furnace ; it is therefore a good plan to commence building up the fire round the crucible-support with a few pieces of ignited charcoal, and then continue it with cold coke in small pieces.   For an ordinary-sized furnace, where the space between the crucible and the walls all round is about 7½ inches, the fragments should not much exceed the size of a large walnut ; by this means the combustion will proceed so gradually that the crucible will run but small danger of fracture during the heating.   When the whole of the fuel has acquired a full red heat, if it be gently touched with a rod, it will sink in

* For another kind of carbon crucible, see Appendix, on the " Production of High Temperatures."

consequence of the charcoal on which it rested having been consumed; more fuel must now be added, and the furnace, if its construction will admit of it, should be filled almost to the top, or at least as nearly so as is practicable, without affecting the free egress of the air and smoke through the flue. In almost all ordinary cases, the operation will be concluded without the addition of any more fuel; but where the experiment requires the protracted application of a very intense heat, more will be required, and it is very necessary to be able to supply it from an adjacent stove, kept burning merely to supply the one where the fusion, &c. is proceeding, as, if cold fuel be added, the temperature of the furnace will fall considerably, the process will be proportionably retarded, and, if it come in contact with the intensely ignited crucible, a fracture will probably result. For these reasons, it is far better to keep on adding red-hot coke by small portions as the fuel sinks, so that the crucible shall always remain covered to the depth of 4 or 5 inches with the red-hot fuel. In protracted experiments, a certain quantity of slag or clinker falls to the grating and closes it up, thereby materially retarding the operation by preventing free ingress of the air; if this be neglected for a short time, it accumulates so much that it will be dangerous to attempt its removal during a fusion, as it would be extremely difficult to do so without disturbing the crucible, and thereby running a risk of losing its contents. For the same reason, if any considerable number of experiments in crucibles at very high temperatures have to be performed, it is proper to take every care to provide the best coke, and to see that the furnace is properly freed from clinkers every time it is to be used. The tendency of some metals and alloys to absorb silicium at these temperatures, must not be overlooked in operations where such an action may exert an injurious tendency.

Sometimes even the best crucibles will open and discharge their contents into the fire during an ignition, especially where fluxes are present; it is therefore good policy to make a point of having the crucible well luted before exposure to the fire.

To prepare this luting, I have always found the following mode of procedure answer extremely well:—Sift some good Stourbridge clay through a tolerably fine sieve (about twelve holes to the inch), and let it be thoroughly beaten in a mortar with some fresh horse-dung to a smooth paste; pass a cloth slightly wet over the crucible so as to damp it, and apply the luting with a knife or spatula; let it be neatly and evenly applied, to the depth of a quarter of an inch, then let the crucible be placed in a moderately warm situation until thoroughly dry, and when this is the case, any cracks which have appeared are to be made good, and after being dried the second time the vessel is ready for use. The same mode of proceeding answers very well for stoneware retorts and tubes.

286. Very frequent operations in laboratories of research are the ignition of oxide of copper, and the fusion of chromate of lead; when these are performed, extreme care is requisite to prevent fragments of coke or coal, or even the smoke of the furnace, finding their way into the crucible. It is best to place the crucible containing the material on the top of the furnace until quite hot, and during this preliminary heating to make up the fire with coke, so that it may be quite clear and free from smoke; the rings (§ 29) may then be removed until an aperture is obtained rather less than the largest part of the crucible, which may then be dropped into the aperture, it being supported by its widest part; it will soon become very hot, and in a fit state to be inserted in the fire, which should be so managed that the fuel does not extend to within an inch of the top of the crucible. If oxide of copper which has been used is being ignited, after treatment with a little nitric acid to reoxidize the reduced metal, it may be lifted out of the fire and stirred occasionally until the whole has acquired a dull red heat, and the nitrate of copper become perfectly decomposed. The fusion of the chromate of lead is accelerated by stirring now and then, as otherwise the bottom part fuses and descends, sometimes leaving the rest above it in the cooler part of the crucible.

287. If proper care be taken, earthen crucibles may be used

for operations which are generally supposed to be necessarily performed in more valuable vessels. If properly freed from iron and other impurities, chloride of calcium may be prepared of the purest white in ordinary English crucibles.

288. Porcelain basins are very well adapted for some fusions, as for instance the white chloride of zinc; the furnaces, figs. 1 and 17, are convenient for this purpose; one or two of the rings being removed, the basin containing a dense solution of the purified chloride may be supported upon it, care being taken to exclude dust and dirt: this method is far more efficacious and economical than the use of gas, especially where large quantities have to be made.

289. In ignitions in porcelain and platinum crucibles over gas- and spirit-lamps, much care is required to prevent loss of the material. Some substances decrepitate violently when exposed to heat; when this occurs, the lid of the crucible should be kept on. The decrepitation, however, may sometimes be prevented by finely pulverizing the matter to be ignited.

290. In the ignition of the platinum and gold salts of the organic alkaloids, it often happens that the metal volatilizes with the vapours, although the temperature had been kept below redness until the organic matters were destroyed. It is necessary, at such times, to cover the salt with pure dry carbonate of soda; and, after the ignition, to wash the latter away on a filter; the whole is then to be re-ignited and the filter-ash deducted from the weight of the metal obtained. Where the salt of silver, gold or platinum is difficult to burn, which very seldom happens, it is sometimes admissible to drop a small fragment of solid and extremely pure nitrate of ammonia into the crucible, to facilitate combustion of the carbon; but great care is requisite in its use, to avoid a deflagration violent enough to project any of the metal. For other precautions necessary to be observed in operations of this class, see §§ 90, 218, & 276.

291. In every case of ignition to remove carbon, care must be taken to allow air to enter the crucible, and this may be done in several ways, the most eligible of which have been already described (§ 86).

292. The method of cooling a platinum crucible with rapidity has been more than once mentioned; if, however, a porcelain vessel were exposed to the same treatment, its fracture would be inevitable; when it is desired, therefore, to cool it as quickly as possible without danger of fracture, it may be placed upon a piece of wire-gauze, supported upon a capsule or other convenient support; or, if its contents are hygroscopic, upon a triangle over a surface of sulphuric acid.

293. In connexion with the furnace operations with crucibles at high temperatures, there are a few precautions which must not be neglected. If, while a substance is in a state of fusion, it is desired to add more, it must be carefully ascertained that no moisture is contained in it, as violent and dangerous explosions, accompanied with projection of the fused matter, may be the result. It is often convenient to remove one of the rings (§ 29) and lay a plate of talc upon the aperture, to enable the operator to view the interior of the furnace and, in some circumstances, of the crucible also.

294. Where it is necessary to melt a more with a less fusible substance, as, for example, in the preparation of brass, the less fusible metal is invariably to be melted first, then the other to be added, and the whole well stirred together. If, in the example given, the zinc were first fused, and the copper added, almost the whole of the former metal would be oxidized or volatilized before the temperature had become sufficiently high to fuse the copper.

295. It is a very common operation in laboratories to have to reduce the silver, gold, and platinum from the constantly accumulating stock of precipitates and filter-papers. It is, however, much better in the case of silver to keep the papers separate and heat them by themselves, as if the mixture of solution and papers be placed in a basin to be dried down, there is sometimes a formation of some explosive compound, apparently derived from the mutual action of nitric acid, nitrate of silver, and the organic matter of the paper, which may be the cause of loss by projection. In the case of the platinum, the whole mixture when dry may be mixed in a red-hot crucible with nitre, and when the

organic matter is destroyed, the platinum may with ease be separated from the residue. With the gold and silver residues, the dried mass may be mixed with soda and borax, and be exposed to a brilliant yellow heat for half an hour, at the end of which time the silver or gold, as the case may be, will be obtained in a button.

296. Mr. How has shown that much trouble may be caused by the silver and platinum washings being inadvertently mixed, as the platinum dissolves in nitric acid when fused with silver. If, however, the nitric solution containing the two metals be evaporated to dryness and fused, water will separate the nitrate of silver, the platinum remaining behind insoluble; if any platinum still adheres to the silver, the latter must be precipitated by hydrochloric acid.

297. It is becoming a common operation in the analysis of inorganic compounds to effect reductions by hydrogen gas in porcelain crucibles; this may be performed in the manner shown in the engraving, fig. 160, where the tube, *a a*, conveying dry hydrogen, passes through a hole in a platinum lid adapted to a porcelain crucible, and descends a short distance into the latter, which may be supported upon a wire triangle over a lamp. It is

Fig. 160.
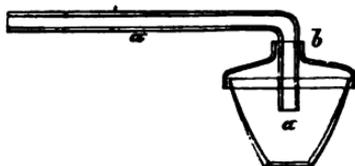
Fig. 161.

sometimes possible to obtain porcelain covers with a tube of the same material, made in one piece, as seen in section, fig. 161, but they are rather difficult to procure.
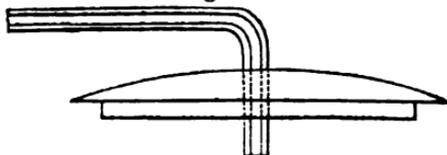
298. *Operations at high temperatures in tubes.*—In the chemistry of the present day tubes are much used as a means of exposure of substances to high temperatures, frequently with a gas of some

kind passing over it.   The process of organic analysis in a current
of oxygen may be instanced as an example.   From the large
surface which is by this means of operating exposed to the action
of gaseous matter, a very advantageous mode of experimenting is
the result, and, in fact, some of the most beautiful and accurate
experiments in modern chemistry are thus performed.   The
material of which tubes are made for this purpose is generally
glass, as it is easily worked to different shapes to suit the various
purposes to which it may be applied.   Earthen tubes are worse
than useless for most experiments of this class, and those made
of porcelain, although not porous like those last named, are so
extremely liable to crack, that it is far better wherever pos-
sible to use glass, the only drawback being its fusibility ; the
hard Bohemian glass (of which the combustion-tubes for organic
analysis are made) is, however, capable of withstanding a full
red heat when supported as in a Liebig's furnace, and is there-
fore sufficiently refractory for all ordinary purposes.

299. Where the use of a very high temperature is unavoid-
able, gun-barrels may very often be made use of, and it will be
shown farther on that they are well adapted for nitrogen deter-
minations by Peligot's modification of the method of Varrentrapp
and Will, where, although the heat required is not very great,
it is seldom possible to use the same glass tube twice ; and as in
many laboratories it is common in the analysis of nitrogenized
manures, soils, &c. to make three or four combustions a-day, the
saving of tubes becomes worthy of attention.   A good gun-barrel
may be used for nearly a hundred analyses before being destroyed.
A piece of iron gas-pipe may often be employed instead of a gun-
barrel, and for some kinds of reduction experiments answers ex-
tremely well.   It is often advisable to protect the glass tube by an
outer one of copper, which may be constructed of a ribbon of the
metal the same length as the tube, or a little shorter, and rather
more than three times its diameter ; after being heated to dull
redness and allowed to cool to anneal and render it easy to
work, it may be rolled round the tube with the hands, a small

piece of iron or copper wire being twisted rather tightly round either end to keep it firmly fixed.

300. It is necessary to be aware of the high conducting power of an exterior tube of copper when applied in this manner, as, if not known and guarded against, it would sometimes prejudicially affect the results. When required merely as a support, a narrow strip of metal may be made to lie upon the vertical supports throughout the whole length of the combustion-furnace, the tube resting upon it being thus prevented from curvature when softened by the high temperature.

301. Figure 7 on page 14 represents the general mode of procedure in experiments where a gas is to be passed over a substance at a red heat, as, for instance, in the reduction of ferric oxide or oxidized copper turnings by hydrogen. The piece of combustion-tubing, a, rests upon a series of vertical supports intended to prevent flexure. The gas evolved from an apparatus not seen in the figure, but which will be described further on, passes through the tube b into the bottle c, filled to about one-third its height with concentrated sulphuric acid, intended to absorb the moisture with which the gas is saturated; from thence it passes through d into the combustion-tube, which latter is closed at either end by corks, e, e, fitted with tubes, the posterior one being attached by means of a tube of caoutchouc to the tube d, evolving the dry gas. It is necessary to allow the gas to stream rapidly through the apparatus for some time before putting the red-hot charcoal in the furnace, in order that the atmospheric air may be perfectly expelled, as otherwise a violent explosion will occur, and of course the fragments flying about are liable to cause serious injury to the operator. It is always necessary to continue the stream of gas until no more water is produced, as may be proved by none condensing upon a cold glass plate held close to the exit-tube, or, in general, by steam ceasing to make its appearance. In all cases it is better to continue the flow of gas until the apparatus is quite cold, when the tube should be closely corked at either end, until the contents are wanted for use.

302. In experiments where a very intense heat is required,

it is necessary to lute the tube, no matter what may be the material of which it is composed; for if of iron, although the temperature may be far short of the point of fusion, the metal is rapidly oxidized and destroyed when exposed to a current of air at a red heat; the same applies to copper, and even platinum is injured by the sulphurous vapours to be found to a greater or less extent in all furnaces. In the case of the latter metal, it is essential to lute the tube to protect it from slag and the fusible impurities abounding in fires at strong heats.

As instances of some interesting furnace-tube experiments, may be mentioned the decomposition of water by metallic iron, the formation of the same by passing hydrogen over reducible metallic oxides, the formation of the beautiful sesquichloride of chromium by passing chlorine gas over a mixture containing oxide of chromium and charcoal, Berzelius's experiments on the separation of antimony, arsenic and sulphur from minerals, by passing chlorine over them at high temperatures, the conversion of toluidine into aniline, Captain Reynold's experiments on the production of propylene from valerianic acid, the formation of the anhydrous chloride of aluminium, the decomposition of some oily bases, with production of others having the power of giving coloured reactions, &c.

It appears from some experiments, that bodies standing high in homologous series may, by passing through tubes heated to moderately high temperatures, be reduced with deposition of carbon and evolution of gaseous hydrocarbons into members lower down in the scale; it need scarcely be said that a careful investigation of these decompositions is absolutely certain to be rewarded by valuable discoveries.

SECTION XVI.

PRESSURE-TUBE OPERATIONS.

303. In the progress of modern organic chemistry a new method of manipulation has been gradually developed, and now become very generally adopted in certain trains of research. It consists in exposing substances to the action of reagents at an elevated temperature under considerable pressure. The reason for this procedure is, in general, that the reactions sought are most frequently sluggish at ordinary temperatures, and as the reagents used are often volatile, it would be difficult to effect the intended change by mere digestion in the ordinary way. It is true that an apparatus might be made, by means of which substances could be exposed to the action of volatile reagents at temperatures not sufficiently great to injure corks, but then it would be impossible to construct it so as to withstand a very powerful pressure; now, by the process about to be described, this objection is removed, and any temperature or pressure may be attained short of that capable of bursting the tube. Before proceeding to describe the process, it may be mentioned that the iodides and bromides of ethyl, methyl and amyl are greatly used in experiments of this description, as in the splendid research of Hofmann on the bases of the alcohol radicals, Frankland's isolation of the hydrocarbons forming the radicals of the same series, &c.

304. It is not always necessary to expose the pressure-tubes to a considerably elevated temperature, that of 212° Fahr. being sufficient in the greater number of instances; sometimes, however, a saline solution or oil-bath is required to raise the heat to the required degree, but then the tubes should be of greater strength than in the former case. It is generally better to have them of rather small bore, and to employ a greater number, than to use a few of considerable diameter, as the former are capable of withstanding greater pressures. To construct a pressure-

tube, it is merely necessary to seal one end and to keep it in the blowpipe-flame, turning it round constantly until it has become of the same thickness as the other parts. It is now to be heated strongly about 12 or 14 inches from the closed end, and dexterously turned in the flame until the glass has become of considerable thickness; it is then to be drawn out until of the form seen in fig. 162.

Fig. 162.

The part *a* is to serve the purpose of a funnel, and, if the liquid to be introduced is poured into it and a little air expelled, by warming *c*, the liquid rushes into the tube as the latter cools and the air consequently decreases in volume; by repeating this two or three times a sufficient quantity will have been introduced, and the tube is then to be closed by directing a blowpipe-flame upon the part *b*. It is sometimes advisable to reduce the amount of air in the tube, so that the only outward pressure, on exposure of the tube in the bath, will be caused by the vapour of the liquid and not by the expansion of the included air. This is readily managed by heating the liquid until it boils, and sealing the tube before the vapour has condensed. The tube is now of the shape seen in fig. 163, and this is a better form than fig. 164, because it admits of having the point broken off, and then being used again and again until the fine tube has become too short. No fear need be entertained of the tube bursting at the small portion if moderate care be used in its construction, as from its small internal diameter it is capable of withstanding a greater pressure than the large one; nevertheless, where very high temperatures are to be applied, it is advisable to thicken the glass of the larger tube at the point where the small one joins on, before introducing the substance. The tubes are now to be labelled, which is easily done by tying on them small pieces of zinc with the name of the contents scratched on, or still better, written on the clean metal with a quill-pen dipped in a weak solution of chloride of platinum, the latter forming an indelible and jet-black stain upon the zinc. If the tubes are to

be exposed only to the temperature of boiling water or a saline solution, they may generally be immersed as Fig. 163.
they are, but if any fear of their bursting is entertained, they may have a piece of rag tied round them, so that if such an accident should happen, the fragments may not be projected about, or the others in the bath be broken by the concussion. It is extremely convenient to have a tin-plate pierced with holes inserted in the bath, so that the tubes may be supported vertically, or, if this is not used, a small piece of lead may be enclosed in the rag used to cover the tubes, so as to sink them in the bath. Where high temperatures are employed, and, consequently, the pressures become very great, it is advisable to introduce the tubes into a pistol-barrel with a plug capable of being screwed in; a piece of stout iron gas-pipe answers very well. A small piece of tow first being thrust to the bottom of the barrel, the tube is to be introduced, then a little more tow, and, finally, the plug is to be screwed in. Where an oil-bath is required, it is frequently convenient to substitute tallow, as it is not so liable to emit unpleasant vapours. If solutions are employed as the media for applying heat, great care must be taken that the bath does not boil dry, as in this case explosions may occur, which, if not dangerous, are liable by the concussion to cause injury to the neighbouring apparatus. An arrangement upon the principle of Gay-Lussac's washing-bottle (fig. 114), may be employed with much advantage to keep the water or saline solution of the bath at a constant level.

Some chemists do not quite immerse the tube in the fluid, but allow the upper portion to project, so that a species of cohobation is continually going on; this is, however, not so rapid a method as by entirely immersing the tube.

No general rule can be given as to the time of exposure, it
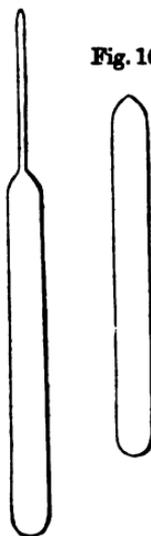
varying from a quarter of an hour or less to a fortnight or even three weeks. Where ammonia is employed, with the intention of removing its replaceable hydrogen, and substituting some hydrocarbon for it, the volatile alkali must invariably be employed in an alcoholic instead of an aqueous solution, as with the latter the reaction is so ˙sluggish, that after a week's exposure, and sometimes even much longer, less effect is produced than in an hour or two with the alcoholic ammonia. This arises from the reagents being soluble in alcohol but not in aqueous ammonia.

305. It is not always easy to know when the reaction is completed, without opening the tube and examining the contents; but a shrewd guess may frequently be given from the appearance of the fluid when cold. If, for instance, the ingredients when introduced are entirely fluid, and crystals appear on cooling the liquid, after an exposure of moderate duration, it is advisable to return the tube for a short time to the bath, and observe if the quantity appears to be increased on a second inspection; if this happens, the reaction may again be allowed to go on, until no further effect is produced.

306. It is better to permit the tube to cool completely before removing the rag, and to avoid incautious handling, or even a slight blow, especially when hot, as the tube sometimes flies to pieces in the operator's hands, and great danger is incurred of receiving severe injury.

For the same reason, when the tube is to be opened, the rag is only to be removed from that part of the tube where the file-mark is to be made; and even then, where gases are evolved, great care is to be taken that the end does not fly off with violence. Where the gases produced are to be examined or analysed, the point is to be broken off under mercury, a gas-jar full of the same metal being immediately over it, so that the gas may pass freely into it.

307. Where the iodides of the alcohol radicals are made to react in excess on alcoholic ammonia, it is usual, when the process is concluded, to distil off the former upon a water-bath

in a retort, as it may, with the addition of a little more, be used again for the same purpose.

308. As the pressure-tubes are generally rather troublesome to clean, it is better to preserve them if the same operation is to be repeated, a label being attached to assist identification.

309. It is generally unnecessary to use new tubes, unless required very strong, as, with the aid of the gas-blowpipe, fig. 48, they may be constructed with facility from the necks of broken retorts, which should always be preserved for this and other purposes.   Other uses of broken retort-necks, &c. will be pointed out in the proper places.

It must be borne in mind that the tubes should always be of pretty considerable thickness, and that test-tubes from their thinness are totally unfitted for experiments of this kind.   Mr. Squire, in his investigation of caprylamine, made use with advantage of soda-water bottles, well corked and wired down; what are termed carrara-water bottles, from their shape, would be more generally convenient, and probably resist a greater pressure.

x

SECTION XVII.

EVAPORATION.

310. The process of evaporation is one constantly employed in the laboratory: its object is to separate fluids from solids by volatilization of the former, and is opposed to distillation, from the fact that in the latter operation it is generally the fluid which is the valuable product, whereas in evaporation it is invariably the solid matter which it is sought to obtain.

It is generally a very easy process; the apparatus is commonly of the simplest and most inexpensive kind, but there are nevertheless many precautions to be taken with which it is essential the student should be familiar. Evaporation is very frequently the first step in crystallization, but as the latter operation is of every-day employment in all laboratories and in all kinds of researches, and is one involving some detail, it will have a section exclusively devoted to it.

311. *Evaporation over naked fire.*—In scientific research, it is not usual to trust fluids under examination in porcelain vessels over the naked fire; it is true that with care most porcelain will endure the temperature without fracture, but then it becomes necessary to devote more attention to the progress of the operation than can generally be spared. Moreover, it is not safe to risk contamination with the smoke and dust which furnaces, unless managed with extreme care, are liable to evolve. For these reasons, evaporation over the naked fire is more generally resorted to in the comparatively rough operations of technical and manufacturing chemistry.

It may be mentioned, however, that the rings of the furnaces (figs. 1 and 17) are well adapted to support basins of different sizes over the fire.

312. The remarks in § 311 apply, although with somewhat less force, to exposure of evaporating dishes to the flame of a lamp; and it may be taken as a general rule, that if a flame

passes over the line formed by the height of the fluid in the
basin, the latter will be fractured. If, therefore, it is neces-
sary to expose a porcelain or glass vessel over a lamp-flame
without the intervention of sand or other medium, care should
be taken to prevent actual contact of the flame with the bottom
of the vessel. If, for the flask supported over the gas-furnace in
fig. 28, a basin be substituted, as in fig. 29, a very effective mode
of evaporation is obtained; but, nevertheless, there are many
analytical operations in which a wide-mouthed flask like that in
the engraving alluded to, may be used with advantage in evapo-
rating over the flame of a gas-lamp.

Where rapidity of evaporation is the chief object, as in eva-
porating saline liquids to dryness to obtain the solid matter, it is
of course desirable that the vessel selected should be as open as
possible, to enable the steam to escape without hindrance; in
these cases, the basins shown in figs. 165, 166, and 167 are

Fig. 165.
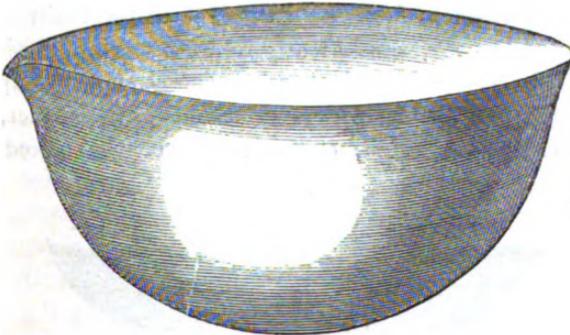
very well adapted for the purpose. They should be of the
Bayeux or Meissen ware, both of which are extremely thin and
light, and are therefore well adapted to withstand sudden
changes of temperature. Their thinness, however, renders great
care necessary in their use, especially in stirring the pasty mass
which is generally obtained towards the end of the process, as
if the stirring-rod is roughly handled, it is easy to push it through
the bottom of the basin.

K 2

313. Almost all liquids containing solid matters in suspension emit while boiling, small drops, which are thrown up to a considerable height; the greater portion of these fall back into the basin, but others are carried over and become lost; this renders it very improper to let liquids in basins boil where the solid matter has to be estimated with precision; it is true, that by

Fig. 166.
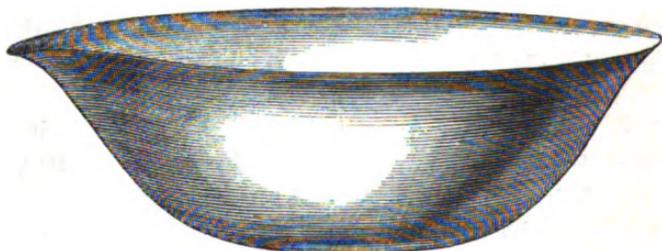
placing another basin somewhat larger, over the one containing the boiling fluid, much of this loss is avoided, but then a large quantity of the steam formed condenses upon the basin used as a cover and falls back, thus greatly retarding the operation, and making it far more convenient, as a general rule, to expose the basin to the heat of the water- or sand-bath. In fact, as has been previously indicated, evaporation over the naked fire is

Fig. 167.

more adapted to the copper pans of the pharmaceutist than to the porcelain vessels of the scientific chemist. Almost all saline fluids, as they become thick and pasty by evaporation, require to be carefully stirred, to assist in the escape of the vapour arising from them; if this precaution be not attended to, violent bursts of steam take place, which are liable to give rise to considerable loss of material by projection, and even to cause the fracture of the vessel. Not only does stirring prevent this, but it

also enables the operation to be completed in a much less time than would otherwise be necessary.

314. Evaporations requiring to be performed without loss, as in the concentration of mineral waters or the estimation of their solid contents, are best performed in flasks during the first stage of the process, that is, until they are so far reduced in bulk that they may be transferred to an evaporating basin, in order that the operation may be concluded on the sand-bath. The evaporating basins for this purpose are best when made of platinum or silver. It must be remembered, that some flasks are constructed of such bad glass that they yield soluble matters with considerable facility when waters are boiled in them for a long time. When this is the case, it is better to evaporate the liquid in porcelain basins over the gas-furnace; it is not generally safe to place them upon the sand-bath.

315. When evaporations are to be conducted in flasks until nearly all the fluid is expelled, or if any effervescence takes place or the boiling is violent, it is a good plan to have a small capsule placed in the neck of the flask, to avoid loss of solid matters without preventing the escape of the steam. It is essential, where evaporations in open basins are taking place, to prevent the ingress of dust; this may be accomplished in many ways, two of which may be mentioned. If a diaphragm of bibulous paper be placed at a little distance above a fluid which is evaporating without ebullition, it will prevent the dust from falling in without much retarding the evaporation, or a plate of glass may be laid on the top of the basin without quite covering it. A very convenient plan is to support a large piece of glass by two bricks at a few inches above the vessel in which the operation is proceeding, or even a plank may be used, but it must be placed so far away that no vapour will condense upon it and fall back into the dish, as it would probably cause the introduction of impurities, which would in some instances involve the necessity of throwing away the material under examination.

316. If the matter operated upon is injured or decomposed by too high a temperature, it may be placed upon the water-bath;

this will prevent undue elevation of the heat, but at the same time retard the process. It must not be forgotten that stirring so greatly facilitates the operation, as often to reduce the time required more than half.

317. In many analytical operations of this class the gas sand-bath (fig. 29) is extremely convenient, and, moreover, allows of the regulation of the heat with considerable nicety.

318. It is not at all an uncommon occurrence to have to evaporate liquids and dry precipitates which are decomposed by even very moderate degrees of heat; in these instances it is necessary to resort to the use of substances which have a great tendency to absorb moisture; among which may be mentioned sulphuric acid, quicklime, chloride of calcium, nitrate of magnesia, chloride of zinc, &c. Those most generally used are the three first, and they may be made available either with or without the assistance of the air-pump. The simplest way of using these desiccating media is by placing them in a porcelain or glass vessel, and supporting the fluid to be evaporated upon a triangle of wire or glass, or a piece of wire-trellis over the drying substance: the whole arrangement is placed upon a piece of ground glass, and is covered with a glass shade or bell-jar having its edge ground true and greased; by this means the damp air is prevented from entering, and as the absorbent gradually removes the moisture from the included air, the fluid parts with its water, and this goes on until the fluid is dried up or the precipitate completely desiccated.

If the apparatus, instead of being merely placed under a bell-jar, be put on the plate of an air-pump and exhaustion is effected, the process will be brought much more speedily to a termination. In either case the operation is necessarily rather slow.

319. It is well known that the point at which liquids boil is the higher the greater the weight of the atmosphere, as shown by the barometer; and from this it will readily be seen that *in vacuo* the boiling-point of liquids is very considerably lower than when under the ordinary circumstances of atmospheric pressure: this principle has been much made use of in many manufacturing operations on the large scale, particularly in sugar-works and in

the preparation of the more delicate and easily injured pharma-
ceutical extracts; it is seldom if ever required to operate in this
manner in chemical research, and a description of the manipula-
tion would be foreign to the plan of this work; but evaporation
in vacuo at ordinary temperatures is, on the contrary, an ope-
ration of every-day occurrence in the laboratory, and will there-
fore be described.

The air-pump, to be practically useful in experiments of this
kind, must not only be capable of effecting a good vacuum, but,
what is equally necessary, be able to retain it for several days, as
the process of exsiccation *in vacuo*, although a very perfect one for
removing mechanically or feebly combined water, is slow, and
some substances require a week's exposure to effect a perfect
drying.

320. One of the most convenient methods of operating, is to place
a glass vessel containing sulphuric acid upon the plate of the air-
pump and cover it with a very coarse brass-wire trellis, on which
the substances to be dried are supported in capsules or watch-
glasses; (it is an excellent plan to have a number of the latter
always at hand, their surfaces having been ground to fit each
other); if, now, the substance to be dried is weighed between them,
and the upper one be removed and put underneath, and both are
placed in the receiver together, it is easy to weigh the apparatus
again in the same manner as at first, after a certain exposure
to the absorbent surface, and by this means all danger of in-
crease from atmospheric moisture during the weighing is pre-
vented (§ 85).

321. It should be remembered, that in all cases of drying by
exposure to desiccating agents, the rapidity is greater the more
extended the surface and the thinner the stratum; it would be
difficult, therefore, to find anything better adapted to purposes of
this kind than watch-glasses; small capsules may, it is true, be
used, but they are generally far less convenient. In order to
ascertain whether the substance is perfectly dried, it may be
weighed and exposed for a day or two and then reweighed; if no
difference is observed, no further exposure is required, but if loss

is found it must be noted, and the substance is again to be desiccated for another day or two, and this alternate drying and weighing is to be continued until two estimations at tolerably long intervals are found to be the same.

322. There are many organic bodies which, although uninjured when heated to 212° in a nearly dry state, are, nevertheless, rapidly decomposed if introduced into the water-bath damp; such substances should be first dried over sulphuric acid until all outward appearance of moisture is removed, and may then be placed in the hot-air chamber or water-bath until perfectly dry. Some substances of a very explosive kind must be entirely dried *in vacuo*, as it would be dangerous to raise them to 212°, although it may be known that in general they require a higher temperature for explosion, as they are frequently very uncertain in their behaviour at moderately elevated temperatures, and it is singular that in a damp state some substances explode more readily than when dry; this is frequently the case with gun-cotton.

Where a great many desiccations have to be effected, it would be inconvenient to use more than one air-pump, and various methods have been contrived to enable one instrument to exhaust several receivers without adding very greatly to the expense; one, but not the most economical, is to have several ground plates capable of being attached to and removed from the pump, and having taps beneath to enable them to be closed before being removed.

323. Another process is that of Mr. Cooper's, recommended by Faraday, which consists of two plates of thick glass ground perfectly true, and having a small hole through each about one-quarter of a diameter away from the edge; these plates, with the holes opposite each other, are placed upon the pump plate, a tolerably plentiful supply of grease being rubbed over them; the receiver is then put in its position and the air exhausted; when a sufficient vacuum is obtained the plates are slightly moved, so that the two holes no longer coincide; they may then be removed without air penetrating into the receiver. Of course, by having several double pairs of plates, any number of receivers may be exhausted with one air-pump.

324. The sulphuric acid used for these purposes becomes diluted by frequent use, and must be replenished as this takes place: it is a good plan to have a mark made upon the glass pan which contains it, in order that the amount of increase may be known. When six parts have become seven, its action is too feeble to be worth keeping in the pan; it should therefore be removed and have fresh acid put in its place. It is advisable not to use this acid for any experiments of importance, as it generally contains many impurities; it will, however, answer very well for making hydrogen, sulphuretted hydrogen, or other purposes which do not require it to be pure.

325. Under certain circumstances, many other preparations having great affinity for water may be used instead of sulphuric acid, they have been alluded to in describing desiccation without the air-pump.

326. It has been said that some organic substances when introduced into the water-bath in a damp state are decomposed, although they bear the same temperature very well if previously air-dried; it is remarkable, also, that the presence of water in some cases tends to confer fusibility. Warren De la Rue found that carminic acid fuses if heated to 248° Fahr., unless it has previously been dried *in vacuo*. It is, moreover, by no means to be taken for granted in all cases, that a substance is sufficiently dry for analysis because it ceases to lose weight *in vacuo* over sulphuric acid, as many substances retain the last portions of water with such obstinacy as to render exposure to a temperature of 212° Fahr., or even higher, absolutely necessary.

SECTION XVIII.

DISTILLATION.

327. It has been said that distillation differs from evaporation, inasmuch as in the former case it is the fluid which is required, while in the latter it is not regarded, but, on the contrary, every facility is given for its escape.

Distillation depends upon the fact, that all liquids when heated to a certain degree, called their boiling-point, become converted into vapour, which, by the application of cooling agencies, may again be condensed into the fluid state. It will readily be seen that, as liquids differ so greatly in the temperatures necessary for their vaporization, and also that, as vapours require such very different degrees of cold (if the expression may be allowed) for condensation, the methods of distillation must be exceedingly numerous to suit all cases; it would therefore be almost a hopeless task to enumerate every contrivance which has been adopted to meet the ever-varying cases which constantly occur in research. But as the subject is one of such great importance and every-day application, especial care will be taken to point out the more salient features in the manipulation.

328. One of the most ancient instruments for the purpose is the alembic, which may be considered the type of all distillatory apparatus, and although seldom used in modern chemistry, it must be confessed that it was admirably adapted to the processes in vogue among the alchemists, by whom it was chiefly used: it consisted of two portions, capable of being separated; the lower, known as the body, cucurbit, bolt head, belly, chamber, and by several other fanciful expressions,

Fig. 168.
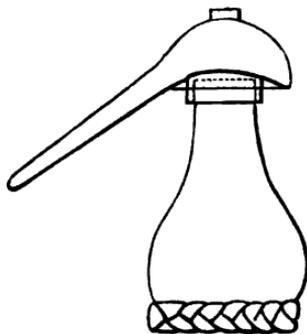
was a gourd-shaped vessel (whence one of its names, cucurbit), well fitted for being cleansed, or to have solids or liquids introduced. The head, or capital, was also singularly perfect in shape for the intended uses; it had a species of channel all round to carry any liquid which condensed in it to the beak, by which it was conveyed to the receiver. Modifications of the alembic are still used, and will be pointed out in the proper place.

329. The simplest apparatus used by chemists for distillation, consists of the retort and receiver, fig. 90, where *a* is the retort having its neck inserted into a receiver, *b*. The retort rests on a triangle, *d*, supported on a small clay furnace, *c*. The receiver is supported by a tripod, *e*, of iron wire. Retorts seldom crack if heated over a charcoal fire in this manner, in consequence of the complete diffusion of the heat over the whole body of the vessel.

Retorts require care in their selection, as they are sometimes so imperfectly formed as to be scarcely adapted for the purpose intended. They should be selected light and free from specks and flaws, which are liable to cause them to crack on the application of heat. They should also be well made about the part where the neck is bent, the curve being as round as possible, and not like a large wrinkle, as is the case with those which are carelessly formed. With tubulated retorts, the tubulature should be directly over the body, so as to permit the entrance of a thermometer; no retort should be used in which the tubulature is formed so far forward, that when in its position a liquid or solid cannot be added without soiling the neck, as is the case with many that are sold. The form usually made in England is more globular and less deep than those imported from the Continent. I am inclined to prefer the latter form for general use. It is a convenient plan to draw out the necks of retorts, which may readily be done in the blowpipe-flame. By this contrivance, the neck may be introduced into receivers without the use of an adapter, an important point in many distillations.

It is constantly necessary during distillation to add liquid or

solid matters without stopping the process, hence one reason for the necessity of having the tubulature directly over the body of the retort. This addition requires considerable care, for several reasons; in the first place, the addition of solid matter to a boiling fluid, by forming a number of points for vapour to be evolved at, frequently causes the fluid to froth over and contaminate the liquid in the receiver, so that the process is retarded, as the fluid has to be returned to the retort, and the distillation repeated. The powder or other solid body must therefore be added very gradually. If the powder be heavy, it falls to the bottom and forms a cake, which, by preventing the proper distribution of the heat, and causing an undue rise of temperature in one spot, is almost sure to cause the fracture of the vessel; if possible, therefore, the distillation should be arrested and the powder introduced by small portions, and by a gentle motion of the retort in the hands is to be thoroughly disseminated throughout the liquid until dissolved; or if comparatively insoluble, a wire should be passed through the cork which closes the tubulature, and being bent into a handle on the outside, be kept in motion during the distillation, so as to prevent the accumulation of the powder at the bottom; and the heat is to be applied with greater care than usual, and less directly upon the bottom.

If, on the other hand, the matter to be added is in the liquid state, it is to be considered whether the addition will cause any chemical action, and if so, it is to be added with sufficient care to prevent the rising of the materials to such an extent as to cause the contents of the retort to boil over into the receiver. It is necessary that care should be taken in the addition of cold liquids to a glass vessel containing a fluid at a high temperature, as it is very liable to cause fracture. If introduced by a funnel, it must not be allowed to penetrate very far into the retort so as to cool the bottom part too much, but rather be added by small degrees, the funnel penetrating only a short distance below the surface; by this means sufficient heat is immediately communicated to the fluid added to prevent fracture of the vessel. Substances in hard lumps must not be added at all during the progress of the distil-

lation, but must be introduced while the retort is held, with the bottom only slightly depressed, so that the pieces added may slide gently down the neck, or through the tubulature, into the body of the retort without any concussion.

330. In distillations of liquids the habitudes of which are not thoroughly known, it is well to have the retort capable of holding twice the quantity of materials to be introduced, in order to prevent the probability of an overflow. In some processes, the contents of the distillatory apparatus are so prone to froth, that vessels of even three or four times the usual size (compared with the bulk of the contents) are insufficient to retain the fluid during the boiling. In the preparation of formic acid from starch or sugar, for instance, the contents of the still sometimes swell to thirty times their original volume, and much annoyance is experienced until the peculiarities of the operation are become familiar to the operator.

Next to the selection of proper retorts for the process about to be undertaken, the receiver best adapted for the purpose claims attention. In the great majority of cases, a common globular flask is all that is required; it is shown in fig. 169. Fig. 170 is a

Fig. 169.
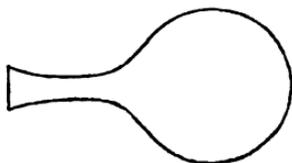
Fig. 170.

a long-necked receiver, very convenient in many instances, and from the distance the vapour has to travel before it can escape into the air, acts well as a condenser. They are also useful where Gay-Lussac's method of ascertaining the value of peroxide of manganese is used. Receivers, the same as figs. 169 and 170, with the addition of a tubulature, are also convenient in many distillations. Figs. 171 and 172 are more complex in shape, but are nevertheless necessary, not only in the preparation of many organic substances, such as those formed by the action of chlorine

or other gases upon alcohol or hydrocarbons, but also in a great number of other processes; and that shown in fig. 171 is often used in ordinary distilla-
tions, from the effective
manner in which the globe
acts as a condenser, and
also as a valve or safety-
tube; for if the end, *a*,
is immersed in the liquid
in a flask, and contraction
takes place in the retort,
the fluid rises in the long
tube, and may, perhaps,
partly fill the globe; but
as soon as it has all passed
in, air-bubbles rise up
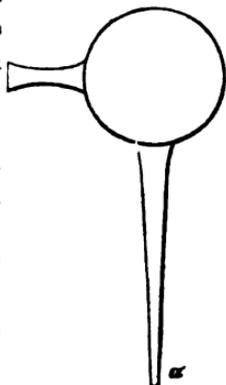
Fig. 171.   Fig. 172.
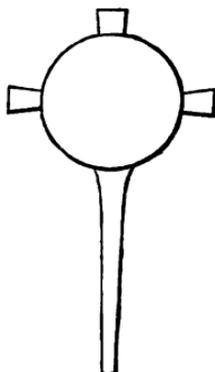
through the column of fluid and restore the balance of pressure. Where in a distillation a gas as well as a fluid is produced, the usual method of proceeding must be somewhat modified; the arrangement to be selected of course depending upon the nature of the gas and fluid formed.

331. It is frequently observed, that, from various reasons depending upon the nature of the distillation, sudden contraction takes place, and if the neck of the retort dips into the distilled liquid, it will infallibly rush back, and the experiment will in all probability be destroyed. Accidents of this kind may be prevented by the use of the safety-tube, several modifications of which are shown in the section on Manipulation connected with researches on Gases.

332. *Substitutes for retorts.*—In many processes of distillation, retorts are by no means the most convenient kind of vessel in which to perform the operation, and it is possible to contrive a great many substitutes. Several that are not shown in the pages immediately following, will be seen by reference to the figures representing various processes involving distillation in the course of the work. The most obvious and commonly used substitute

for a retort and receiver, is constructed from two flasks connected by a tube fitted with corks.

Small distillations may sometimes be advantageously effected by means of test-tubes connected in the same manner. The tube delivering the vapour passes through a cork in the recipient, the aperture in which holds the tube tolerably tight, but allows the air to escape as it expands by the heat. The tube acting as the condenser may be kept immersed in cold water to facilitate condensation of the vapour.

333. Tube-retorts may be made of a great variety of forms, and are extremely valuable in experiments of research, from the facilities which they afford for working upon quantities of liquid so small that they would be lost in retorts or other distilling apparatus of the usual size; they are therefore much employed in investigations on the products of decomposition of organic bodies, particularly such as are only procurable with difficulty or at great expense. In experiments of demonstration they are equally useful, where the results are only to be observed by one or two persons; and combinations and decompositions may be observed in them as readily, and sometimes more so, than in working on much larger quantities.

The student will do well to practise the construction of these vessels, which will be found extremely easy after a little experience. Faraday, whose dexterity as an operator in tube chemistry was proverbial before he devoted himself to electrical and magnetic investigations, was perhaps one of the first to publish the methods of using vessels constructed of tube for most of the operations in chemical research, and since that time their use has become greatly extended. And when the student is reminded that the magnificent and highly difficult investigation of cacodyle, by Bunsen, was almost exclusively worked out in tube apparatus, he will be able to form some idea of their value.

In the section on Glass-blowing, descriptions will be found of the various methods of bending, blowing, and cutting glass tubes, and of constructing retorts used in tube chemistry; also a few

general directions as to the best methods with which the author is acquainted of forming various articles of glass apparatus.

334. Figs. 173 to 177 represent a few of the most commonly used tube-retorts, but several others will be seen on referring to

Fig. 173.
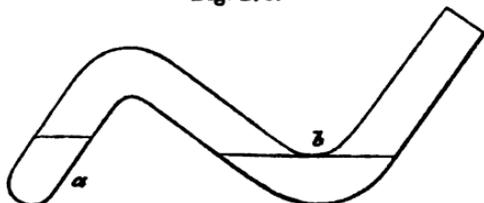
the engravings of apparatus scattered throughout the pages of this volume.

Fig. 173 shows a form of retort easily made, and sometimes

Fig. 174.
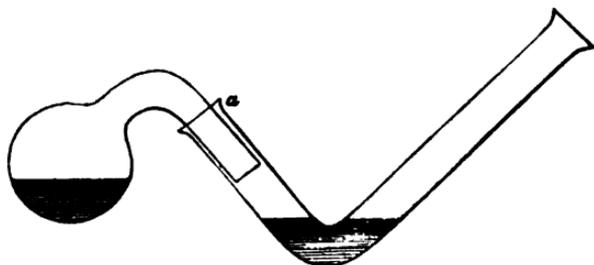
very useful. The fluid to be distilled is made to occupy the part a, and gentle heat is applied just sufficient to raise the vapour,

Fig. 175.
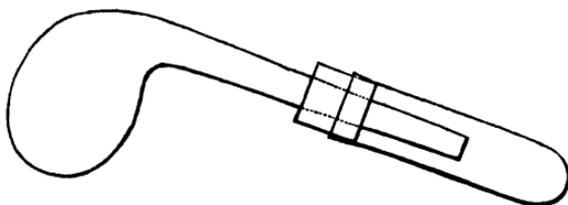
the retort being held vertically. The part b is kept cool by a piece of moistened rag, or any other convenient method, and this

is continued until the portion of the substance introduced which contaminates the sides is washed down; the retort may then be placed as in the figure, and the distillation be proceeded with, the angle, b, still being kept cool; a retort and receiver are thus formed in one piece, and as the distillate may easily be removed by a pipette, the instrument is seen to be managed with ease, the only disadvantage being the loss of time in washing out the liquid to be distilled from b. Clarke's retort and receiver, fig. 174, are in some slight degree like the last; the chief differences are in the shape of the retort, and in the arrangement consisting of two pieces instead of one; the form of the receiver is the same, and it also resembles the first in being open. It is generally, however, made much larger, and intended to hold about two fluid ounces. The receiver must of course be kept cool; a short test-tube full of water may be inserted at the open end, to assist, by the coldness of the fluid, in effecting condensation. The neck of the retort fits with sufficient stiffness, at a, to render it merely necessary to support the receiver by the vertical clamp (§ 238) or otherwise. If the neck of the retort fits too loosely, it may be tightened by rolling a piece of paper round it.

335. The small retort and receiver, fig. 175, are easily constructed out of the fragments of tubing which are constantly accumulating in the laboratory: it is a useful arrangement where the quantity of fluid under examination is extremely small. The liquid may be introduced by immersing the point in the fluid to be inserted, and alternately heating and cooling until the object is effected. It is preferable, however, to make the neck sufficiently large to admit a small funnel drawn out of a piece of tubing. A small test-tube makes an excellent receiver, the neck of the retort being held steady by passing through a cork, which, however, does not fit so tightly as to prevent the escape of the expanded air on the application of heat.

Fig. 176 shows another way of constructing these little vessels, which is more especially useful where a sublimate is formed which would choke up the small orifice of that last described, or

if it is desired to clean it out for a repetition of the experiment, or other purposes.

Fig. 176.
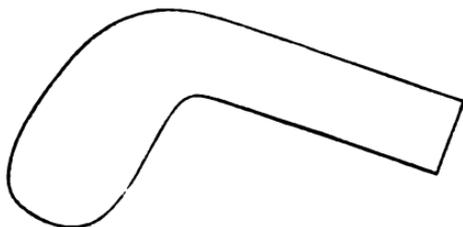
336. Fig. 177 shows an arrangement of the retort and receiver of a somewhat different kind to those previously described; it is used where it is neces-sary to pass the vapour of a substance over some solid matter to effect a change in the vapour previous to collecting it. There are many pro-blems of this kind con-stantly occurring in the laboratory; if, for ex-ample, it is wished to dry

Fig. 177.
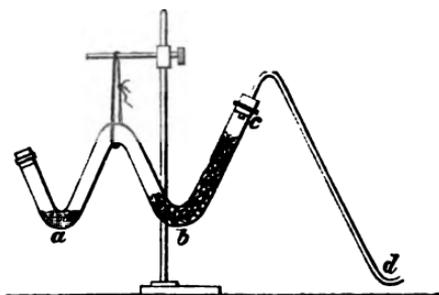
a gas formed on applying heat to some substance in a, it may be conveniently effected in many instances by passing its vapour through the desiccating agent contained in fragments at b c; or oil of vitriol may in some cases be placed at b, in just suffi-cient quantity to close the bend of the tube, the end being corked; the gaseous products are conveyed away by the tube, d. Hydrobromic acid is sometimes prepared in this apparatus by having bromine at a, the vapour of which is passed through pieces of phosphorus at b, and fragments of glass wetted with water, from b to c; the acid gas is evolved by the tube, d, and may either be collected in the mercurial trough, or be absorbed by water.

337. The common alembic has been alluded to at p. 202; it was, however, omitted to be stated there, that it is well adapted for operations where a sublimate is formed simultaneously with a fluid, as the latter drains off through the channel previously described, and leaves the solid matter comparatively pure, at least as regards contamination with the liquid products of distillation. Small alembics blown at the lamp are sometimes employed; they are made in two pieces, the head being fitted to the body by grinding, and the former having a tubulature to allow of more fluid being introduced during the distillation. They are, however, too fragile and expensive for common use. In alembics, the chief condensation is in the head, its globular shape well fitting it for that purpose. It is perhaps strange that alembics are so little used, as, if made with the beak at a much less acute angle than as generally seen, so that they may be attached to a condenser, they are exceedingly convenient for many operations, from the facility with which they may be cleaned. This is particularly the case with those made of stoneware described further on.

An extremely convenient mode of effecting distillations on the small scale, is by the use of a U-tube for a receiver, having one arm bent and bordered for the reception of a cork, into which the neck of the retort is inserted, fig. 178. The other end of the receiver has a small

Fig. 178.

opening, to allow of the expansion of the vapour. A beaker containing a freezing mixture may be used, if necessary, to cool the condenser; in most cases cold water is sufficient, if changed when it becomes warm to the touch.
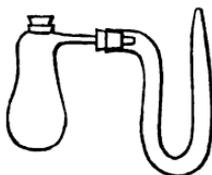
338. The ordinary still and worm to be found in almost all laboratories, is constantly in use for a great number of operations. It is frequently required for preparing distilled water; and if the head be removed, the boiler, if of a capacity of from twelve to twenty gallons or more, is very useful for preparing decoctions of plants, previous to an examination of their constituents, evaporation of large quantities of liquids, preparation of various

substances, &c.   Many varieties of stills are now in use, and
considerable ingenuity has been displayed in adapting them to
the purposes for which they are required; it is seldom, how-
ever, that in a laboratory of research more than two stills are
required, and these are generally of the simpler description, the
more complex ones being almost exclusively used in technical
operations, and a description of them does not, therefore, come
within the scope of this work.

339. The still shown in fig. 179 consists of a stout copper
boiler, *a*, inserted in brick-work, and furnished with a tap to run

Fig. 179.
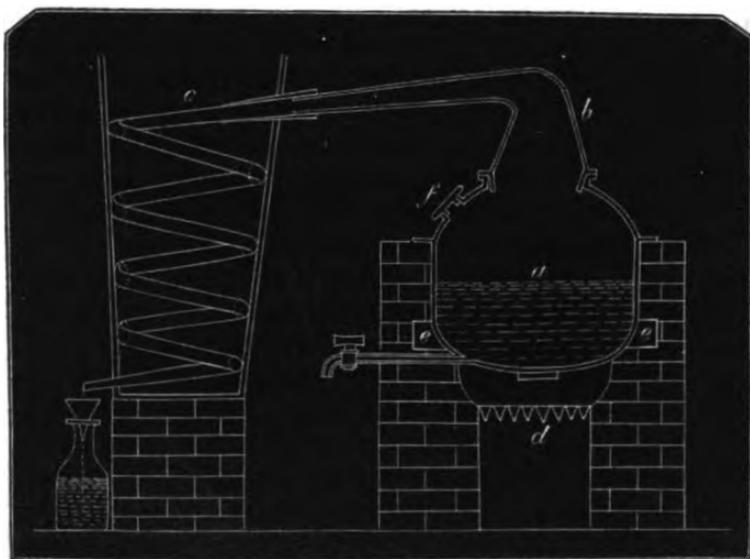
off the liquid when necessary; *f* is the man-hole, which serves
to introduce fresh quantities of fluid without removing the head.
It is also sometimes used to insert a thermometer, when it is
desired to ascertain the temperature, as in preparing formic acid
from starch, and many other operations.   The head is seen to be
provided with a flange, which rests on the rim surrounding the
top of the boiler; the tube leading from the head fits into the

enlarged end of the worm-pipe, and the points of junction here and where the head fits in to the boiler, are made good with a luting of almond- and linseed-meal. The worm-tub is kept well supplied with cold water during the distillation by a pipe leading to the bottom, the heated water by its diminished density floating on the top and flowing away by another pipe; neither of these are shown in the engraving. The flue is so constructed that it winds once or twice round the pot, as at *e e*, and finally escapes into the chimney; by this contrivance a great saving of fuel is effected. It is not advisable, as a general rule, to fill the boiler higher than is shown in the figure, especially where there is a tendency to froth. The fire-bars are seen at *d*; the supports on which they rest are not shown; they are the same as in fig. 4, p. 12.

340. It is proper where very volatile liquids, such as ether, are distilling, to place a piece of moist bladder over the exit-pipe of the worm and the funnel into which the liquid drops, to prevent evaporation.

Where it is wished to distil as rapidly as possible, the head should be kept hot by covering it with a cloth, which effectually prevents condensation there, and causes almost the whole of the vapour formed to pass at once into the worm.

341. The operation of distillation is in general one of great ease and simplicity, and few precautions are required; it is, however, necessary to avoid urging the fire too fiercely, as, if the steam is formed with too great rapidity, the head is liable to be blown off, there being considerable resistance offered to its escape by the worm. The distillate should never be perceptibly warm as it issues from the condenser; when such is the case, the fire must be slackened and the supply of cold water increased.

342. If spirituous fluids are being distilled, to increase the quantity of the more volatile ingredient in the distillate, the fire should be kept low, so that the fluid may issue very slowly; it is sometimes better that the liquid in the still should not boil in these operations, in order that the amount of water coming over with the spirit may be as little as possible. If a weak spirit

is to be concentrated, as in distilling off the alcohol or ether from the residues constantly accumulating in the laboratory, it is better to have a water-bath made to fit inside the still, the head fitting tolerably tight. The weak spirit is to be placed in the bath, the body of the still being filled to the usual height with water; the head is then luted on, and the water in the still made to boil; the fluid in the bath never reaches quite to 212°, and the ether or alcohol comes over readily; when this stops, the contents of the bath will be found to contain very little spirit and may be thrown away, except where some valuable substance is contained in it.

343. When a substance has been dissolved in alcohol or ether for the purpose of obtaining it in crystals, and the first crop has been separated, it is generally necessary to concentrate the fluid to obtain a second crop; the value of alcohol and ether renders it usual to perform this by distillation, in order that the spirit may be recovered and used again for similar purposes; as this is usually an operation performed upon very small quantities, it is best to distil from a flask placed upon a small water-bath, and attached by a glass tube to one of the condensers to be described further on.

Fluids containing mixtures of spirit and water are liable to boil with concussion, or, as it is usually termed, "bumping;" this may be obviated in several ways, most of which have for their object the production of surfaces containing points, in order to permit with ease the evolution of the vapour; pieces of wire, preferably platinum, fragments of glass or quartz, &c., may be used for this purpose: even fragments of cork or wood thrown into the retort to some extent assist the evolution of the steam.

It must be observed, however, that if the liquid in the retort commenced bumping before the platinum wire, &c. was introduced, it must be allowed to cool 20 or 30 degrees before attempting to retrieve the oversight, as, if fragments of metal, wood, cork, glass, &c. be thrown into a retort at or even a little below the boiling-point of the contents, it frequently happens that so large a quantity of vapour is suddenly formed that the fluid boils over and may do considerable injury, especially in the case of such inflammable liquids as alcohol and ether.

344. It is necessary, as a general rule, to note the quantity of fluid introduced into a still, because from the opacity of the vessel it is impossible to see when the contents are getting low, but if it is known how much is contained in it, and the quantity coming over is observed, no fear need be entertained of proceeding so far as to injure the bottom of the vessel.

345. In the distillation of vegetable matters with water, it is a good practice to place them upon a perforated false bottom raised a few inches above that of the still, in order to ensure them from burning. Where herbs are to be distilled to procure essential oil, it is proper to add some salt to the water, in order to raise its boiling-point a few degrees, as by this means the oil is procured with more facility, and, according to some distillers, in larger quantity.

346. One disadvantage of the ordinary worm-condenser is the difficulty with which it is cleaned, and one product is liable therefore to be contaminated with that which has been previously distilled. In all cases where a fluid has passed over which is not readily removed by running cold water through the worm, the latter should be closed by a cork at its lower end, and filled up with some solvent capable of removing the obnoxious matter.

The solvent to be used of course varies with the different matters to be removed; alcohol, wood-spirit, benzole, dilute solution of caustic potash, or acetic acid, are the substances most commonly resorted to for this purpose; where wood-spirit or benzole has been used, it is necessary afterwards to empty the worm-tube and blow steam through it until the odour is removed, before proceeding to distil. In fact, this operation alone will frequently remove impurities from the worm without the use of any solvent.

347. The difficulty of cleaning the worm has led to the invention of several modifications of it, the greater number of which are only employed in technical operations. One of them, however, may be mentioned here; it is extremely simple in principle, but requires considerable care in its manufacture to answer the purpose perfectly, as, if the workmanship is not good, it will be found difficult to prevent leakage. The ends of the worm (which is merely a zig-zag) project from the tub at each bend, and are connected together

by pieces of tube which slip on tightly, and are made good, if necessary, by a little luting. It is evident that if the joints are taken off, it is easy to pass a bottle-brush or other convenient cleanser down the tubes, so as to remove any dirt with facility.

348. Retorts require somewhat more care in their use than stills, from the fragility of the material of which they are constructed; if used properly, however, it is seldom that they break during a distillation. The remarks upon the proper degree of stoutness in material given with regard to flasks, apply with equal force to retorts; they need not therefore be repeated. In general it is essential to apply the heat exactly under the centre of the bottom of glass vessels, as, if the sides become heated many degrees above the liquid, the comparatively cold fluid, if thrown upon it during the ebullition, is liable to cause fracture. There are, on the other hand, instances in which it is necessary to place the lamp a little on one side of the retort, so that the full heat may not play directly upon the bottom: some liquids which boil with violent concussions, although a considerable quantity of platinum may be in the retort, may be brought over quite quietly by this means. When a liquid is introduced into a retort and heat is first applied, it is usual to find water condense on the outside of the glass; it is advisable to remove this with a cloth. Care must be taken so to regulate the heat that the fluid may never be distilled too rapidly for the means of condensation, as, in the case of volatile liquids, considerable loss may be occasioned. If the fluid being distilled has a very high boiling-point, it is better to cover the dome of the retort with a hood of some kind to prevent condensation there, because if this be neglected the operation is much and unnecessarily prolonged, and with liquids decomposable by protracted ebullition, loss is incurred; where, however, the object is to separate a more from a less volatile fluid, this procedure is injurious to the success of the experiment, as the less volatile portion is retained by the condensing power of the dome, while the more volatile one passes over.

349. Where the substance being distilled is very volatile, or contains a difficultly condensable ingredient, and efficient means

of cooling are not to be had, the receiver may be attached to the retort by a well-fitting cork, through which, or the tubulature of the receiver, a small tube passes, and dips a short distance under mercury, or, in some cases, a fluid capable of absorbing the volatile product; the mercury allows any permanently elastic matter to escape, and so prevents disruption of the joints, while any fluid condensable with the aid of a slight pressure is retained. Where this precaution is adopted, it is necessary to ensure against the possibility of the fluid whose pressure is made use of, rushing back into the receiver. This may be easily effected by the use of one of the safety-tubes described further on.

It is advisable, as a general rule, to which there are, however, some exceptions, not to allow the beak of the retort or other distillatory vessel to dip under the surface of the distillate, as, in the event of the heat being suddenly lessened, contraction takes place and the liquid will in all probability rush back into the retort; this is almost sure to happen under the circumstances indicated, unless the neck of the retort is so large as to more than contain the distilled fluid, because, as soon as the fluid has all entered the neck, air-bubbles pass through it and equalize the pressure in the same manner as with the quilled receiver previously mentioned.

Fig. 180.
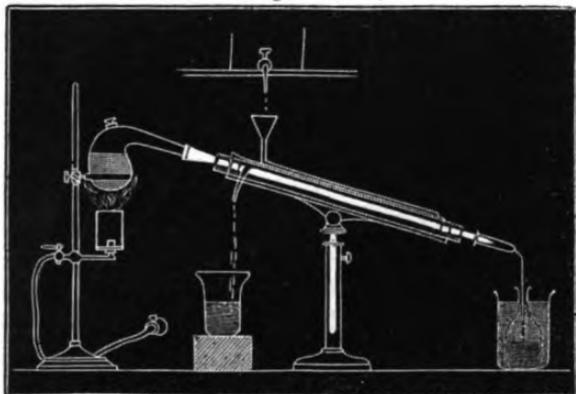
350. An excellent method of condensing in distillations with retorts is by the use of Liebig's condenser, fig. 180. It is seen in

L

other places in this work.   A tube of tin is closed at each end by a cork through which a glass tube passes; the tin portion is to contain the cold water, which by means of the funnel enters at the lower end, and, after becoming heated, escapes by the upper aperture.   Simplicity of form is one of the chief merits of this apparatus, enabling it to be cleaned with facility after any operation.

351. It frequently happens that the neck of the retort is too large to enter the recipient; one method of obviating this has been already given, p. 203; another is by the use of adapters, which are tubes, generally of glass, rather wide at one end and small at the other, the wider end to admit the retort-neck, the other to enter the receiver.   The simpler shapes are easily made with the blowpipe and some large tubing, which, for this purpose, is preferably of flint-glass.   Figs. 181 to 186 show several varieties of adapters fitted for different purposes.

Fig. 181.   Fig. 182.

Fig. 183.

Fig. 184.
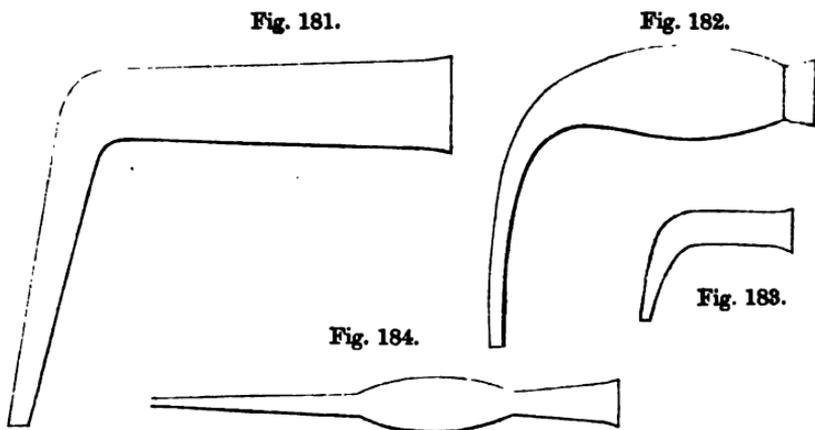
If it is merely desired to connect the exit of a Liebig's condenser with a bottle or flask intended to contain the distillate, figs. 181, 182, and 183 are the best; but, if the fluids being distilled do not require much refrigeration, and it is simply intended to connect the retort or other distilling apparatus with the receiver, figs. 184, 185, and 186 are convenient.   It is

often an effectual method of condensation to arrange the apparatus

Fig. 185.
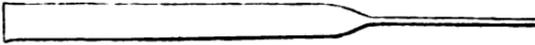
Fig. 186.
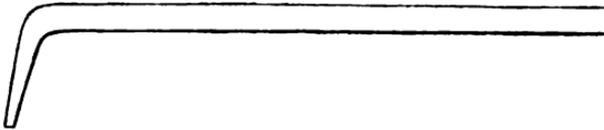
as in fig. 187, where it will be seen that a retort, *a*, is fitted at *b* with a cork into a long adapter, *c c*, similar to fig. 186; the bent

Fig. 187.
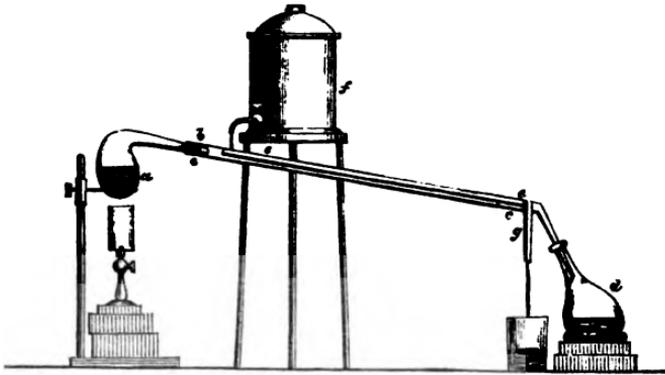
point enters a flask, *d*; at *e e*, a piece of bibulous paper is placed along the adapter and receives the water which falls from the tap of the water-bottle, *f*. At *g* another piece of paper is placed across the adapter, its ends hanging down, in order to conduct the water which has performed its office into the vessel beneath. It must be observed, that if the tube, *c c*, is placed too slanting, the paper, *g*, will be unable to prevent the water from passing *g* and entering the flask, *d*. In some cases it is impossible to prevent great obliquity of the conducting tube, *c c*, as in connecting with re-

L 2

ceivers those alembics the beaks of which have a "quick dip," as it is termed, or, in other words, make too acute an angle, with a vertical axis passing through the vessel, it is then necessary to pass a pierced but tightly-fitting cork over the conducting-tube, making it occupy the place of g in the above figure; the water will then be conducted by the cork into a vessel placed beneath it.

In distilling fluids which are not corrosive, it will be found exceedingly convenient to have some adapters made of tinned iron, somewhat of the shape of fig. 186. In order to prevent the condensing water passing into the recipient, a piece of tin, shaped like a heart, is pierced in its centre to permit it to be passed over the bend for a short distance. It is then soldered in its place, and all the water running along the condenser stops short at the impediment thus placed in its course, and runs down in a stream from the lower end into a pan placed to receive it.

352. When the liquid to be distilled is very volatile, or if a mixture contains a very volatile ingredient, several expedients may be resorted to in order to effectually condense the whole of the vapour. Sometimes, after passing through a Liebig's condenser, it is conducted into a flask immersed in snow and salt, or some other convenient freezing mixture, or into the arrangement seen in fig. 188, where the tube, a, is supposed to come from a condenser, and enters a series of U-tubes, $b\,b$, immersed in a freezing mixture contained in the vessels perforated at the bottom, to allow the passage of the conducting tubes, $c\,c$, which are attached to the U-tubes,

Fig. 188.

and terminate in the flasks, $d\,d$, which may likewise be placed in a freezing mixture.
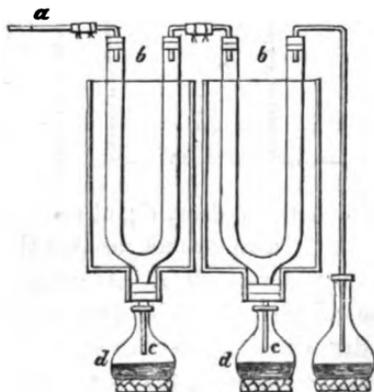
This is, however, an expensive arrangement, and one that may generally have substituted for it a far simpler one constructed of flasks, and connected by glass tubes fitted into corks. Where no freezing mixtures are at hand, it is sometimes necessary to avail ourselves of the property of evaporating fluids to carry away a large amount of heat, which becomes latent as they are converted into vapour; for this purpose alcohol, ether, wood-spirit, and some other volatile fluids are employed; their use is, however, limited, and it is far better to avoid them if possible. Fused nitrate of ammonia, when dissolved in water, developes cold, and as it may be evaporated down and used again any number of times, it becomes a very useful auxiliary in many researches.

Fig. 189.

An extremely convenient mode of cooling in distillatory experiments on the small scale, is by means of the contrivance seen in fig. 189. It consists of an adapter, $a\,b$, having at its lower end, b, a piece of vulcanized india-rubber tube, $b\,c$, which passes through a square hole mortised in a block of wood, f. A small piece of hard wood, d, lies in the cavity, and, on turning the screw, e, is pressed against the tube, so as to collapse it to any required extent, and consequently regulate the flow of water. These compression stop-cocks are adapted to a multitude of purposes in the laboratory, and are very easily made by any person with the aid of the tools to be described further on. A piece of glass tubing, g, is tied at the lower end of the vulcanized-pipe, which latter is securely fastened by silk at h and c.

353. *Fractional distillation.*—It frequently happens in organic researches, that mixtures containing several substances of different boiling-points present themselves, and the only available means of separation sometimes consists in what is termed fractional

distillation. This process is not only one of great labour, but, unfortunately, it has little claim to accuracy as regards the *absolute* separation of bodies, it being, perhaps, almost impossible to procure one substance out of a mixture of homologous fluids in such a state that it can be said to contain no admixture of its associated compounds. This arises from the fact that the boiling-point of an organic fluid is dependent upon the relative number of the atoms of carbon and hydrogen present, the former element raising while the latter lowers the degree at which it is converted into vapour; it will therefore be seen, that on endeavouring to separate bodies by this means, where homologous groups are present, it is possible to obtain fluids having the theoretical boiling-point, and proportion of carbon and hydrogen in the hundred parts, and yet being admixtures of the fluids above and below in the homologous series, the deficiency in the carbon and hydrogen of those lower in the series being exactly counterbalanced by the excess in that portion present belonging to a higher position in the group. This mode of separating bodies is always, therefore, to be considered as by no means preventing the necessity for further modes of purification being adopted in all possible cases, and it is only with some neutral hydrocarbons that any great difficulty occurs in this respect.

354. Where only one substance is sought to be obtained from a mixture, and there is ample material to work upon, it is possible to obtain it in a state of *comparative* purity, although with considerable loss*, by distilling it several times in a retort with a thermometer in the tubulature, and each time rejecting all liquids boiling below or above the point known to be that theoretically belonging to the fluid under examination ; by this means a large quantity of the mixture may be made in general to yield sufficient of the substance sought for an examination of its chief properties. It is far better, wherever practicable, to submit the liquid to a complete fractionation, which is performed by distilling it with a

* This loss is not absolute, but as a considerable portion of the substance sought becomes by the process disseminated through a great mass of the other bodies, it may be said to be lost for all practical purposes.

thermometer in the tubulature, and changing the receiver at, say, every 10° Fahr., or 5° Centigrade; by this means fractions are obtained, which are to be again distilled into a fresh series of bottles in the same manner, which forms the second fractionation. It will be seen that where a fluid begins with a low boiling-point and rises very high towards the end, this process involves an immense amount of labour: if we suppose the fluid to commence ebullition at 200° Fahr. and rise to 400°, there will be twenty bottles required, the contents of each to be again distilled, and generally towards the beginning of the operation, each fraction, when redistilled, spreads itself over four or five bottles, requiring therefore constant attention; and when the liquids are completely fractionated fifteen times, as was the case in the investigation of the bases from Dippel's oil by Dr. Anderson, and in my own experiments on the naphtha from Boghead coal, 300 distillations become necessary as a minimum; in each of those researches, however, at least 1000 distillations were made, involving an amount of labour, patience and attention, which few who have not worked out such processes can imagine. By the method given, there are only two series of bottles required during the operation, one containing the fluids being distilled, and another receiving the products of the distillation. As each distillation reaches its close, a point is attained when it would be unsafe to proceed further, the quantity of liquid in the retort being too small; this should, in a careful operation, be very little, but as it is constantly occurring, it must not be wasted, and it is generally, perhaps, the best plan to draw it off with a siphon or pipette when the retort is nearly cold, and (as most fluids become coloured by ebullition) place it in the bottle corresponding with the second fraction above it of the series then being distilled, not the series being distilled *into*; by this means, the last distillates are always colourless, if the liquid does not come over coloured.

355. It is a disputed point whether the bulb of the thermometer should be immersed in the liquid of the retort during a fractional distillation, or in the vapour; but if we consider that the vapour represents the fluid distilling, which is always a

nearer approach to homogeneity than that in the body of the re-
tort, which is always of a higher temperature, it will be admitted
that the bulb should be as near the fluid as may be, but not in
it, to indicate the boiling-point of the fluid distilling over.   This
does not apply to pure liquids: for then the bulb should be
thoroughly covered with the boiling fluid.   In fractional distilla-
tions no regard need be had to the influence of atmospheric pres-
sure, as the fractions are all produced nearly under the same cir-
cumstances; this does not apply to ascertaining the boiling-points
when the fluids are pure.   For the influence of the barometric
indications upon the result, see p. 55.   Fractional distillations
will generally be commenced with a large retort, but as the liquid
becomes dispersed over a number of bottles, and consequently
the quantity of fluid in each distillation is much lessened, a smaller
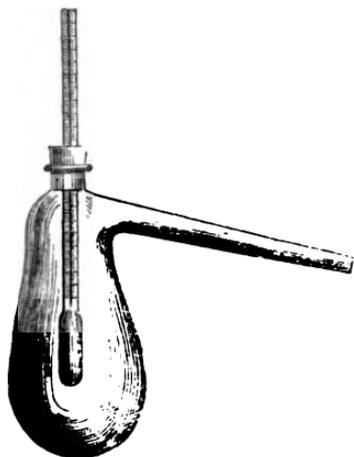
retort must be used, and if the
fluid is small in quantity and
very valuable, that figured in the
margin will be found extremely
convenient, and as it is made from
tubing at the glass-blower's lamp,
it is light and not liable to crack.
The thermometer is held verti-
cally by the cork.   Where it is
merely intended to isolate a more
from a less volatile fluid, an ap-
paratus, the same as, or on the
principle of, that employed by
Wurtz to separate the butylic
alcohol from the amylic and others

Fig. 190.

of the same series in fusel oil, is of great assistance.   The less vola-
tile fluids are condensed in a bulb placed over the flask, while the
more volatile pass over; by an arrangement of this kind much
labour is saved.   When liquids have been fractionated several
times, portions are almost invariably obtained, boiling many
degrees below the original point of ebullition, which fact has been
mistaken by some for a breaking up of the liquid with production

of fluids of more simple constitution; but this is not the case, at least in the majority of instances, the lowering of the boiling-point simply arising from the successive removals of the more carburetted and consequently less volatile portions of the mixture. It is not intended to assert that breaking up never takes place, for it has been said by some chemists that certain fluid hydrocarbons, when distilled until their boiling-point has become nearly constant, and then kept for a considerable time, boil at a very different temperature than at the time of preparation, the differences in height of the barometer of course being allowed for. If, therefore, some hydrocarbons break up at normal temperatures, it is to be supposed that they would be far more liable to do so at the point required for distillation; the alleged phenomena, however, require confirmation. Mansfield, whose experience in the fractionation of fluid hydrocarbons from coal-naphtha gives weight to his opinion, denies that any breaking up takes place in those examined by him. It would be interesting, therefore, to expose fluids of this class, the boiling-point of which is constant, to a tolerably high temperature in sealed tubes, and then examine the fluid, as by this means the question might probably be decided. It is doubtless the case that when organic fluids, more especially those with somewhat high boiling-points, are distilled, decomposition takes place to a greater or less extent, as is made evident by the colour which is at last acquired by liquids which were perfectly limpid before the operation; the change, however, appears to depend upon a gradual oxidation of the hydrogen of the substance, water being formed and carbon eliminated, and differs entirely from a molecular breaking up. This is confirmed in many ways, amongst others by the fact that water becomes evident as the distillation proceeds, no matter how carefully exposure to the damp air has been avoided; and also, that when a current of dry hydrogen, carbonic acid, or nitrogen is substituted for air, the decomposition is prevented. It must be remembered when distilling in a current of gas, that if it is one less dense than air the boiling-point will be lowered, and *vice versâ*.

356. When volatile organic bases are fractionated, those with the very high boiling-points become decomposed with a formation

of pyrrol, the presence of this substance being shown by its characteristic reaction of dyeing red, slips of deal wood moistened with hydrochloric acid.

357. A method of separation of volatile organic acids of the series $C^n H^n O^4$, dependent upon an entirely different principle to the method last alluded to, has been proposed by Liebig, and has afforded excellent results in the hands of several chemists. The process consists of partial saturation and distillation, and is thus performed:—The mixture of, say butyric and valerianic acids, is divided into two portions, one of which has potash added to it until neutralized, the other is then added, and the mixture distilled; if, now, the quantity of alkali added is less than is required to neutralize the valerianic acid, nothing but valerianate of potash remains in the retort, a mixture of vale-rianic and butyric acids, containing much less valerianic acid than before, distilling over. If, on the other hand, the quantity of potash added is more than enough to neutralize the valerianic acid, the surplus will of course be saturated with butyric acid, and thus a mixture of valerianate and butyrate of potash re-mains in the retort, the former salt being in the greater quan-tity, while the distillate contains only butyric acid. When acetic acid is present, the reactions are somewhat different; but for de-tails the reader is referred to the paper itself*.

358. *Special cases of distillation.*—There are many fluids which, either from peculiarities in their methods of boiling, or from their action upon vessels constructed of ordinary materials, require particular precautions in the operation of distillation. Only a few of these need be instanced as types of the general methods to be adopted.

One of the most dangerous and troublesome fluids to distil is sulphuric acid; its great causticity, and the suffocating nature of the vapours formed by its contact with carbonaceous matters at high temperatures, make the destruction of a retort contain-ing it, while over the fire, a serious accident, and one which must be avoided by every means in our power. The manufacturers of ·

---

* Liebig's 'Annalen,' Sept. 1849, and Chem. Gaz. 1850, p. 24.

this important acid have been induced from this cause to use stills of platinum, which, although of such great expense in the first instance, are found much more economical in the end. Sulphuric acid possesses in an eminent degree the unpleasant property of concussive boiling previously alluded to, and it is necessary therefore to have a considerable quantity of fragments of glass or platinum in the retort, to facilitate the escape of vapour. It is, moreover, not only unnecessary but improper to apply any artificial refrigeration to the receiver, as the extremely hot acid coming into contact with the cooled vessel would almost infallibly cause its fracture ; and, moreover, its boiling-point being so high, if we have a tube, 4 or 5 feet long, to connect the retort with the recipient, no fear need be entertained of the acid vapours escaping into the laboratory. It is perhaps scarcely necessary to caution the operator against allowing any organic matter to find its way into the acid to be distilled, as a decomposition takes place with formation of sulphurous acid, the presence of which may prove highly prejudicial in many operations in which the acid is likely to be used. With sulphuric acid, advantage is gained by preventing the heat from playing immediately upon the bottom of the retort; this has already been mentioned as a means of preventing concussive ebullition in other cases, and Berzelius applied the method to the distillation of sulphuric acid, by placing the bottom of the retort upon a truncated cone, which in its turn rested upon a hearth, and a charcoal fire was made round it, so as to apply the heat in such a manner that the boiling commenced from the sides instead of the bottom.

359. Hydrofluoric acid requires a special apparatus for its production, in consequence of its great tendency to combine with silica rendering it impossible to use glass vessels, as they would be destroyed in a very short time, and, what is far more serious, prevent the possibility of obtaining a pure product. Perhaps the most convenient apparatus for the production of hydrofluoric acid, where it is required to be frequently made, is that represented in fig. 191.

It consists of two hemispherical iron pots with broad flanges, which permit them to be laid mouth to mouth, and afford the space to pierce holes for the admission of the screws, the nuts of which are seen in the engraving. The pots are lined throughout with lead; in fact, two leaden vessels of the same shape as the

Fig. 191.
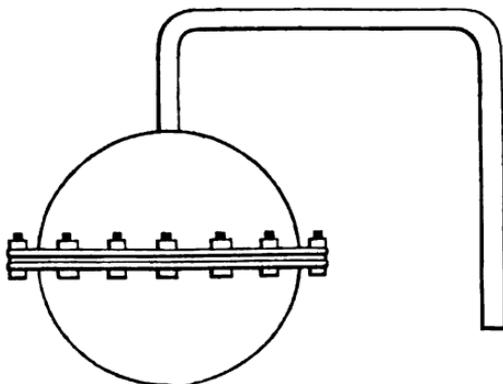
iron ones are constructed, which exactly fit inside them, and are also provided with flanges, as by means of the screws the two leaden surfaces are brought into such close contact that scarcely any leakage occurs, and what there is may be effectually stopped by a little plaster of Paris. A hole is made through both lead and iron at the top, to admit the leaden pipe, which is ground in quite tight. The chief advantages of this apparatus over those usually described, consist in the facility with which the sulphate of lime may be removed after the action, the economy with which the leaden lining can be replaced, and the protection afforded to it by the iron exterior; moreover, the iron pots are to be obtained with ease, as they merely consist of the larger sizes of sand-pots mentioned at the commencement of the work (p. 13).

360. There are several cases of distillation of frequent occurrence, in which a liquid has to be saturated with a gas evolved by the reaction of certain substances upon each other; the pre-

paration of hydrochloric acid may be taken as illustrating the general features of the operation, and showing the precautions necessary. The chloride of sodium is placed in the retort, *a*, and

Fig. 192.
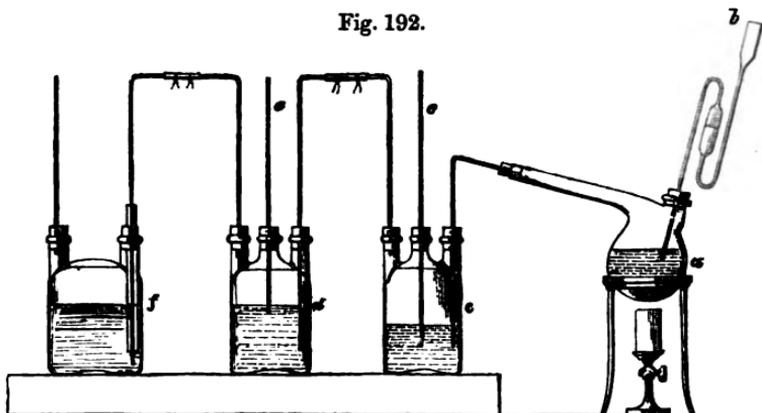
sulphuric acid is introduced very gradually by the funnel, *b*; the muriatic acid gas passes at first into the bottle, *c*, where any impurities mechanically carried over are deposited; it then flows into *d*, by a tube which dips under water; these bottles are seen to be provided with safety-tubes, *e e*, which, by admitting air, if any contraction occurs, prevent the contents from being forced back: the mode of action of these tubes, and the varieties of them in use, will be explained in the section on Gaseous Manipulation. In the same manner as the last, the gas, if any is unabsorbed by *d*, passes into *f*; at first the water in *c* and *d* absorbs all that comes over; but as it becomes saturated, it passes into the other bottle. As heat is developed during the absorption, it is proper to immerse the bottles in cold water. It is unnecessary to apply heat to the retort at the commencement of the operation, that developed by the reaction being sufficient; but as the flow of gas becomes slackened, a small lamp-flame may be placed beneath it and gradually increased. The bottle, *f*, is fitted up in a manner different from the others: the mode of action will be explained further on.

361. When mixtures are to be distilled which it is expected

might explode by a temperature of 212°, the contrivance shown
at p. 45 may be used with advantage.

362. Mercury may easily be distilled in small quantities in
plain glass retorts, which should not be too large; for if the
dome of the retort is far above the mercury, it will be necessary
to heat it to a degree that may endanger its safety, in order to
drive the metal over. From the high temperature required, it
is improper to use tubulated retorts, as if closed by a stopper
they are liable to fracture, and corks are rapidly carbonized.
The steady heat of a small charcoal fire is perhaps the most
convenient for the purpose. Where larger quantities are to be
distilled, an iron retort is preferable to any other, and the bot-
tles in which the metal is imported, if fitted with a bent iron
tube, answer the purpose extremely well. The addition of
copper filings much facilitates the process, where it is desired to
obtain as pure a product as possible. The exit-tube in either
case must be plunged under water.
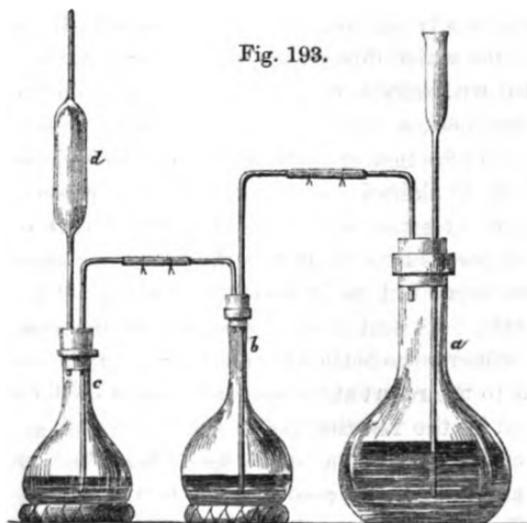
Fig. 193.

363. It has already been mentioned, at p. 225, that fluids
distil at a lower temperature in a current of hydrogen than when

the operation is conducted in the usual manner.   This method of
operating has to be resorted to in several cases; in the first place,
it is not unfrequently necessary to expel a more from a less vola-
tile fluid in the purification of the latter, as, for instance, where
it is desired to drive off ammonia from a fluid base having a com-
paratively high boiling-point; to effect this, the apparatus shown
in fig. 193 may be used, where a represents a bottle fitted up
with tubes for the preparation of hydrogen gas, which is dried by
passing through sulphuric acid contained in b, from whence it
streams through the basic liquid in c.   Sometimes it is required
to heat the latter, in which case the volatilized base is condensed
in d and falls back into the flask, the dry hydrogen carrying away
the ammonia and water present in the fluid.   The operation is
generally a somewhat protracted one.   It is often required to
distil fluids of no great stability in an atmosphere of some gas
having little or no tendency to impart oxygen.   The ebullition
of fluids is often by this means considerably facilitated.   Phos-
phite of ethyl, which boils at 191° Cent. (375°·8 Fahr.) in air,
comes over at 188° C. (370°·4 Fahr.) in a current of hydrogen gas[*].
Where it is merely wished to prevent oxidation, or to facili-
tate the ebullition of fluids of no great stability, but not sponta-
neously inflammable, a current of dry hydrogen evolved from an
apparatus similar to that shown in the last cut, passes into a
retort the neck of which is drawn out and bent, so as to enter a
U-tube, which, if necessary, may be immersed in a freezing
mixture and have a conducting tube passing into a flask (in the
manner of those in fig. 188), likewise kept cold.   Sometimes the
current of hydrogen carries away so large a quantity of the fluid
that its loss would be serious; it is then necessary to connect the
first with another, or even two or three more U-tubes or other
condensers, according to circumstances.

364. If the fluid is spontaneously inflammable, as is the
case with many organic compounds containing antimony, arsenic
and other metals, it is necessary to have the joints made by fusion,
and the apparatus is then preferably constructed from glass tubes.

[*] Railton, Chem. Soc. Quart. Journ. Oct. 1856.

Fig. 194 gives an idea of one of the simpler kinds of apparatus
for the purpose.   The substance is formed by the action of heat

Fig. 194.
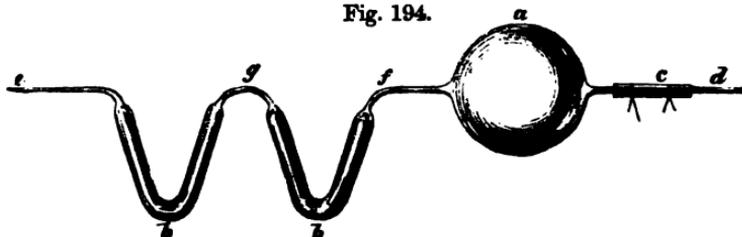
upon the ingredients in *a*, and is condensed in the V-tubes, *b b*,
the second of which is drawn out to a point at *e*.   Before the
reaction is commenced, a current of dry hydrogen is passed through
the whole by means of the tube, *d*, connected with a gasometer
or other source of the gas; *d* is connected in its turn with *a*, by
a caoutchouc tube, *c*, containing a piece of glass rod, almost large
enough to fill it.   When all the air in the apparatus has been
expelled by the hydrogen, the tube, *c*, is tightly tied, and *d* is
removed.   The bulb, *a*, is then heated until the substance has
distilled over into the V-tubes, *b b*, which are kept very cold
during the operation.   When no more fluid is condensed in the
receivers, a powerful blowpipe-flame is directed upon the parts,
f and *g*, in succession, which are thus closed and removed until
wanted for examination; finally, the point, *e*, is closed by fusion.
From what has been said, it will easily be seen that the above is
far from being a universal method, the method of manipulating
requiring various modifications according to the nature of the
substance operated on.

365. When it is necessary to observe the temperature at
which a fluid distils in a current of hydrogen or other gas, it is
sometimes proper to use a flask provided with three apertures:
one for the tube delivering the gas, another for the exit of the
distilled liquid, and a third, generally in the centre, for the ther-
mometer.   By this arrangement, however, a considerable surface
of cork is exposed to the action of the heated vapour, and with
fluids the boiling-point of which is above 300° Fahr., it soon

becomes brittle, and even rotten, so that it is difficult to keep it from leaking; but if the surface of the cork is comparatively small, this does not occur, or at least with the same rapidity. There are small three-necked Woulfe's bottles, blown from tube at the lamp, to be procured from the dealers in chemical apparatus, which, from their thinness, are well adapted for this purpose.

366. In some distillations it is advisable to allow the ingredients to digest for some time before applying the fire, particularly if fluids are to be dehydrated by contact of quicklime, chloride of calcium, or other substances used to remove water. The less active the matter intended for the purpose, the longer the digestion is required to be. In most instances, the object may be effectually attained by putting the ingredients together over night, and distilling in the morning.

367. In making formic acid by the more common processes, the starch or sugar, oxide of manganese and water are introduced into the still, and a fire being put under it until the fluid has obtained a temperature of about 100° Fahr., or a little higher, the sulphuric acid is added by degrees, the fire being previously removed; an immense quantity of carbonic acid gas is evolved, and sometimes the action is so violent, that, although the fire has been taken out, the mixture froths over; in any case, it is better to allow the ingredients to digest for five or six hours before distillation, when, by careful regulation of the heat, the dilute acid may be brought over without any further danger of frothing. The formiate of lime produced in a subsequent stage of the process is best distilled with sulphuric acid, to obtain the strong acid, in the stone alembic, p. 239.

The formic acid, as thus obtained, invariably contains a certain amount of sulphurous acid, which may be rendered sufficiently fixed to allow of distilling over the formic acid in a state of comparative purity, by adding just enough of a solution of chromate of potash to convert the sulphurous into sulphuric acid. If this is done with moderate care, no fear need be entertained of lessening the product by decomposition of the formic acid.

The salt alluded to is moreover useful as a test of the presence of sulphurous in formic acid, as a very small portion converts the yellow colour of the chromate into a beautiful green, even in the cold, by reduction to the state of green oxide.

368. For a great many purposes, but more especially in the production of chemical reagents on a somewhat large scale, as is so frequently required in certain investigations, a stone still and worm are much employed, and will be found exceedingly useful. It is scarcely safe to use a sand-bath for them, although some withstand that method of applying heat very well. It is better therefore to use a chloride-of-calcium bath, the heat given by which is sufficient for almost all the purposes to which a stoneware still is likely to be applied. For the preparation of prussic and valerianic acids on the large scale, they are indispensable. The

Fig. 195.

worm should be inserted into a wooden tub, the spout projecting at the bottom. This is the most easily fractured part of the apparatus, and requires especial care. It is a good plan, as a means of protection, to have two stout pieces of wood nailed to the tub, and standing out to the same extent as the exit of the worm, but not placed so close as to prevent easy access.

369. When these stills are in operation, it is necessary to cover the head with a cloth, to prevent condensation and con-

sequent loss of time and fuel. The juncture of the head with the body is closed by means of almond and linseed luting. It is absolutely essential that great care be taken to prevent the chloride-of-calcium bath becoming dry, or even too low, as in that case the addition of cold water would infallibly break the still; in fact, when water has to be added to keep up the height of the fluid, it should always be nearly if not quite boiling.

370. The best method of supporting the still in the bath is seen in fig. 196. A hole is punched out in a circular piece of strong sheet-iron, just large enough to permit the easy entrance of the still as far as the flange, *a*, which supports it in the bath. The iron pot is at least 6 inches larger all round than the still. A hole about 2 inches across is punched in the iron ring, to allow of the addition of hot water to replenish the bath. As the solution of chloride of calcium is liable to froth up and boil over at times, it is better not to allow it to fill the pot to a greater height than that indicated by the line in the figure.

Fig. 196.

371. The stone worms are so cheap, that it is better, where they are required frequently for any particular purpose, to keep them for that exclusively, especially if from its nature there is any difficulty in cleaning them out, their opacity throwing great difficulty in the way of ascertaining their freedom from dirt or impurities.

372. *Destructive distillation.*—The products of the destructive distillation of coal, and various animal and vegetable substances,

The salt alluded to is moreover useful as a test of the presence of sulphurous in formic acid, as a very small portion converts the yellow colour of the chromate into a beautiful green, even in the cold, by reduction to the state of green oxide.

368. For a great many purposes, but more especially in the production of chemical reagents on a somewhat large scale, as is so frequently required in certain investigations, a stone still and worm are much employed, and will be found exceedingly useful. It is scarcely safe to use a sand-bath for them, although some withstand that method of applying heat very well. It is better therefore to use a chloride-of-calcium bath, the heat given by which is sufficient for almost all the purposes to which a stoneware still is likely to be applied. For the preparation of prussic and valerianic acids on the large scale, they are indispensable. The

Fig. 195.

worm should be inserted into a wooden tub, the spout projecting at the bottom. This is the most easily fractured part of the apparatus, and requires especial care. It is a good plan, as a means of protection, to have two stout pieces of wood nailed to the tub, and standing out to the ... worm, but not placed so ...

369. When these ... cover the head ...

sequent loss of time and fuel. The juncture of the head with the body is closed by means of almond and linseed luting. It is absolutely essential that great care be taken to prevent the chloride-of-calcium bath becoming dry, or even too low, as in that case the addition of cold water would infallibly break the still; in fact, when water has to be added to keep up the height of the fluid, it should always be nearly if not quite boiling.

370. The best method of supporting the still in the bath is seen in fig. 196. A hole is punched out in a circular piece of strong sheet-iron, just large enough to permit the easy entrance of the still as far as the flange, *a*, which supports it in the bath. The iron pot is at least 6 inches larger all round than the still. A hole about 2 inches across is punched in the iron ring, to allow of the addition of hot water to replenish the bath. As the solution of chloride of calcium is liable to froth up and boil over at times, it is better not to allow it to fill the pot to a greater height than that indicated by the line in the figure.

Fig. 196.

371. The stone worms are so cheap, that it is better when they are required frequently for any particular purpose to keep them for that exclusively, especially if from its nature there is any difficulty in cleaning them out, their quality depends...

...ne top of the head is useful for

have furnished chemists with many of their most interesting products. The number of these already obtained would, to recount their history, require a volume; but a few will be mentioned, in order to show that a description of the apparatus required, and the methods of using them, are deserving of a place in this work.

373. Wood, by destructive distillation, yields, in addition to acetic acid, methylic alcohol, acetone, xylite, lignone, paraffine, kreosote, the beautiful pittacal, and the host of substances studied by Reichenbach, several others which are as yet imperfectly known. Small as the per-centage of nitrogen in ordinary wood is, the author found methylamine to accompany the ammonia formed by destructive distillation of the impure acetate of lime made on the large scale, from the acetic acid produced simultaneously with wood-spirit.

Coal, by destructive distillation, yields the whole series of fluid hydrocarbons homologous with the starting-point, benzole, many gaseous ones, being still far from well known, and numerous organic bases, viz. aniline, the pyridine and chinoline series, and the somewhat mysterious body, pyrrol, known by its characteristic reaction of staining fir-wood moistened with hydrochloric acid, bright red or crimson. Indigo yields aniline and other substances. Boghead coal, and probably Burmese naphtha, yield hydrocarbons of more than one class, one appearing to be identical with the alcoholic radicals.

374. These few substances mentioned (for they are few compared with the multitude inviting study) are sufficient to indicate that a wide field for investigation remains comparatively unexplored in the products of the destructive distillation of organic matter; and also that no apology is due for devoting some pages to a consideration of the apparatus best adapted for researches on the subject.

375. Where it is intended to distil large quantities, recourse will doubtless be had to the cast-iron retorts used at gas-works; but, on the small scale, the stout iron pots to be obtained at the iron-wharves, and shown in figs. 197 and 198, are very convenient.

The pot, *a*, in the latter figure, is provided with a very broad flange, supporting an iron cover made after the manner of a saucepan-lid, and perforated with an aperture of about 6 inches

Fig. 197.
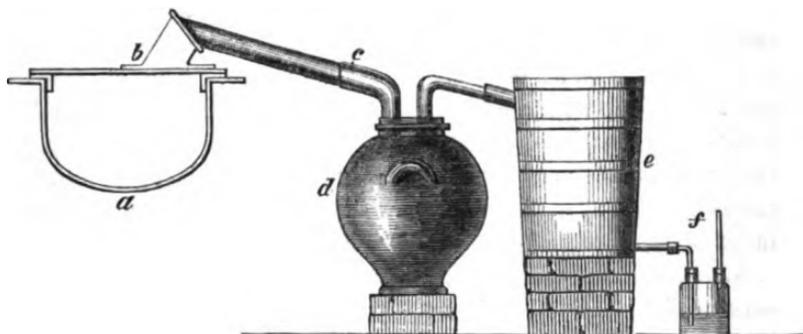
diameter, to admit the head, which is to be riveted on. The exit-pipe is made large until it enters the first recipient, *d*, with which it is connected by the adapter, *c*. The vessel, *d*, may very well consist of a six-gallon stone jar, closed with a large bung pierced with two apertures. All the tar and other semi-solid and easily condensable matters having been deposited here, the more volatile products pass into the worm, *e*, which is kept constantly supplied with a stream of cold water having lumps of ice floating in it. All the fluid hydrocarbons, and most other matters, are completely condensed by this means; but if very volatile bases are present, they require further precautions; the exit-pipe, *f*, is therefore made to dip into dilute muriatic acid contained in a second bottle, which effectually retains all the basic products. The iron pot is set in brick-work, just in the way of an ordinary still, no particular precautions being necessary, except that of being able to remove the fire with rapidity in the event of the products coming over too rapidly. It is to be remembered that the great danger is not of having too little, but too much heat; and it is a good general rule, to bring over the products at the lowest possible temperature, the fire being increased as the evolution of volatile products slackens, this being easily

seen by watching the rapidity with which the bubbles of gas pass through *f*. Where the gas is very fœtid, as is the case when most substances containing a large per-centage of nitrogen are distilled, it may be passed through a rather thick solution, prepared by stirring up chloride of lime and water to a creamy consistence, or the gas may be ignited or passed by means of a long tube under the ash-pit of the furnace. The lid of the still is luted up with a mixture of finely-sifted fire-clay and fresh horse-dung beaten to a plastic mass in an iron mortar. To apply the luting in the most successful manner, the lid being inverted, the luting is to be placed all round, and the lid being then put in its place, is to be kept down by placing heavy weights on it.

376. In some operations, a neater but more expensive apparatus for distillation is made by drilling a series of holes round the rim of a carron pot, and fastening the lid down by screws and nuts, as seen in section, fig. 198. The exit-pipe is made of wrought iron, and is inserted into the lid by having a screw tapped on its end to fit a hollow screw made in the plate which covers the pot. This arrangement is excellently adapted for the preparation of sulphurous acid from bruised charcoal and sulphuric acid.
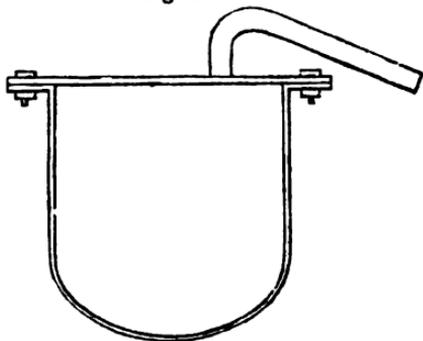
Fig. 198.   Fig. 199.
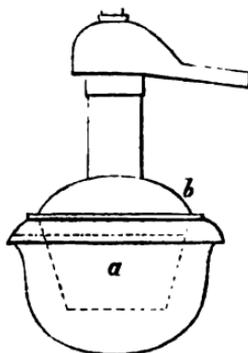
377. Where destructive distillation is to be performed on a much smaller scale, as in preparing aniline from indigo, chino-line from cinchonine or quinine, trimethylamine from narco-

tine, &c., the arrangement shown in fig. 199 may be used.
It is constructed of stout sheet-iron, and has the head, be-
longing to a stoneware alembic similar to fig. 200, luted to it
with the almond and linseed luting previously alluded to.   By
far the best way of heating these alembics is by means of a
species of hot-air bath, formed of an iron pot similar to those
used to melt lead in, but with the three feet removed, which may
be done by filing them three parts through, and then giving a
smart tap with the hammer.   These pots are covered with a lid
fitting somewhat tightly on; it has a hole in the top large
enough to admit the alembic, which is supported by the flange
which joins the body, *a*, to the dome, *b*.   A small hole, about
1 inch in diameter, is left in the lid of the hot-air bath, to enable
the operator to observe when it reaches a red heat.   The pot is
to be heated by placing it on the largest hole of the furnace,
fig. 1, all the rings being removed.

The great advantage possessed by this arrangement, is the
rapidity with which the temperature can be regulated as com-
pared with a sand-bath.   In the latter case, the sand takes a
considerable time to acquire the requisite temperature, and when
it has done so, it requires a still longer time to cool, whereas the
pot can be heated to redness as rapidly or slowly as may be
required, and may be cooled with equal facility.

The manner in which the alembic is surrounded prevents
accession of currents of cold air, so that even when constructed
of earthenware they may be raised to a red heat and cooled
again a great number of times without fear of fracture.   The
stoneware alembic alluded to is shown in section in fig. 200.
They are somewhat difficult
to obtain, but their extreme
convenience in many opera-
tions renders it well worth
while to have them made of
the potters, so many of whom
are to be found in Lambeth,
near London.   The aperture in the top of the head is useful for

Fig. 200.
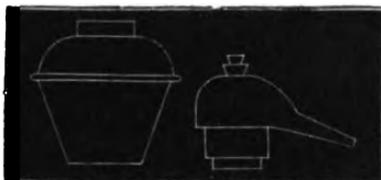
the introduction of fluids, &c. after the joints have been luted up, or during the progress of a distillation.

378. It has been said that, as a general rule, the lowest possible temperature should be used in destructive distillations where the object is to examine the products obtained; this rule holds good in the process for procuring aniline from indigo; the latter substance, being finely pulverized, is to be mixed with a very concentrated solution of potash, and the whole is to be evaporated with constant stirring, in an iron pot, until a faint odour of aniline is perceptible; directly this is observed, the mass is to be rapidly transferred to the iron alembic with the stone head, fig. 199, which is then to be inserted in the hot-air vessel, and the apparatus being placed on the aperture in the furnace-plate, and ample condensation being ensured, the fire is to be very gradually raised until no more aniline is procured.

It is important in the construction of these alembics to have the beak made at a much more obtuse angle with the body than is usually done (see also p. 219), as, if this is attended to, much greater ease is found in attaching them to condensers. The caprylic alcohol, which has become an object of interest lately, is readily and conveniently prepared from saponified castor-oil in an apparatus similar to fig. 199.

379. There are many occasions in organic and inorganic chemistry where it is desired to effect distillation under reduced pressure, and consequently at a lower temperature than if performed in the ordinary manner. This is easily managed by the use of the apparatus seen in fig. 201. A glass retort, a, has its neck inserted into a tubulated receiver, c, with which it is connected, air-tight, by the caoutchouc tube, b. The tubulature of the receiver is fitted with a cork and tube, d, which connect it with a small air-pump. The air is then exhausted as far as may be requisite, the degree being made evident by the rise of the mercury in the tube, e, which dips into a small basin of the metal; if, now, a lamp-flame be applied at d, the tube is soon closed by the pressure of the atmosphere, and the distillation may then be commenced.

In distillations of this kind there are several methods of pro-
ceeding, which will suggest themselves to the operator, as they

Fig. 201.
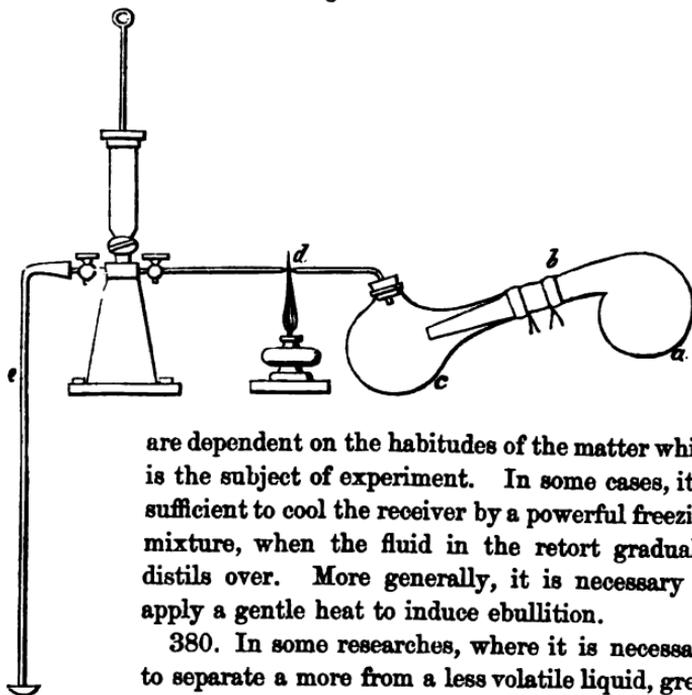
are dependent on the habitudes of the matter which
is the subject of experiment. In some cases, it is
sufficient to cool the receiver by a powerful freezing
mixture, when the fluid in the retort gradually
distils over. More generally, it is necessary to
apply a gentle heat to induce ebullition.

380. In some researches, where it is necessary
to separate a more from a less volatile liquid, great
assistance is gained by using the double-headed
stills shown in figs. 202 and 203. The method of using them
consists in placing within the chamber, *b*, which surrounds the
head, *c*, a fluid, the boiling point of which is higher than that
of the more volatile product which it is wished to obtain, and
below that of the liquid which is to remain behind in the still.
If, for instance, it is desired to obtain benzole from coal-naphtha,
it is sufficient to fill the chamber, *b*, with water, and proceed with
the distillation in the ordinary manner; it is evident, that, as
the temperature of the head can never exceed 212°, the hydro-
carbons, which require a higher point for volatilization, will be
condensed on arriving at that part of the head which is sur-

M

rounded with water, and return to the body a, but that the liquids which boil at or below 212° will pass the head and proceed to
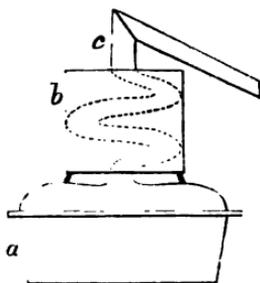
Fig. 202.　　　　　　　　　　　　　Fig. 203.
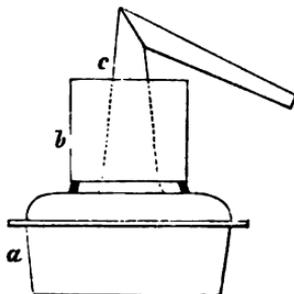
the receiver.　Sometimes it is unnecessary to have a worm passing through the water, a rather considerable elongation of the head being sufficient to prevent the passage of fluids of high boiling-points, as in fig. 203.

381. If retorts or flasks are to be exposed to temperatures so high as to endanger their safety, or where fluids are to be operated on which, either from their inflammability or value, it is particularly essential to prevent being spilled if any accident should occur, we may employ vessels covered by the electrotype process with a thick coating of copper: the method of effecting this will be found in the section on Electrical Manipulations.

382. In operations on very limited quantities, where the use of ordinary retorts, or even the small ones described in the section on Fractional Distillation, would be impossible, recourse may be had to the apparatus shown in figs. 204 and 205; it consists of a very small tubulated retort made from a piece of large tubing; when the bulb has been blown on the end of it, and the neck bent as in fig. 204, the point of the blowpipe-flame is directed on the part a, fig. 205, and a piece of red-hot glass rod is placed against it and immediately withdrawn; it thus forms a thin tube, which may be bent as at $a\,b$.　This construction enables us to introduce the fluid to be distilled without soiling the neck of the retort, an advantage not generally found in these instruments as constructed from

tubes; the fluid is made to enter by dipping the end, *b*, into it and applying suction to *c*, carefully avoiding the entrance of mois-

Fig. 204.

ture: when a sufficient quantity has entered, the point, *b*, may be closed by the blowpipe.   This method is especially useful in experiments where it is wished to operate upon known quantities.

Fig. 205.
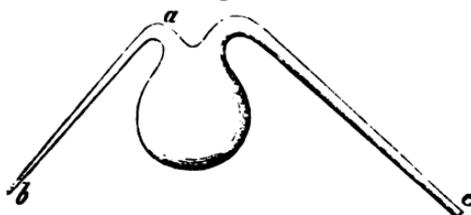
383. Where an extremely volatile fluid is one of the products of a distillation or reaction, the appliances shown in figs. 206 and

Fig. 206.
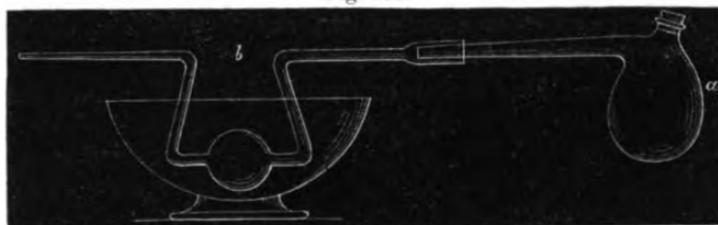
207 may be made use of with advantage.   The retort, *a*, in which the materials are being heated, is connected with the bulb apparatus, *b*, immersed in a freezing mixture.   The product may be transferred to the little tube apparatus, fig. 207, in which

it is to be preserved; it may be introduced by the method de-
scribed in the section on Pres-
sure-tube Operations (§ 304).

Fig. 207.

384. It not unfrequently hap-
pens that it is wished to submit
a fluid to the action of a sub-
stance at a moderately high tem-
perature (generally a little above
the boiling-point of the liquid)
for a considerable time, as, for
example, in the preparation of
some hydrocarbons by the action
of sodium on iodine or bromine
compounds. In this case it is
convenient to use the appa-
ratus shown in fig. 208. The
flask, *a*, contains the substance to be co-
hobated, and, in the example given, a
quantity of sodium; it is immersed in the
copper tallow-bath, *c*, which is heated by
the gas-lamp, *d*. The vapour which rises
condenses in the long wide tube, *b*, which
has a capillary opening at its upper end,
and falls back into the sodium; by this
means the whole of the iodine or bromine
may be removed in an hour or two, and
the tube, *b*, and its cork being removed, it
is to be replaced by a bent tube connected with a receiver, and
the pure hydrocarbon or other fluid distilled over.

Fig. 208.
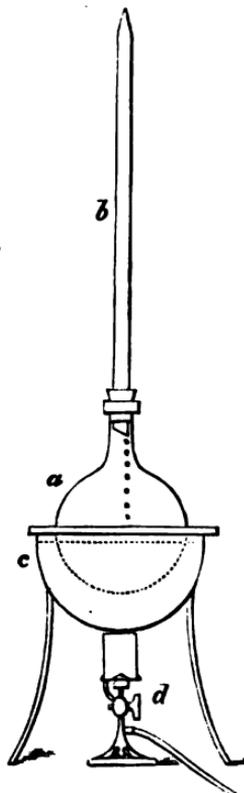
SECTION XIX.

SUBLIMATION.

385. Sublimation differs essentially from distillation in the fact, that the product of the operation is obtained in the solid instead of the fluid state; the apparatus used is generally extremely simple, and presents far less variety than that employed in distillation.

386. Very frequently, in manipulating with the small quantities used in research, the arrangement recommended by Berzelius (which for simplicity leaves nothing to be desired) will answer equally well with far more complicated appliances; it merely consists of two platinum crucibles, one rather larger than the other, the larger being inserted so as to penetrate a short distance inside the smaller. The upper one is filled with cold water during the process, which, if required, may be removed with a pipette as it becomes heated, and be replaced with fresh. Two porcelain crucibles may sometimes be substituted with advantage for the platinum; but in this case it is generally unsafe to fill the upper one with water, as such a proceeding would, in all probability, be the cause of fracture. Two porcelain or earthen basins, placed mouth to mouth, and having a strip of paper pasted round the line where they join, for the twofold purpose of confining the vapour and keeping the vessels together, is frequently a good arrangement. In all cases of sublimation it is essential to have a small aperture in some part of the apparatus to allow of the expansion of the air, as, if confined, it would, on heat being applied, break the connexions. It is seldom, however, that it is necessary to make this aperture purposely, as the apparatus for sublimation is seldom quite air-tight.

387. In subliming iodine on the small scale, with a view to its purification, it may be placed in rather large and shallow evaporating-basins, covered with others, which are to be inverted and placed with their mouths downwards against the under ones.

The place of juncture is to be made tight (with the exception of a very small air-hole) by means of the almond and linseed luting frequently alluded to in the section on Distillation. The apparatus, after being put together, is placed upon a moderately hot part of the sand-bath for some hours, and is then to be removed to a cooler portion, and allowed to become cold very slowly. When perfectly cold, the basins are to be taken apart and the iodine removed with a strip of glass, or even with a strong feather; it is, however, better to avoid the contact of organic matter. The largest crystals are generally found upon the bottom dish, in the form of magnificent sword-blades, sometimes several inches long, when the quantity sublimed is large. If a considerable quantity of pure iodine is required, as in many researches, the ordinary porcelain dishes in use in the laboratory are too small to be really serviceable, and it is better to use the large earthenware dishes known as milk-pans: the arrangement is precisely the same as with the evaporating-basins.

388. Many organic substances, such a naphthaline, pyrogallic acid, &c., may be very conveniently sublimed in the apparatus shown in fig. 209. It consists of an evaporating-basin having a beaker inverted over it, the join being made with paper pasted round. Rings are then made of annealed iron-wire, of the exact size of the inside of the glass: these are covered with muslin, which is sewn on. The object of these discs (which are placed in the beaker in the positions indicated by the lines) is to retain the sublimate and prevent it falling into the dish again.

Fig. 209.

389. As a general rule, it is proper to employ a gentle and steady heat, only just sufficient, in fact, to vaporize the substance, many volatile bodies of unstable composition being partially, or even entirely decomposed by an undue elevation of temperature. This is particularly the case with pyrogallic acid, previously alluded to. No matter
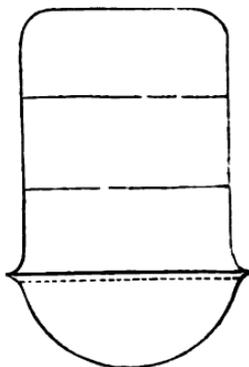
how carefully the operation may be performed, a certain quantity of this, at present, useless metagallic acid is formed, but by careful management the amount may be considerably reduced.

390. With fusible sublimates much is absorbed by the diaphragm; this must never be lost sight of, as in some instances it may be recovered by solution in alcohol or ether, and subsequent crystallization. In the case of the curious substance obtained from sulphopianic acid, as much, or more, is obtained in this manner as in the state of sublimate.

· 391. Indigo may be sublimed between two porcelain dishes, or by mixing it into a paste with plaster of Paris, forming the mixture into a cake, and placing it in a warm place to become dry; when this has been effected the temperature is raised, and crystals will form on the surface of the plaster, and may be removed with a feather. Biniodide of mercury may be obtained in magnificent scarlet crystals by careful sublimation between porcelain capsules.

There is a well-known peculiarity of the last-named substance which has been only imperfectly accounted for, namely, that when first sublimed it is of a beautiful pale-yellow, which, by contact with a glass rod, becomes scarlet, a peculiar motion taking place at the same time among the crystals, indicating some structural change. This difference in colour between substances before and after sublimation is by no means uncommon: bisulphuret of mercury, if formed by precipitating corrosive sublimate with sulphuretted hydrogen, is quite black before, but brilliant red after sublimation, and is then known as vermilion. Changes of this kind are, however, not peculiar to the process of sublimation : many colours prepared by the wet method acquire different tints by digestion at certain temperatures; the arsenite of copper prepared in the manner adopted for the beautiful emerald-green, acquires its beauty by the maceration of the ingredients for some time. The wet method of preparing vermilion is also an example of the same kind of change.

392. A current of air or certain gases appears to greatly facilitate the crystallization of some substances: if naphthaline is heated to the subliming-point, and air is drawn through the

apparatus, the product is denser, and apparently whiter and purer, than when sublimed in an apparatus with diaphragms, such as is represented in fig. 209. If the crude mixture of chrysène and pyrène be heated in a test-tube, it melts and creeps up the sides, but does not volatilize even at a very considerable temperature; but if air is drawn through the apparatus, a dense yellow vapour rises, and may be condensed at some distance; it is possible, however, that some decomposition takes place in this case. In the process for forming the sesquichloride of chromium, much trouble is sometimes found in obtaining the crystals at a sufficient distance from the mixture of oxide and charcoal; if, however, a very powerful current of chlorine is employed, and the heat is sufficiently raised, this difficulty does not appear.

393. Sublimations on the small scale are often conveniently observed in glass tubes, as for instance, in the opera- Fig. 210. tion of testing for arsenic. Great care should be taken in selecting tubes for this purpose, as if the ordinary flint-glass containing lead is used, and it has to be exposed to a reducing flame, or even if heated in contact with carbon in any way, the lead becomes reduced, and much uncertainty may arise from this point alone. In the sublimation of mixtures containing arsenic in minute quantities, according to the directions found in elementary works, very small tubes are employed of the size and shape seen in fig. 210; and a little care is required in so inserting the charge at *a*, as not to leave any upon the tube. Perhaps the best way of doing this is to place the mixture upon a little paper gutter, and, the tube being held horizontally, the gutter is to be placed in it; the tube is now to be raised, when the whole of the charge will fall about *b*, a small portion, however, dropping in its place at *a*; the rest is to be got down the narrow tube by the use of a small wire and a gentle tapping. If the substance is sufficiently dry and in fine powder, no difficulty will be found in effecting this. After the charge is inserted in the

Fig. 210.

little bulb, any traces which may be found to adhere to any part of the tube are to be carefully removed from the narrow portion by means of a wire with a small piece of linen or thread tied to it, and from the large tube by a piece of wood having something similar but on a larger scale attached. In many operations of qualitative analysis an open tube is used, in order that air may have free access, for the double purpose of oxidizing the metals sought for, and, by establishing a current of air, carrying the vapours forward: in this operation a piece of ordinary tube, from $\frac{1}{8}$th to $\frac{1}{4}$th of an inch in diameter, about 5 inches long, and open at both ends, is employed; it is held almost horizontally at first, the specimen under examination occupying a position about 1 inch from the end exposed to the flame. A spirit-lamp should be used in order to prevent smoke. The heat employed, gentle at first, should be gradually increased, in order to observe all the phenomena that may present themselves. It is to be noticed that the current of air through the tube is greater, the more the position in which it is held approaches the vertical; much command is therefore obtained over the process of oxidation by this means. Every point is to be noticed: the ease with which the sublimate rises, its colour, odour, its appearance when chased by the flame from one part of the tube to the other, whether it melts, or globules are formed, &c. If water is evolved, care must in all cases be taken to prevent its running back upon the hot glass, and thereby causing its fracture. Sometimes, but this is comparatively seldom, the flame of a spirit-lamp is insufficient to volatilize the substance; when this occurs, the blowpipe must be used to urge the flame; this is generally necessary with tellurium, which requires a powerful heat for volatilization.

394. Sublimation is sometimes conveniently effected in common, or preferably, Hessian crucibles; two are taken, one a little smaller than the other; the one is inverted inside the other, and, if necessary, luted to prevent escape of the sublimate.

SECTION XX.

CRYSTALLIZATION.

395. The process of crystallization is one of the most important in the whole range of chemical operations, and, to perform successfully, requires considerable attention to minute detail. It is by means of it that most inorganic and organic substances are obtained in a state of sufficient purity for analysis; and it is this circumstance that makes it so great a source of pleasure to the chemist to find the substances he is investigating capable of being procured in well-defined crystals; and it may be taken as a general rule, to which there are few exceptions, that the solid objects of chemical research which possess the greatest points of interest are capable of assuming the crystalline state. Moreover, the forms of crystals are a most valuable means of identifying substances, and it is this fact which renders it so necessary for every chemist to possess a moderate knowledge of crystallography.

396. It has long been a favourite object among some chemists to obtain regular crystals of large size, and of late years this art has been carried to a degree of perfection which perhaps those who have not seen what may be done in this way would hardly believe possible. It is difficult to lay down any general rule for obtaining crystals; that which is generally given in books, namely to evaporate the solution requiring to be crystallized until a pellicle forms and then set aside, is, it is true, adapted for most cases which occur in rough technical operations, but as a means of operating in research it would be difficult perhaps to find a worse guide. Liquids evaporated until a pellicle forms, generally, in fact almost invariably, give a confused irregular mass of crystals; where it is merely required to obtain a large crop, and size is not an object, the rule may be said to answer, but in no other case. In fact this rule, from having been so generally adopted, has caused some articles of commerce

to be only fit for the market when in very small crystals; a product in which the crystals were well developed being rejected, and probably considered impure. It is somewhat amusing to know that morphia is only saleable in powder, and if offered in a state that would to some extent be an evidence of its freedom from adulteration, would be refused.

397. The methods by which very large crystals are procured differ generally in minute but essential points, according to the habitudes of the salt worked upon. Some are readily obtained in very large crystals without much trouble; others, on the contrary, are extremely difficult to procure in large crystals, which show distinctly the characteristic form. Of all classes of salts, perhaps the alums are the most easily managed in this respect. Gigantic crystals, in regular octahedra, the longer axis 5 inches long, are to be seen in some museums. Chrome-alum is particularly easy to procure in fine crystals. In the process for making valerianic acid by oxidation of fusel-oil with bichromate of potash and sulphuric acid, it is by no means uncommon to obtain chrome-alum crystals 1 inch in length along the chief axis. But when substances are obtained in such extremely large specimens, it is generally at a sacrifice of perfection in form; they are frequently covered in certain directions with striæ, or the solid angles are not sharp at the extremities. This must be submitted to as unavoidable, unless a large quantity is made, so as to permit selection of the best.

If a saturated solution of chrome-alum is allowed to deposit its first crop of crystals, and the mother-liquid is set aside to evaporate spontaneously, at the end of a few days a number of crystals will be found, some of perfect shape; these are to be selected and put into a shallow vessel by themselves, being every day turned with a piece of wood on to a different face. At the expiration of every few days, the liquid is to be replaced by a fresh, cold, saturated solution.

Many other solutions give almost equally fine crystals, especially sulphate of copper and common or even iron-alum.

398. Crystallization is dependent upon the change from the

fluid to the solid state, and it is the mobility among the particles conferred by fluidity that, enabling the forces to act freely, causes bodies to assume the crystalline form. The more slowly this change is effected, the greater the freedom with which the force is exerted, and consequently the greater the regularity of the crystal. If, therefore, in ordinary crystallization it is desired to have a crop, the characters of which shall be well developed, every precaution must be taken to retard the cooling; the slower this takes place the more successful will be the operation. Where small quantities of solutions of salts are to be cooled slowly, the capsule may be placed overnight upon a warm brick, but as this would cause evaporation, and consequently by concentrating the solution injure the operation, the vessel containing the solution to be crystallized should be covered with another, the convex portion being downwards, in order that the fluid raised by the heat may drop back and preserve the original strength of the solution.

399. Mixtures of baryta- and silver-salts of different acids, more especially if belonging to homologous series, may be separated by what is termed fractional crystallization, that is, the gradual separation of the more from the less soluble salts. After one crop has deposited, the mother-liquid is evaporated gently, until a crop will be deposited after standing some time, but no further; it is then set aside, and after a sufficient interval, depending of course upon the circumstances of the case, for which no general rule can be laid down, the crop is removed for examination, and the operation repeated.

400. The same remarks apply to platinum- and silver-salts. In the former case, however, the evaporations must be made without the agency of heat, which appears to result in the gradual production of bases in which the platinum, instead of merely occupying the position of a metal in a double salt, becomes an integrant particle of a new alkaloid which is formed, possessing analogies with the platinum bases examined by Reiset, Magnus, Peyrone, Gros, Ræwsky, Gerhardt, and others. It is almost equally necessary in the fractional crystallization of platinum-salts, to

avoid prolonged contact of a great excess of bichloride of platinum, as a decomposition is thereby set up, and gradually becomes more evident as the time becomes longer; it is therefore advisable to perform the evaporations *in vacuo* over sulphuric acid, and with only a moderate excess of platinum.

401. The crystalline forces sometimes act with sufficient energy to cause double decomposition; thus the Chili saltpetre, nitrate of soda or cubic nitre, as it is sometimes called, is converted into nitrate of potash by mixing it with an equivalent of chloride of potassium and crystallizing, the decomposition being effected in consequence of the superior tendency to crystallize possessed by nitrate of potash over nitrate of soda. Large quantities of chloride of potassium were imported into Russia during the commencement of the late war for that purpose, and it is but recently that the object has become evident to the authorities, and the exportation prohibited.

402. Crystals are not necessarily identical in composition because they are so in shape, certain substances having the power of replacing each other in any quantity without regard to the usual equivalent proportions; thus three parts of sesquioxide of iron may replace three parts of alumina in alum without alteration of structure, or three parts of sesquioxide of iron, and three parts of green oxide of chrome, may replace six parts of alumina in the same salt. The consideration of the laws of isomorphism being foreign to the plan of this work, they are merely alluded to in order to show the importance of a knowledge of the subject in manipulating where isomorphous substances are present. The fact of the same substances crystallizing in two forms of incompatible kinds is at times observed, and constitutes what is termed dimorphism. But where, more especially in organic chemistry, substances believed to be the same, yield crystals unlike the usual form, the circumstance is always to be looked upon with suspicion, and should induce careful examination.

Substances crystallized from water frequently retain that fluid in the state termed water of crystallization, in which the water always stands in atomic relation to the equivalent of the sub-

stance. Many salts that are properly anhydrous have water mechanically held between the plates or particles of which they are composed, and on breaking large crystals which appear dry outwardly, it may frequently be seen. This property of retaining foreign substances is common even to the finest and best-looking crystals, and particularly happens with the platinum-salts of the organic bases; the latter, even when of perfect shape and considerable size, having a tendency, when powdered, to hang together as if moist, but if washed with a mixture of alcohol and ether this disappears (§ 90). It has been found that salts treated this way invariably afford more correct results on analysis than where it has been omitted. Salts crystallized from alcohol sometimes retain that fluid in a state analogous to water of crystallization.

403. Some substances tend to assume the crystalline state with greater facility at one temperature than any other, and this property may sometimes be employed as a means of separation. Where alcoholic solutions crystallize with difficulty, and the matter experimented on is too insoluble in water to allow of the use of that liquid as a solvent, it is sometimes possible to obtain crystals by adding water to the alcoholic solution until precipitation takes place, but only so long as it is capable of being redissolved on the application of heat; if too much water has been added to allow of this, a little alcohol will enable the point to be reached; the fluid is then to be set aside to cool and crystallize. The same remarks apply where ether is capable of precipitating from alcoholic solutions, or *vice versâ*; but in the latter instance there is more often a tendency to assume a resinous than a crystalline state. Sometimes, where a substance is excessively soluble in water, but not at all, or comparatively little, in strong alcohol, as in the crystalline hyposulphite of gold and soda of Fordos and Gelis, the crystallization may be determined by the careful addition of spirit to the aqueous solution, a quantity sufficiently great to cause precipitation being avoided.

404. The beautiful condition of the pharmaceutical preparations of certain compounds of ferrous and ferric oxides with ammonia,

potash, quinine, &c., are not instances of crystallization, although the precautions in obtaining them are sometimes even more difficult to fulfil; this subject, however, from its technical character, will not be considered here.

405. Some salts are almost equally soluble in hot and cold water; they are therefore best procured in the crystalline state by very slow evaporation, as, for instance, on the sand- or water-bath, the fluid not being allowed, as a general rule, to attain a higher temperature than 100° Fahr., and, in most cases, considerably below it; formiate of lime and chloride of sodium are perhaps the most familiar examples of this kind of salt.

406. A very good method of obtaining the platinum-salts so frequently alluded to in good crystals, is to add the bichloride of platinum to a very strong aqueous solution of the chloride of the base as long as precipitation takes place, then to add boiling water until the precipitate at first formed is redissolved, and then to place the capsule on a warm brick, so as to permit the cooling to take place with extreme slowness. Some platinum-salts crystallize with such extreme readiness, that very little precaution is required to obtain them of large size, even when the quantity of liquid is extremely small.

407. Where it is desired to prevent any vibration from disturbing the capsule containing the salt which is undergoing crystallization, it may be suspended from the ceiling by strings; this is said to be essential to the success of the process for obtaining Herapath's sulphate of iodo-quinine in a state fit for use as artificial tourmalines.

408. When cantharides, or pepper, and several other animal and vegetable substances have been exhausted with ether, or benzole, to obtain cantharidine, piperine, &c., the solution when evaporated yields crystals of the body sought, but always contaminated by a large quantity of resinous and oily impurities; these latter may be removed by washing the crystals with cold ether or solution of potash, which dissolves the resin much more readily than the proximate principles.

Substances belonging to extensive homologous series always

show extremely marked differences in their tendency to crystal-
lize, as the number of atoms of $C^2 H^2$ increase in the compound.
The great group commencing with formic, and gradually rising
to the wax acids, affords a very distinct instance of this; for
whereas formic acid requires to be reduced below 32° to crystal-
lize, acetic acid, the next step, keeps its crystalline state until
the thermometer reaches 60°; after this, the next step in the
series, propylic acid, begins to assume the character of a fat acid,
at least in its salts, and the rest become more and more oily,
until pelargonic acid is reached, which shows unmistakeable
signs of being a fatty acid, being solid and greasy at low tem-
peratures; and the next, namely capric acid, is solid below 80°,
the fusing-points becoming higher with every additional incre-
ment of $C^2 H^2$.

409. In this last-named series, it is the acids themselves
which more and more approach the solid condition as they
rise higher in the scale; but their salts decrease in tendency
to crystallize in the same ratio, the acetate of soda being
highly crystalline; but after this, the salts which these acids
yield with the alkalies, become more difficult to crystallize;
there are, however, many anomalies in the crystalline tendencies
of these and all other homologous series; the salts of the dif-
ferent acids becoming in some cases less and less crystalline up
to a certain point, then one perhaps will be found exceedingly
easy to obtain in that state, and after this the tendency to yield
crystalline compounds will again decrease. A very marked in-
stance of the increased development of a character with each
additional increment of $C^2 H^2$, is seen in the baryta-salts of the
oily acids of butter and cocoa-nut-oil, butyrate of baryta being
readily soluble, caproate not so soluble, the caprylate sparingly,
while caprate and laurate of baryta are nearly insoluble. The
fractional crystallization of the salts of baryta is the only means
of separating these acids with any success.

If the ammonia-salt of the mixed caprate and laurate of baryta
is decomposed by chloride of barium, and the precipitate is
boiled with a large quantity of distilled water and the solution

filtered, the bright liquid becomes turbid before cooling if laurate, but not until cold if only caprate of baryta is present [*].

410. The platinum-salts of organic non-oxidized bases belonging to the pyridine and aniline series become less readily crystalline as they rise in boiling-point, and consequently in the per-centage of carbon.   Chinoline and lepidine present remarkable exceptions to the law of decrease of crystalline tendency as the point of ebullition rises[†].

411. It is often an important object to ascertain the fact of a substance being crystallizable or not, and also what menstruum is the most favourable for the purpose.   To effect this, a little of the matter may be boiled in a test-tube with the liquid to be tried, and the solution, if necessary, filtered; if, on cooling, crystals are not obtained, the fluid may be placed in a watch-glass and evaporated a little; if there is no result, the evaporation may be continued almost to dryness, or the fluid may be artificially refrigerated.   Motion in some cases greatly facilitates crystallization.   There are organic acids which, when dissolved in water, remain a long time without crystallizing, if kept quite quiescent; but on the fluid being stirred with a glass rod, the whole becomes almost solid.   Fluids which resist every method adopted to induce them to deposit crystals, will sometimes do so after being kept for a long time.   Many organic salts when first precipitated are in a resinous or pasty condition; but on keeping them for a few days, they frequently become hard, crystalline, and in a state fit for pulverization.   It is curious that digestion in ether sometimes converts a soft and resinous body into a hard and pulverizable condition.   It is not an uncommon thing to find precipitates which are quite amorphous when first formed, become granular or crystalline on boiling for some time.   It is always better to obtain them in this state, unless decomposition is caused by ebullition, as they are so much easier to wash and procure in a state fit for analysis.

[*] Georgey, Ann. der Chem. und Pharm., lxvi. p. 298; and Chem. Gaz., 1849, vol. vii. p. 82.

[†] Trans. Roy. Soc. Edinb., vol. xxi. part 2.

412. The presence of small quantities of resinous matters sometimes impedes crystallization to a degree which would appear quite disproportionate to the amount of impurity present; and some salts, even those whose characters are the most marked, become so disguised by this means as to be taken for new ones; and it would not be difficult to point out instances where chemists of the greatest skill and experience have been deceived through not being sufficiently alive to this source of error.

413. As a general rule, solutions intended for crystallization should be put aside in a quiet place, where no dust can find entrance, and where there is as little vibration as possible. If a solution, in the act of depositing crystals, is even slightly agitated, it frequently deposits a second crop on the first in such a manner as to render it unsightly. It is necessary to be aware of the remarkable way in which the crystals of inorganic salts are modified in shape by the presence of organic substances. It is well known that common salt crystallizes in octahedra if a little urea is present in the solution. Sulphate of potash is also sometimes so altered in appearance by the presence of impurities in the solution, that it might at first sight be easily mistaken for an organic product.

414. Crystallization is often remarkably facilitated by hanging pieces of string or catgut across the pan or basin in which the operation is proceeding; and as the crystals deposited upon the catgut are sometimes remarkable for their symmetry, it is a good method of obtaining the small and perfect ones intended to be grown by the process given at p. 251.

415. Crystallization is sometimes only to be effected at high temperatures; this is the case with bismuth, sulphur, and other fusible substances. The general method is in almost all cases the same, namely, the substance to be crystallized is fused in an earthen crucible in considerable quantity, and made to cool very slowly; as soon as it has solidified on the surface, a hole is made in the crust with an iron rod, and the fluid in the interior is poured out, when the sides, on being removed, are generally found studded with crystals. Sulphur and bismuth may be successfully operated on in this manner.

416. Very fine crystals of sulphur are sometimes obtained on digestion of an alcoholic solution of hydrosulphuret of ammonia with nitrobenzole, in the process for preparing aniline, and also from a solution in sulphide of carbon.

417. Coloured crystals may generally be bleached by filtering the hot solution through animal charcoal. It is considered by some that the bleaching property of charcoal is increased if added in small quantities by sprinkling into the solution containing the salt to be decolorized during ebullition. If the solution is acid, and in fact, as a general rule, the animal charcoal should have been freed of its phosphate of lime, insufficiently burnt matters, &c., by hydrochloric acid before use. Great care must be taken to wash away the last traces of acid from the charcoal. The hydrochloric acid, if precipitated after the operation with ammonia, yields a large quantity of phosphate of lime in a state of considerable purity.

418. Prolonged exposure of any organic substances to even moderately high temperatures, preparatory to crystallization, is to be carefully avoided, as much loss is frequently caused by this means through decomposition, or rather, perhaps, modification; quinine, for example, is gradually converted into a dark-coloured mass of the same composition in the hundred parts, but quite altered in its external characters. The remarkable results of Pasteur's experiments on the artificial production of racemic acid by the action of heat on the tartrate of cinchonine, &c., should also be remembered, as showing an instance of the same kind of action.

419. A beautiful instance of the use of crystallization is afforded by the method of preparing pure benzole from the hydrocarbons of coal-naphtha: if the fraction boiling between 165° and 180° Fahr., after about ten complete fractionations, is immersed in a mixture of snow and salt, about half of it freezes to a beautifully white and highly crystalline solid, which may be drained for a short time, and the process repeated two or three times, or less if the apparatus for removing the non-crystallizable portion by atmospheric pressure, described by

Mansfield, is used.   By thus purifying the benzole, a product of constant boiling-point is much more readily obtained than by any other means.   A more rapid way of obtaining the benzole in a state fit for being crystallized, than by fractional distillation, is given in § 380.

Benzole is often the best mentruum that can be employed for crystallizing organic preparations insoluble in other fluids.   Not the least of its advantages is the ease with which it can be driven off by exposure of the substance to a temperature of 212° in the water-bath.   Chrysène, which refuses to crystallize well from most of the fluids usually employed as solvents, yields magnificent yellow spangles resembling iodide of lead, when a hot saturated solution of it in benzole is cooled slowly.   Laurent's bichloride of naphthaline crystallizes from benzole in large rhombic crystals which cannot be distinguished by the eye from iceland spar, and, like that substance, possessing the power of double refraction.

SECTION XXI.

ON VOLUMETRIC MANIPULATION.

420. By volumetric analysis is understood the use of mea-
sured bulks of test-liquids containing known quantities by
weight of certain substances, capable of producing with a solu-
tion of the assay sufficiently marked effects to show with pre-
cision the complete conversion of the substance sought to be
estimated, into a compound the nature of which is perfectly
known. The quantity of the matter sought is ascertained by
observing the number of measures of test-liquid used. This
method of research has become of almost universal application
for the estimation of certain substances, the names of which are
given below, and several others which are not necessary to be
specified, as they are more usually determined in other ways.

421. The objection has been raised to all methods of volume-
tric analysis, that it is impossible to measure with accuracy; and
this has been sought to be proved by the difficulty of so filling
a measure with any liquid twice that it shall each time weigh
exactly the same. But it is unnecessary, in reply to this, to do
more than say, that the solutions are used in so dilute a state,
that not only does any error of admeasurement become too small
to have any influence whatever upon the results, but that ac-
curate estimations may by this means be effected on quantities
so small as to render it impossible to make use of the balance.
This might, if necessary, be instanced by numerous cases; but
it will be sufficient to allude to the paper of Bunsen "On a
method of volumetric analysis of very general applicability*," to
show the really wonderful accuracy of which the method is
susceptible.

422. There are one or two advantages of a general kind to be
gained from the use of *measured*, which do not apply to *weighed*,

* Liebig's Annalen, lxxxvi. p. 265.

quantities.   In the first place, the results are invariably obtained
with far greater rapidity, all the operations of quantitative ana-
lysis which cause delay, as, for example, the washing, drying,
and weighing of precipitates, being dispensed with.   There is
also another advantage which is peculiarly a feature in volume-
trical estimations, namely, that when two experiments are made,
the second is, if the solutions are properly prepared, almost
absolutely correct.   This feature will be more particularly dwelt
upon further on.

423. The instruments most commonly used for the purpose
are the burettes, figs. 211, 212, 214 and 215, test-mixers, and
calibrated pipettes.

Guy Lussac's burette, fig. 211, is to-
lerably convenient, from the facility with
which minute additions of liquid can be
made, by gently inclining the instrument,
the end, *a*, being closed during the pro-
cess by the pressure of the thumb, which
is relaxed when necessary, to allow of the
atmospheric pressure upon the liquid in
the tube, *a b*, so as to permit its exit by
the aperture, *c*.   The chief objection to
this instrument is its fragility, the tube,
c d, being extremely liable to be broken
off by the slightest carelessness.   If,
however, a small piece of cork is inserted
between the two tubes at *c*, and a string
is bound round them both, the danger of
breakage is so far lessened that in care-
ful hands a burette of this kind will last
in every-day use for years.

424. *Mohr's alkalimeter*.—This form
of burette consists of a graduated tube
open at both ends, *a b*, fig. 212, and
fitted with a compression stopcock made
of vulcanized india-rubber.   It is fixed upon a vertical support,
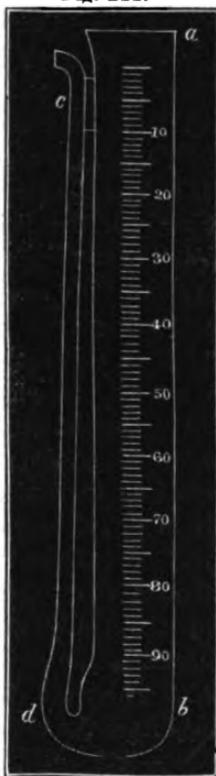
Fig. 211.

and when it is intended that the liquid shall flow, pressure is applied to the two knobs, *c d*, which causes them to open. The clasp is represented on a larger scale, and slightly open, in fig. 213. The instrument is sometimes made with a stopcock of glass, as in fig. 214; this, however, adds greatly to the expense, without increasing its efficiency. An apparatus of this kind, but ungraduated, is, however, in some researches invaluable as a separator, where very volatile and rare fluids are to be removed from water, acid, or alkaline solutions, &c.

Fig. 213.

Fig. 212.

Fig. 214.

425. Binks' alkalimeter, fig. 215, is the most convenient of all the forms of burette; its construction is simpler than either of the others, and it is far less liable to injury. Strange to say, Dr. Mohr, of Coblentz, entirely misunderstanding its mode of use, describes it as incapable of being used without danger of spilling its contents. If made to hold 50 cubic centimetres, and of a length of 2 feet, very open divisions will be obtained, which will enable the operator to obtain extremely accurate results with considerable rapidity. It is generally the custom to graduate these instruments in such a manner that it becomes necessary to hold it in the right hand during the operation of adding the test-liquid; it is much better, however, to reverse this, as a little practice will enable the operator to use the left

hand with equal facility, and then the right is at liberty, so that it may be used to stir the liquid, direct the course of the test-liquid with the glass rod, apply test-papers, regulate the gas-flame when heat is required, &c. If Binks' alkalimeter, full of

test-liquid, is held in the left hand, in such a manner that the thumb closes the aperture, *a*, while *b* becomes the lowest part of the tube, the end, *a*, being elevated at an angle of 20° or 30°, no fluid will escape, but upon relaxing the pressure of the thumb, and allowing air to enter, it will rise in a succession of bubbles through the liquid, which latter escapes by the orifice; in this manner the rapidity of the flow may be regulated with the utmost nicety. When the effect sought has been obtained, and it becomes evident that the test-fluid has been added in sufficient quantity, the burette is placed in a vertical position in the stand, *d*, and allowed to remain until all the fluid has drained from the sides, and the liquid in the burette ceases to rise from this cause. After the operation has been concluded, it is invariably found that a small quantity of liquid remains in the spout, *b*, being retained by capillary attraction; it is necessary to make this unite with the rest of the fluid, by applying a mo-

Fig. 215.

mentary suction with the lips to *a*, before putting the instrument aside to drain.

426. It is a matter of indifference what part of the curve formed by the water in the tube is employed as the line to read off from, if the same portion is taken invariably in the preparation of the standard liquid, and when using it. It is most common, however, to read from the lowest part of the curve.

427. Many contrivances have been adopted to render the readings extremely accurate, and lessen the errors of observation; and even tables have been constructed to correct for the influence of variations of temperature in altering the volume of the liquid; but it is better, as a general rule, to use tubes of small calibre and very dilute solutions, so as to reduce the error of observation to a point so far below the unavoidable errors of experiment as to be inappreciable; and it is more easy to do this than is generally supposed. Further on, experiments will be detailed to show the amount of accuracy attainable in several kinds of testing.

428. The alkalimeter on a foot, fig. 216, is, when made narrower than those usually sold, a convenient instrument for delivering test-liquids; the rapidity of flow is determined by the position of the grooves in the stopper; its use requires no particular precautions.

The volumetric method of estimation has been applied to the determination of the per-centage

Fig. 216.

values of a great number of substances; it will be unnecessary, however, to describe them all, the manipulation with a few being

N
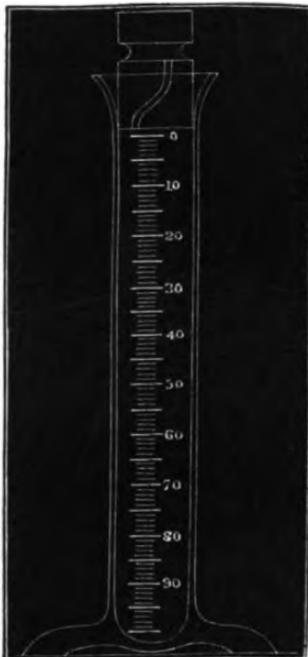
understood, will render it easy to acquire facility with the others described in works on analysis.

429. *Volumetric determination of acids.*—The volumetric method, as applied to acids, almost invariably depends upon the amount of an alkali required to neutralize them, and, with a little care, most persons will be able to estimate their strength with a degree of accuracy leaving nothing to be desired. It is usual to employ a different alkali in the case of hydrochloric and acetic acids to that used with the sulphuric, because with the former it becomes impossible to heat the solution to drive off the carbonic acid, the presence of which interferes with the reaction. But as it is inconvenient to have several alkaline test-liquids in the laboratory, I have been in the habit of using the same for all, it being equally applicable to the determination of fixed and volatile acids. The liquid alluded to is the solution of lime in sugar-water, recommended by Peligot in his modification of the nitrogen process of Will and Varrentrap, described in a subsequent part of this volume.

Lime is well adapted for the neutralization of acids, the only impediment to the use of lime-water being the small per-centage of earthy base. But if, instead of using pure water, a tolerably strong syrup is substituted, the portion dissolved becomes much greater; and the fluid is extremely convenient for the estimation of the strength of acids, from the fact, that, being free from carbonic acid, it is unnecessary to employ heat. This will be adverted to at greater length under the head of Alkalimetry.

The solution of lime in syrup, if very concentrated, has a yellowish colour, but the equivalent of lime being low, it will bear considerable dilution. A solution of caustic soda is also a very convenient standard alkali. As the solution is intended to be used for all the acids, it becomes a question which to select to prepare it from, and no hesitation need be had in adopting sulphuric acid for the purpose. As it is necessary in every laboratory to have a standard sulphuric acid, it being required not only for estimating the value of the carbonates of potash and soda, but also for nitrogen determinations, it will be selected as the starting-

point for the other acidimetrical and alkalimetrical solutions.   The preparation of this acid will be found described at p. 269.

The strength I am in the habit of employing is such that 50 cubic centimetres, equalling 100 divisions of the burette, are exactly equal to 20 grains of carbonate of potash; each division, therefore, is equivalent to ·2 grain of carbonate of potash, and as the instrument has very open divisions, it is perfectly easy to read off to half a division, equal in value to ·1 grain.   If preferred, any other strength may be employed.   As all caustic alkalies in solution are altered in value by keeping with a rapidity proportional to the amount of exposure, no good can result from making a very large quantity of the lime-syrup or caustic soda up to any exact standard, as it is necessary every few weeks to determine its saturating power.   This does not deteriorate the value of the method, because the process of ascertaining the strength of the alkaline solution does not occupy five minutes.

430. The apparatus depicted in fig. 217 is admirably adapted for keeping the solutions of caustic soda and lime-syrup, and enabling the burettes to be filled with little exposure of them to the air.   It is, I believe, the contrivance of Dr. Price.   A glass bottle is fitted with a sound cork, through which pass two tubes, *a* and *b*.   One of these reaches to the bottom of the fluid, and, when not in use, is closed by a small tube and cork, *c*.   The other fits into a hole in one of the hollow vulcanized india-rubber balls used as a toy.

Fig. 217.

On applying pressure to the ball, the solution rushes up the tube *a*, and is forced into the burette or other vessel used to receive it. On removing the hand, the ball resumes its original shape, and a volume of air equal to the fluid expelled enters by *a*.   The fact

N 2

that the volume of air entering is never greater than that of the liquid ejected, is one of the great merits of the instrument, because the quantity of carbonic acid in such a small bulk is so inconsiderable, that the solutions keep a long time unaltered.

If we find the number of divisions of lime-syrup required to neutralize the burette full of standard acid, we have the data for ascertaining the quantity of all other acids which the burette full of syrup is equivalent to. Suppose, for example, that the 100 divisions of the burette of lime-syrup or soda are just sufficient to neutralize 100 divisions of the sulphuric acid, it is evident, that as the 100 divisions of sulphuric acid are equivalent to 20 grains of carbonate of potash, that the 100 divisions of lime-syrup are also equal in saturating power to 20 grains of carbonate of potash; and to ascertain how much of each of the acids the 100 divisions of lime-syrup are capable of neutralizing, it is only necessary to calculate how much of each acid is equivalent to 20 grains of carbonate of potash.

The following equations give the values sought:—

$$KOCO^2 \quad : \quad SO^3 \quad :: \quad KOCO^2 \quad : \quad SO^3$$
$$69 \quad : \quad 40 \quad :: \quad 20 \quad : \quad 11\cdot594$$

$$KOCO^2 \quad : \quad NO^5 \quad :: \quad KOCO^2 \quad : \quad NO^5$$
$$69 \quad : \quad 54 \quad :: \quad 20 \quad : \quad 15\cdot652$$

$$KOCO^2 \quad : \quad \overline{A} \quad :: \quad KOCO^2 \quad : \quad \overline{A}$$
$$69 \quad : \quad 51 \quad :: \quad 20 \quad : \quad 14\cdot782$$

The 100 divisions of lime-syrup are equal, therefore, to 11·594 dry sulphuric, 15·652 dry nitric, and 14·782 dry acetic acids. The quantities of the other acids may be calculated in the same manner, by substituting their equivalents for the second term in an equation like those given above.

431. To perform the analysis, 50 grains of the acid are weighed in a small capsule or flask, the quantity being adjusted by means of a pipette; the contents of the capsule are then washed out into a small basin; a little tincture of litmus, sufficient to give a brilliant scarlet to the fluid, is added, and the lime-syrup is slowly poured in until the colour begins to change; when this takes

place, the addition is made more slowly still, the fluid being kept constantly stirred. A point is at last reached when one drop more syrup is capable of turning the liquid from red to blue; the operation is then finished, and the small quantity of liquid remaining in the beak of the alkalimeter is made to join the rest by suction applied at *a*, fig. 215, and when the fluid has all run down, the volume remaining is read off.

432. It is proper in all cases where great accuracy is desired, to repeat the operation, care being taken to add the test-liquid very slowly when the point attained in the first experiment is nearly reached.

In order to calculate the result, it is merely necessary to consider that, as 100 divisions of the burette are equal to a certain amount of dry acid (which amount has been found by an equation similar to those on the previous page), so the number of divisions used in the experiment indicate the number of grains of dry acid in the specimen. Therefore, calling the amount of dry acid equal to the 100 divisions of the burette, *a*, and the number of divisions used, *b*, we have

$$\frac{a \times b}{100} = x.$$

$x =$ the number of grains of dry acid in the quantity analysed, from which the per-centage can immediately be deduced.

433. *Volumetric determination of alkalies.*—There are many ways of ascertaining the quantity of caustic and carbonated alkalies in any given specimen, and the methods of manipulation will be found in their proper places in this volume. The mode of determining the quantity of alkali in carbonates by the weight of carbonic acid evolved on heating the sample with an acid, will be described in the section on Gas Manipulation.

434. The volumetric process, while susceptible of equal, if not greater precision than that last mentioned, is less troublesome, and occupies not half the time. It is, however, necessary in the first place to prepare a test-acid, and as this latter is also the standard from which the lime-syrup previously alluded to is made, great care should be taken that it is of exactly the proper strength.

To prepare it, concentrated sulphuric acid is diluted, say with twenty times its bulk of water; 20 grains of pure anhydrous carbonate of potash* are then weighed out, dissolved in water in a porcelain basin, and some tincture of litmus added; the whole is then supported over a lamp and heated nearly to ebullition: a burette being filled to 0° with the acid, the latter is to be slowly added until the colour of the litmus changes to a red; if the operation has been carefully performed, it will be found that this red is only due to the liberated carbonic acid acting on the litmus, and if the solution is briskly boiled for a very short time, the blue colour which the litmus had before the addition of the acid will return; by thus adding the acid carefully, and boiling the solution, a point is at last reached when the smallest further addition of the acid will convert the solution from a distinct blue to a brilliant scarlet, which indicates the conclusion of the process. A little practice will enable any person to perform this with success. The operation is to be repeated, the test-acid being added with very great care as the point first obtained is approached; the second result is to be taken as the true one. The number of divisions used, of course indicates the quantity of the diluted acid equivalent to the 20 grains of carbonate of potash; and to make the standard acid from this, it is merely necessary to dilute the solution until the quantity thus obtained is made up to 100 parts. Thus, supposing 60 divisions of the burette to have been required, it is evident that to obtain the standard fluid, 60 volumes of the diluted acid are to have 40 volumes of water added. For this last operation any tall cylindrical jar will answer, if it is accurately graduated into 100 parts. It is better, after this has been done, to again make an experiment on 20, or any other number of grains of carbonate of potash, to ascertain whether the dilutions have been accurately made. If the liquid is still a little too strong, it may be again diluted on the same principle, but if too weak, more sulphuric acid must be added, and this involves a repetition of the whole process.

* For precautions necessary in weighing deliquescent substances, see §§ 84, 91, 278.

435. If the above operations have been skilfully performed, results almost absolutely accurate may easily be obtained with the test acid. It is essential that the carbonate of potash used in this process should be carefully examined as to its purity. It is not sufficient to merely establish the absence of sulphates, chlorides, silica, &c.: its freedom from soda must be carefully ascertained, as it has been found that specimens of carbonate of potash considered as absolutely pure, have contained sufficient soda to cause serious errors to creep into analyses made with a standard acid, the strength of which has been determined by it.

A standard acid is also used in Peligot's modification of the process of Will and Varrentrap for estimating nitrogen.

436. *Volumetric methods in general.*—The volumetric method has been applied successfully to the determination of a great number of substances besides those enumerated, including, among others, baryta, bromine, chlorine, copper, manganese, tin, uranium, silver, iron, indigo, prussic acid, urea, and chloride of sodium in urine, &c. Baryta may be determined by the standard sulphuric acid; the process is, however, not so generally applicable as the conversion of it into a known weight of sulphate of baryta and weighing. Bromine may be very exactly determined, even when in presence of hydrobromic and hydrochloric acids, by means of a standard solution of pure oil of turpentine in alcohol*, turpentine having the property of combining with bromine into a colourless oil, when present in the proportions of 34 of the former to 80 of the latter, being in the ratio of single equivalents, supposing the formula of turpentine to be $C^5 H^4$†. What-

* Chemical Gazette, vol. xii. p. 432.

† Although 34 parts of turpentine decolorize 80 parts of bromine in presence of water, it is not necessary to assume $C^5 H^4 = 34$ as the formula and atomic weight of turpentine; in fact $C^{20} H^{16}$ appears to be the formula of the oil; for if we multiply 136 (which is the atomic weight; supposing $C^{20} H^{16}$ to be the formula) by ·0346, we obtain 4·7056 as the vapour-density for four volumes, and 4·76 has been obtained by experiment. The fact that the atomic weight of any organic substance, if multiplied by half the density of hydrogen, gives its vapour-density for four volumes, becomes obvious on a little reflection, and has already been mentioned in the section on Vapour Densities (§ 127).

ever the real formula of turpentine may be, the fact that 34 parts
of pure turpentine are capable of decolorizing 80 parts of bromine
(when the reaction takes place under the conditions given in the
paper alluded to), is quite sufficient for all the purposes of the
quantitative estimation of free bromine.

Chlorine, as it exists in chloride of lime, is capable of being
volumetrically determined in several ways, the manipulation
connected with which will be found in analytical treatises.
Copper is determined by a solution of sulphuret of sodium, a pre-
liminary assay being always made upon a known weight of pure
metal, the solution of the sulphuret being prepared fresh each
time by dissolving the crystals in distilled water; the method is,
however, but little practised.

437. Uranium may be estimated by a solution of a phosphate of
known constitution, the process being based upon the insolubility
of the uranic phosphate.

438. Urea is determined by the new process lately introduced
by Liebig, and which is founded upon its tendency to form definite
compounds with corrosive sublimate.

439. The quantitative determination of silver by a solution of
chloride of sodium is susceptible of the greatest precision. A
standard solution of common salt is made of such a strength that
100 divisions of the burette are equal to 10 grains of silver, each
division being equivalent to $0\cdot1$ grain, and a second solution is
also made ten times more diluted, so that one division is only
equal to $0\cdot01$ grain. The first assay is made with the strong
solution, and is repeated, the process being stopped when the point
is nearly reached, and the estimation is finished with the weak
solution. The solution of the silver in nitric acid is placed in a
rather capacious stoppered flask, which is briskly shaken after
each addition of the test-liquid. As long as silver still remains
in solution, the latter is milky, even after considerable agitation;
but when the operation is finished the solution becomes clear.
The milkiness alluded to is a great assistance in the process, as it
enables the operator to know that sufficient test-solution has not
been added, and fortunately it is not opaque enough to prevent

the cloudiness caused by each addition of the normal fluid from being seen.

440. In the French Mint very elaborate precautions are taken to ensure perfect accuracy in the measurements, tables of correction for the influence of temperature upon the bulk of the solution being used; such modifications are, however, merely useful where a great number of operations have to be performed daily, and are never adopted in scientific research, the silver in the latter case being almost invariably weighed as chloride.

441. *Test-papers, &c.*—There are several substances used in qualitative and quantitative experiments to determine the presence of excess of alkalies or acids, by the changes of colour produced in them. The most common of these, and perhaps the most generally useful, is litmus, which appears to be prepared from two or three species of lichen by a process which is by no means thoroughly known. As it appears in commerce, it consists of small square pieces about $\frac{1}{4}$ of an inch long by $\frac{1}{6}$ broad; these fragments, besides litmus, contain a great many substances, among which may be found ferric oxide, alumina, sulphate of lime, silica, and some others. Upon digesting this mixture with distilled water at a gentle heat, a blue solution is obtained of considerable intensity; this solution must have about a quarter of its bulk of alcohol added to it to prevent decomposition, which would otherwise take place on keeping. If pieces of white filtering-paper are saturated with the fluid thus prepared, and hung upon clean strings in a place free from dust and vapours, what are termed litmus-papers will be obtained; they should be cut into strips about $\frac{1}{6}$ an inch broad and 3 or 4 inches long, which may be kept in small test-tubes, corked, for almost any length of time without injury. These papers are so valuable, and of such constant use in the laboratory, that no trouble should be spared to obtain them of the best quality. If the litmus, as sometimes happens, contains an excess of alkali, it is less sensitive as a test for acids, a portion of that present being expended in its neutralization before the remainder can act upon the colouring matter. This difficulty may be got over by adding a very dilute acid to the solution before

N 5

dipping in the paper, and when the fluid has begun to show the acid reaction, bringing the blue colour back with a little carbonate of potash.

Litmus-papers are preferred by some to the tincture in alkali-metrical experiments; the solution to be tested is applied to the paper with a glass rod, and if a red coloration is observed, the paper is gently warmed until dry, in order that if the reddening is caused by carbonic acid the latter may be dissipated by the heat, and the blue colour restored. When litmus-paper is intended to be used as a test for alkalies, it should be previously reddened by holding it in a moderately damp state over the vapour of acetic acid until of a distinct red, but not longer; the blue is readily restored by even very diluted alkaline fluids or the vapour of ammonia. The neutral-tint paper, sometimes prepared as a test for both acids and alkalies, is an unnecessary addition to the collection of test-papers.

442. *Turmeric-paper* is best prepared by macerating ground turmeric root with moderately strong spirits of wine, filtering off the bright liquid and saturating white filtering-paper with it; in consequence of the volatility of the spirit, the papers soon dry, and may then be preserved like those coloured with litmus. Turmeric-paper thus prepared, is of a brilliant yellow colour, which is turned to a reddish-brown or intense red by alkalies, according as they are more or less strong. The dilute alcohol is by far a better menstruum for the colouring matter of the turmeric than water, especially if the papers are intended for use at lectures, where it is desired to make the change of colour evident at a distance. Turmeric paper is much used to detect ammonia, but for this purpose it should be slightly moistened, in order that the volatile alkali may be absorbed and thus more effectually act upon the colouring matter.

443. *Lead-paper,* used for detecting the presence of sulphuretted hydrogen, is made by saturating filtering-paper with solution of acetate of lead, and, after drying, may be preserved in the same manner as the others. It is blackened by very minute traces of sulphur. If lead-paper be held over a bottle of sulphide of

ammonium until black, it becomes an excellent test of ozone in essential oils; for if a little turpentine, or other oil which has been exposed to the air until ozonized, is dropped upon the paper so blackened, and the latter be held over the furnace-plate or other source of heat until the turpentine begins to volatilize, the black stain disappears in the places where the ozonized oil has been, and the original appearance of the paper is restored. This change is due to the conversion of the black sulphuret into the white sulphate by the oxidizing tendency of the ozone.

444. *Logwood.*—The colouring matter of this substance is preferred by some to litmus for detecting the presence of excess of alkalies, an acid aqueous solution of the colouring matter being turned from red to blackish purple by small excess of alkali. It is especially used in neutralizing the sulphuric acid in Peligot's nitrogen process.

445. *Slips of fir-wood,* moistened with hydrochloric acid, are much used as a test in experiments on the volatile organic bases. The method of testing for pyrrol has been mentioned before, p. 236. A great number of volatile bases, when quite free from pyrrol, have the property of giving a bright yellow stain to fir and hydrochloric acid; the reaction is therefore not distinctive of any specific substance.

Carbolic acid is recognized by its property of giving a deep blue tint to slips of fir, moistened with moderately strong nitric acid; the blue colour soon passes, however, into a brown. It also gives a blue with fir-wood and hydrochloric acid.

446. Paper saturated with tincture of guaiacum assumes a blue tint when exposed to most oxidizing vapours, such as chlorine, bromine, nitric acid, ozone, &c.

EXPERIMENTS SHOWING THE ACCURACY OF THE METHODS GIVEN.

447. *Alkalimetry.*—A test-acid having been prepared, 100 divisions of the burette being equivalent to 20 grains of carbonate of potash, a little of the latter, which was ascertained by careful analysis to be chemically pure, was heated to redness in a platinum crucible, and on being weighed with the lid on, to

prevent moisture from being absorbed during the operation, was
found to be equal to 10·8 grains. The contents of the crucible
were washed into a porcelain basin, some tincture of litmus and
a little more water being added, to make up about 2 ounces: the
fluid was now heated nearly to ebullition, the test-acid being slowly
dropped in, with constant stirring; after a time the solution be-
came distinctly red, but on boiling for a few minutes the blue was
restored; at last a point was reached when a single drop con-
verted the boiling solution from a blue to an intense scarlet, which
was not altered by prolonged ebullition. The burette was then
replaced on its stand, the drop of fluid remaining by capillary
attraction in the beak, sucked in so that it joined the rest of the
fluid, and, after a few minutes being allowed for the sides to
drain, the volume was read off, when 46 divisions still remained
in the burette, and 100−46=54, the number of divisions used to
neutralize the 10·8 of carbonate, and

$$100 : 20 :: 54 : 10·8.$$

In another experiment, 7·4 grains carbonate of potash required
37 divisions:—

$$100 : 20 :: 37 : 7·4.$$

448. *Estimation of silver by standard solution of common salt.*
—The burette, which was divided into 100 parts, held 50 cub.
cent., and the jar for making the test-solutions held just ten
times that quantity.

Now, to ascertain how much chloride of sodium is to be dis-
solved in 50 cub. cent. of water to make a standard solution, 100
divisions of which shall be equal to 10 grains of silver, we say—

$$\begin{array}{cccc} \text{Ag} & \text{NaCl} & \text{Ag} & \text{NaCl} \\ 108 & : 58·5 :: & 10 & : 5·41. \end{array}$$

The latter is therefore the quantity of common salt to be added
to 50 cub. cent. of water to make the standard solution, but to
make ten times the quantity as a stock, 54·1 would be necessary.
In order to allow for impurities in the salt, 64 grains were dis-
solved in the jar of water. To determine the strength of this
solution two experiments were made.

I. 10 grains pure silver took 81 divisions.

II. 10   „   „   81   „

The 81 divisions were therefore made up to 100 with water.

I.   5 grains of pure silver took 51 divisions.

II. 10   „   „   100   „

III. 10   „   „   100   „

Per cent.

I.	II.	III.
102	100	100

In the first experiment an excess of one division was added, which, although only equal to 0·10 grain when calculated to 100 parts, gave an excess of 2 per cent. The other experiments are exact, and with moderate care may be obtained equally correct every time. It must be mentioned that the experiments above quoted are taken at random from the laboratory note-book.

Estimation of free bromine by oil of turpentine (weighed quantities being used).—47·7 cub. cent. of bromine-water, treated with solution of turpentine in alcohol (containing 10 per cent. of the oil) until the colour of the bromine had disappeared, gave in eight experiments—

I. 4·16 of bromine.	V. 4·23 of bromine.
II. 4·16 „	VI. 4·23 „
III. 4·35 „	VII. 4·16 „
IV. 4·35 „	VIII. 4·16 „

Six estimations as bromide of silver gave—

I. 4·15	IV. 4·25
II. 4·15	V. 4·35
III. 4·26	VI. 4·14

Mean six estimations by turpentine.	Mean six estimations as bromide of silver.
4·225	4·216

Almost the same results were obtained in presence of hydro-bromic and hydrochloric acids*.

449. To show the necessity of carefully examining the carbonate of potash used for determining the strength of the test-acid, to ascertain its freedom from soda, the following analysis, made upon a specimen of carbonate of potash, sold as absolutely pure at an extravagant price, may be quoted:—

Carbonate of potash	. . . . .	91·35
„ soda	. . . . . .	7·80
Loss	. . . .	·85
		100·00

A specimen of salt of tartar of commerce gave—

Carbonate of potash	. . . . . .	75·7
„ soda	. . . . . .	3·4
Sulphate of potash	. . . . . .	3·2
Chloride of potassium	. . . . .	1·5
Water	. . . . :	15·9
		99·7

450. The best method of ascertaining the existence of small quantities of soda in the presence of a great excess of a salt of potash, is to heat a fragment of the suspected mixture in the blue flame of the blowpipe, and see if the yellow flame, characteristic of soda, is obtained. A mere trace of soda may be detected in this manner, as it quite overpowers the peach-blossom flame produced by pure potash salts.

* Chemical Gazette, vol. xii. p. 433.

SECTION XXII.

GAS MANIPULATION.

451. Experiments with gases are of everyday occurrence in all laboratories, many processes of research being dependent upon the operator's knowledge of their peculiarities, and familiarity with the methods of working with them. It will be convenient to divide the subject into five parts, namely, 1. Preparation of gases. 2. Storing of them. 3. Estimation of them: *a*, by volume; *b*, by weight. 4. Analysis of gaseous mixtures.

PREPARATION OF GASES.

452. *a*, Sulphuretted hydrogen; *b*, carbonic acid; *c*, hydrogen; *d*, oxygen; *e*, chlorine; *f*, sulphurous acid; *g*, cyanogen and chloride of cyanogen; *h*, nitrous acid; *i*, muriatic acid.

453. *a. Sulphuretted hydrogen.*—This is by far the most commonly employed of the gases in analytical research; its uses are numerous, but the property which, of all others, renders it indispensable to the analyst, is the exceedingly characteristic nature of its behaviour with solutions of the metals.

454. In fact, the latter may be divided into two great groups, by the manner in which their acid solutions react with it, some being precipitated and others not. Among the former are found antimony, arsenic, bismuth, cadmium, copper, gold, iridium, lead, mercury, palladium, platinum, rhodium, silver, tellurium, and tin. Moreover, its reactions are in some instances so marked, that a shrewd guess may be made as to the identical metal. It is also invaluable for the precision with which certain metals may be isolated from complex organic mixtures, even when existing in them in very minute quantity.

455. It is also much used as a deoxidating agent, many solutions of the higher oxides of metals being reduced to the protosalts with precipitation of sulphur. Its deoxidating properties are also turned to valuable account in organic research.

Iodine and bromine in contact with water may be converted by it into the corresponding hydracids. A minute consideration of these points belongs, however, to works on general chemistry.

456. Sulphuretted hydrogen may be prepared from either the sulphide of iron or that of antimony.

457. *From sulphide of iron.*—This is generally the more convenient of the two methods of preparation, as it does not involve the application of heat. The material from which it is obtained is the protosulphuret of iron, which, for the purpose, ought to be in small fragments: fig. 218 represents the apparatus most usually employed for this purpose.

The metallic sulphide is contained in the large flask provided with a thistle-funnel, and a tube by which the gas is conveyed into the washing-bottle. It will be seen that the tube leading from the generating-flask is divided and connected with a caoutchouc tube, to allow of freedom of motion in the apparatus. The washing-bottle is used to retain any sulphuret of iron, or

Fig. 218.

solution of the sulphate or other impurities carried over mechanically by the current of gas. To effect this washing, the tube evolving the gas just dips under the surface of the water in the washing-bottle. It is not advisable for it to be immersed deeper than this, as such a procedure of course creates a pressure in the flask, causing the fluid in it to ascend in the pipe of the thistle-funnel, and, if allowed to penetrate deeper into the water in the washing-bottle, this pressure, added to that in the vessel containing the fluid to be acted on, may prove inconvenient. By increasing the length of the thistle-funnel the gas may be passed a considerable depth under the surface of any fluid, it being always remembered that the height to which the fluid in the generating-flask will rise in the tube of the funnel, is equal to the depth
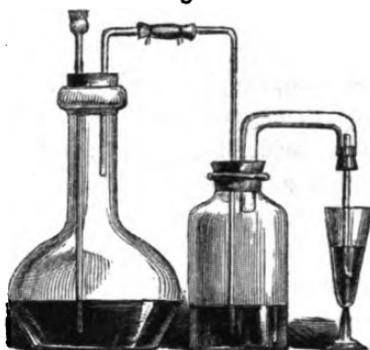
which the tube penetrates under the surface of the water in the washing-bottle, plus that which it dips in the liquid being acted on.

458. The apparatus, fig. 219, is for enabling a current of sulphuretted hydrogen to be obtained at any time, and yet to prevent

Fig. 219.
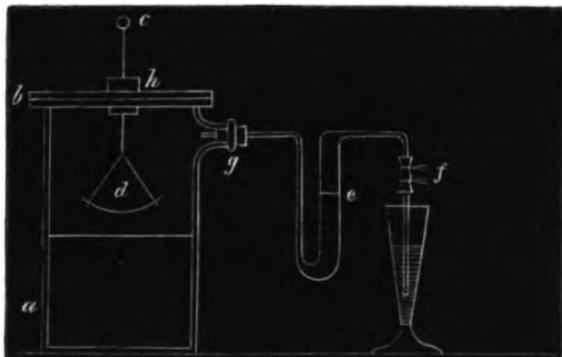
the sulphuret of iron from being dissolved after the required amount of gas has been obtained. It moreover prevents the escape of gas into the apartment after the experiment is finished. It was first described by the late Mr. Kemp of Edinburgh. A glass vessel, *a*, has a lateral opening, *g*, to which is attached the washing-apparatus, *e*. A plate-glass circle, *b*, fits air-tight upon *a*, the two surfaces being adapted to each other by grinding. The plate has an aperture drilled in it to admit a cork, *h*, which allows the wire, *e*, to slide up or down. The basin, *d*, is attached to the wire, and is intended to support the sulphuret of iron. It is made of lead or porcelain, and is perforated. The washing-apparatus, *e*, is attached to *g* by a cork. The form in the engraving may be modified in many ways to suit the operator's convenience. A piece of caoutchouc tubing, *f*, enables a clean exit-tube to be attached when required. The vessel, *a*, may be filled to about a third of its capacity with dilute sulphuric acid. To obtain a current of gas, the basin, *d*, is depressed until it just touches the liquid. If the quantity of gas required is very small,

d is to be raised again immediately, as the acid adhering to the fragments will be sufficient.

459. The fluids on which the action of the gas is to be tried must always be tolerably dilute, and, if it is intended to separate the metals contained in it into groups in the usual manner, should be distinctly, and even pretty strongly acid; a great excess, however, being avoided, as it involves the introduction of an inconveniently large quantity of ammoniacal salt when the fluid has to be rendered neutral or alkaline in a subsequent stage of the analysis. The production of a precipitate is not invariably owing to the presence of a metal capable of being thrown down by the gas, as when sulphuretted hydrogen is passed into solutions of salts of some of the higher oxides, pure sulphur is thrown down as a milk-white powder; an acid liquid containing persalts of iron giving a copious precipitate of sulphur, according to the equation

$$Fe^2 O^3 + HS = 2FeO + HO + S.$$
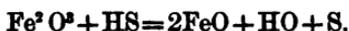
460. It is necessary to perform operations with this gas in places where there is good ventilation, in consequence of its deleterious nature, and also to prevent it from acting upon the other substances contained in the laboratory. All salts of lead will be blackened if even a minute quantity of the gas escapes near them. Baryta salts are (from the almost invariable presence of a trace of lead in them) generally discoloured by it, as also metallic apparatus.

461. Where there is much testing with sulphuretted hydrogen, it is a good plan to use water saturated with the gas, instead of the latter itself, and, in fact, in all cases where it is not necessary to expose the fluid under examination to the action of a continued stream.

462. To obtain a knowledge of the appearances caused by the action of a stream of this gas upon various metallic solutions is of great importance to the analyst, as it frequently enables a pretty accurate guess to be made at the nature of the substances present. For this purpose it is well to practice upon solutions of known composition, until the reactions are familiar.

463. A blue colour is formed by sulphuretted hydrogen in solutions containing vanadium. The precipitates formed in solutions of copper and lead, and perhaps many other metallic salts, vary greatly in colour with the concentration and degree of acidity of the fluid, and with the mixtures present. If, for example, sulphuretted hydrogen is passed into a solution containing lead and arsenic acid, the first precipitate will be black; and if this is filtered off, or allowed to settle, a yellow one results. In this case, the phenomena are caused by the ease with which the lead is precipitated, the sulphuret of that metal being formed immediately, the yellow compound of arsenic and sulphur, corresponding to arsenic acid, being formed with greater difficulty; it is usual, therefore, to reduce the arsenic to the state of arsenious acid before precipitation.

464. A metal may be thrown down by this gas with quite different appearances, according to the state of oxidation in which it exists in the solution; protosalts of tin, for example, giving a dark-brown precipitate, while the persalts are thrown down of a bright yellow colour.

465. A peculiar appearance is caused when the gas under consideration is passed into a solution of corrosive sublimate. It may be mentioned, that at first, when the gas is in small quantity, a white compound of mercuric sulphide with the chloride is formed; and as the precipitates pass through various shades of colour, from white through yellow and red to black, it would appear that several compounds momentarily exist, but are all rapidly decomposed, the ultimate product being mercuric sulphide of a black colour until sublimed, when vermilion is obtained.

466. When insoluble salts are to be decomposed by sulphuretted hydrogen, as very frequently occurs, more especially in organic chemistry, it is necessary to keep stirring up the precipitate, in order that it may be thoroughly exposed to the action of the gas, as, if allowed to remain at the bottom of the beaker, or other vessel in which the operation is performed, the decomposition would be very incomplete even after a considerable time.

467. It is sometimes required to prepare hydriodic acid by passage of this gas into a mixture of water and iodine; agitation is particularly essential in this instance, from the way in which the iodine becomes enveloped with the precipitated sulphur, masses accumulating which are troublesome to get rid of when once allowed to form.

468. It will be seen on reference to the engraving in p. 280, that the large tube proceeding from the washing-bottle has a small tube fitted to it with a cork; this is in order that when it is wished to test solutions of different kinds one after another, it should not be required to wait until the tube last used is cleansed from the adhering metallic sulphide before proceeding to the next experiment; a few of these tubes may always be kept in reserve. It is sometimes more convenient to attach them to one of vulcanized caoutchouc.

469. An alcoholic solution of sulphuretted hydrogen is much used, conjointly with ammonia, in some branches of organic chemistry, for the purpose of reducing the nitro-compounds of certain hydrocarbons, with the intention of converting them into organic bases; the following equation, showing the manner in which this decomposition takes place in the case of the formation of aniline from nitrobenzole, may be taken as expressing the general nature of the process, even where the hydrocarbons are of a different constitution :—

$$C^{12} \begin{cases} H^5 \\ NO^4 \end{cases} + 6HS = \begin{matrix} C^{12}\ H^5 \\ H \\ H \end{matrix} \Bigg\} N + 4HO + 6S$$
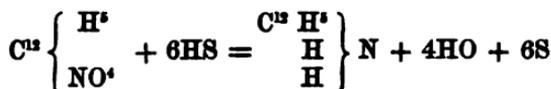
The amount of sulphur deposited being directly in the ratio of the quantity of base formed.

470. *b. Carbonic acid.*—Carbonic acid, although of far less general applicability in research, is, nevertheless, often required to be prepared in the laboratory. It is usually obtained by acting on fragments of marble with hydrochloric acid. It is much better to use the marble in fragments than in powder, as in the latter case the gas is evolved too tumultuously, while in the former it is procured in a steady and easily manageable stream, well

adapted for acting on solutions or other matter exposed to its influence. It is improper to use black marble in experiments where a tolerably pure gas is required, as it evolves sulphuretted hydrogen at the same time as the carbonic acid. The apparatus seen in fig. 218, p. 280, is adapted to the preparation of this gas. The operation is precisely the same as in the case of sulphuretted hydrogen, the only difference being that carbonate of lime in the state of marble fragments is substituted for the ferrous sulphide, and hydrochloric acid for the sulphuric.

471. It is easy in all cases where a gas does not require heat in its preparation, to connect two ordinary glass bottles with glass tubes and corks, so as to form a very efficient apparatus for the purpose; the method of putting it together is obvious from fig. 218. In this, and, in fact, in all cases where gases are prepared and passed into fluids under any pressure, it is necessary to take considerable care in the selection of corks, in order to avoid the necessity of making good the joints with luting. Nevertheless, when large quantities of the gas are required, it is impossible to avoid the use of luting unless an expensive apparatus is employed.

A very effectual arrangement for the preparation of carbonic acid, sulphuretted hydrogen, or pure hydrogen on the large scale, consists of a large stone jar closed with a bung, through which pass two tubes, namely, a large one of glass, having a glass funnel fitted to it with a cork, and a piece of tin gas-pipe passing under the surface of water contained in a washing-bottle, from whence it is conveyed into the liquid to be acted on.

472. When the fluid which is to be submitted to the action of the gas is of a nature to receive injury from contact with a metallic pipe, it is very easy to adapt a piece of glass tube to the metallic one. In this arrangement it is necessary to have recourse to luting, and the best for the purpose is the almond- and linseed-meal mixture previously mentioned.

473. Carbonic acid is, it has been said, less frequently used than sulphuretted hydrogen in research, but, nevertheless, it is indispensable in many operations. It is used to convert the

ordinary carbonate of potash into the bisalt, and to precipitate lime and baryta from alkaline solutions. As produced by the combustion of coke, it has been employed to precipitate soluble salts of lead with it, to form white-lead. It is not unfrequently used as a non-oxidizing atmosphere in some chemical operations, such as the distillation of fluids easily decomposed by contact with air. Where the chloride of calcium in the spongy state, used in organic analysis, is alkaline, it is usual to pass a gentle stream of carbonic acid through the chloride-of-calcium-tube for about half an hour, in order that none of the carbonic acid gas produced during the combustion of the organic substance should be absorbed during its passage before reaching the potash-bulbs. It is necessary, of course, to remove the remaining carbonic acid from the chloride-of-calcium-tube before connecting it with the combustion-tube, &c.; this is best done by gentle suction with the lips, applied by means of a suction-tube, or by simply applying them to the tube itself, of course avoiding to wet the outside of it, or, if such should happen, it must be carefully wiped off preparatory to weighing.

474. In operations where lime, &c. is to be precipitated by a current of carbonic acid from any solution, the property of this gas to dissolve the precipitate again when in sufficient excess must not be forgotten. Where it is suspected that such an error has been committed, it may be corrected by boiling the solution for a short time, by which means the excess of carbonic acid is expelled, the earthy carbonate being again precipitated.

475. *c. Hydrogen.*—In the preparation of this gas, the same system of apparatus given for sulphuretted hydrogen and carbonic acid may be employed; the substances by which the water is decomposed to furnish the gas, with the assistance of sulphuric or muriatic acids, being iron or zinc. The manipulation required demands no specific notice. There are, however, some particular cases in which precautions must be taken. If, for example, it is required to reduce a metallic oxide with hydrogen, it is necessary to dry the gas before passing it into the tube in which the reduction is performed. In the instance of the preparation of the metallic

copper used in organic analysis to reduce the oxides of nitrogen, and sometimes for other purposes, it is merely necessary to substitute a flask of concentrated sulphuric acid for the washing-bottle in fig. 218; see also p. 187.

476. The uses of hydrogen in analysis have been much . increased lately by the researches of MM. Rivot and St.-Claire Deville, and it is probable that they will be still further extended. It is important in experiments where the reducing property of hydrogen is to be made use of on mixtures of a heavy with a comparatively light substance, not to have too rapid a current of the gas, as it is liable to carry away mechanically a portion of the less weighty matter.

477. When the loss of weight consequent upon the passage of hydrogen at a red heat over a mixture of a reducible and non-reducible metallic oxide is to be ascertained, it is unnecessary, where the mixture has been obtained by precipitation, to employ the whole of the precipitate. If the weight of the latter is accurately known, a portion is introduced into the bulb of the reduction-tube, figs. 129 and 220, which is weighed before and

Fig. 220.
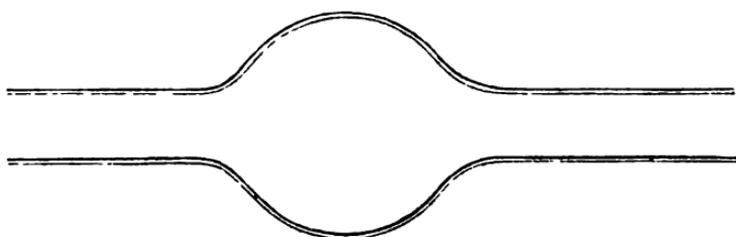
after its introduction. By this means the loss of weight consequent upon the passage of the gas over a known portion of the mixture may be calculated upon the whole quantity, and as accurate a result will be obtained as if the entire amount had been introduced. In fact a more exact experiment is generally made thus, because where a considerable quantity of substance is treated in the manner alluded to, a portion is liable to escape the action of the gas from its being covered by the superin-

cumbent mass, and in all cases the larger the quantity worked upon, the more troublesome the reduction becomes to effect completely.

478. The use of hydrogen in distillation to prevent oxidation has been previously alluded to, § 363, p. 231.

479. In taking the densities of the vapours of substances liable to oxidation at elevated temperatures, results are obtained greatly varying from the numbers required by theory. To obviate this, the flask in which the density is to be determined, has its neck inserted into a vessel through which a stream of hydrogen gas is passed for some hours; by this means the diffusive property of the gas enables us to get rid of the whole of the oxygen from the globe, and thus avoid the source of error caused by the oxidation of the vapour.

480. When it is required to obtain hydrogen gas absolutely pure, it is sometimes procured by the electrolysis of water; the apparatus required for this purpose will be found in its proper place.

A very pure hydrogen may be procured on passing the gas evolved by the action of dilute sulphuric acid on zinc, first through water, then through a solution of nitrate of silver; after this it bubbles up through a tolerably concentrated solution of caustic potash; and lastly, it is dried by sulphuric acid. A considerable time must be allowed to elapse before the gas is collected, as the quantity of air in so complex an apparatus as that required for its complete purification is considerable; and the stream must be tolerably rapid, and well sustained, to ensure the removal of the last traces.

481. Hydrogen is frequently prepared by means of an apparatus on the principle of that seen in fig. 221, and known as Dœbereiner's lamp. The chief advantage in its use is, that it allows of a supply being obtained at any moment, and with the addition of a small brass cup containing spongy platinum, constitutes an instantaneous light. It can also be used very conveniently as a Marsh's apparatus.

The instrument consists principally of two vessels, a and b:

a is a globe with a long neck, and provided at the bottom with a

Fig. 221.
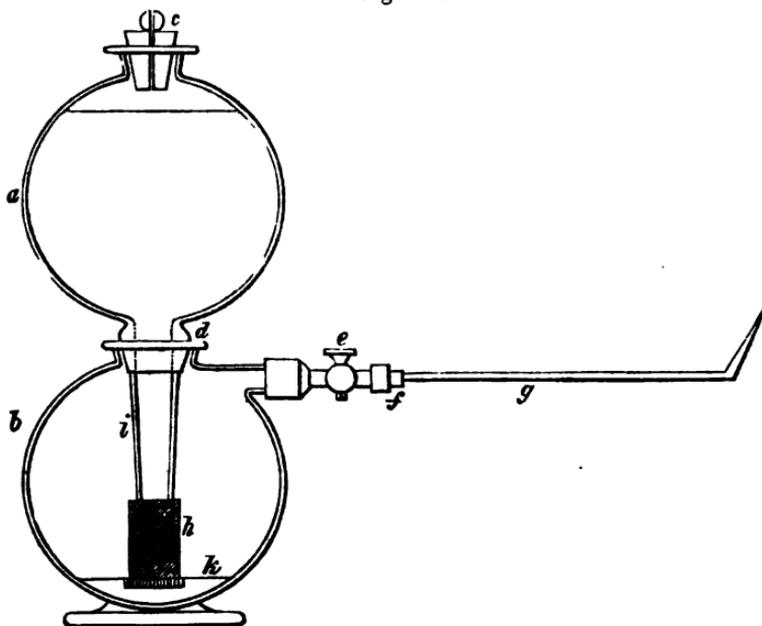
flange, to enable it to support a cylinder of zinc, *h**; it has a
stopper at *c*, which is, however, perforated. It fits tightly into
b, by means of a thick portion ground conical to fit accurately into
the neck of the lower vessel at *d*. The lower portion of the
lamp has a pipe projecting from it, furnished with a tap, *e*,
which is so made as to allow of the other pieces of apparatus,
presently to be described, being attached. The mode of action of
the instrument is very simple. Dilute sulphuric acid, sufficient
to fill the lower vessel when the zinc is in its place, is poured in,
and the upper portion is inserted, care being taken that it fits
properly at *d*; the acid meeting with the cylinder of zinc held
round the tube by the flange, generates hydrogen with tole-
rable rapidity; *e* being closed, the gas is unable to escape, and

---

* It is preferable to have a moveable cork flange to support the zinc.

o

causes sufficient pressure to force the liquid up the tube, i, into
a; the level of the liquid in b is now at k, and the acid being no
longer in contact with the zinc, all evolution of gas ceases; and
by opening the stopcock, e, the pressure of the column of fluid
causes the gas to escape with rapidity. If it is desired to
use the lamp as a Marsh's apparatus, the fluid suspected to
contain arsenic is introduced into a, and allowed to descend
into the lower compartment, so that the hydrogen may act on the
arsenic at the moment of its formation. A piece of hard glass
tube, free from lead, drawn out and bent upwards, as in figure
221, is attached at f, by means of a perforated cork, and as
soon as the air is expelled (by allowing the liquid to descend
twice, and again making it rise into a, by means of the stop-
cock, e), the gas is inflamed at the point of the tube, and a
cold porcelain plate is depressed upon it until the presence or
absence of arsenic is determined.

The process is sometimes modified, by heating the tube, g, in
the centre by means of a spirit-lamp, when the arseniuretted
hydrogen is decomposed with deposition of the metal. When it
is intended to use the instrument as an instantaneous-light ap-
paratus, the appliances seen in fig. 222 are attached. It con-

Fig. 222.
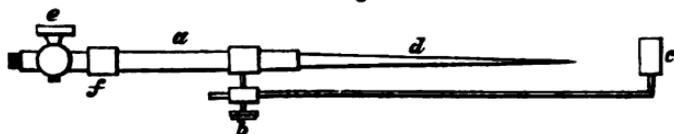
sists, essentially, of a brass tube, a, upon which slides stiffly a
small piece of tube, carrying a rod, to which is attached a nut,
perforated to allow a wire to slide through it, which is capable
of being fixed in its position by a screw with a milled head, b.
This wire has a small brass cup, c, fastened to its extremity,
the concave part of which is directed towards the fine orifice of
the nozzle, d; this cup contains a little spongy platinum. If
the tap, e, be turned when the vessel, b (fig. 221), is full of
gas (the apparatus in fig. 222 being substituted for $f\ g$, fig.

221), the hydrogen escaping by the aperture of *d*, plays upon
the platinum, and being by the peculiar structure or con-
dition of the metal brought into intimate contact with con-
densed oxygen, its union takes place with formation of water,
and the action is sufficiently energetic to cause the ignition of
the platinum, which in its turn inflames the excess of hydro-
gen.   This takes some time to describe, but the effect, as the
name of the lamp implies, is, when all things are in good order,
instantaneous.

482. If, as not unfrequently happens, it is wished to collect
the hydrogen over mercury or water, the arrangement seen in
fig. 223 is adopted.   It merely consists of a glass delivery-tube,

Fig. 223.
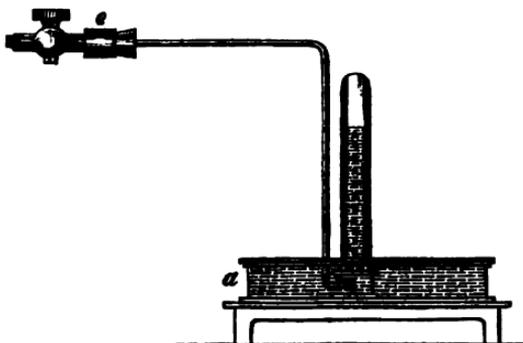
which may be attached by a cork to the stopcock, *e*, instead of
the tube *g* in fig. 221.

483. *Oxygen.*—The uses of oxygen in research are very limit-
ed, and, with the exception of its power of converting carbon
into carbonic acid at a red heat, I do not remember any applica-
tion that requires particular manipulation, except in experiments
for the lecture-table, and in eudiometrical processes, to be al-
luded to in another section.

The method of applying it to the purpose first mentioned, will
be described under the head of Organic Manipulation.   For all
purposes where a good quality of gas is required, it is prepared

o 2

by heating chlorate of potash mixed with about one quarter of its weight of powdered oxide of copper or manganese. This addition enables the gas to be obtained at a lower temperature than would otherwise be necessary. In heating the mixture either in flasks or large test-tubes, care should be taken to apply the heat very gradually, or a fracture is almost sure to take place. A charcoal fire is, for this reason, better than a lamp, as the temperature is more diffused and gradual. The delivery-pipe must not be immersed too deeply in the water of the pneumatic trough, or the pressure will cause the tube to blow out, in consequence of the softening of the glass caused by the high temperature. Many other points in the manipulation connected with this gas will be alluded to under other heads.

484. *Chlorine.*—This gas is used in a multitude of cases, each requiring a different system of apparatus, or a modification peculiar to the circumstances of the experiment in hand. Great care must be taken to avoid breathing it, as its effect upon the lungs, even when much diluted with air, is very distressing; should such an accident occur, most rapid relief is obtained by inhaling the vapour of hot water, the face being placed upon a jug so as to permit of the steam being easily breathed: a very little ammonia added to the water greatly increases its efficacy. Another reason for preventing its escape into the laboratory, is the great injury done by it to all metallic instruments. Where a continued stream of the gas is required to be passed for hours through a solution, as in Rose's excellent process for separating nickel and cobalt, the exit of the gas must be into a chimney, or some other place where no inconvenience can arise from it.

If an exceedingly large quantity of gas is to be passed for hours through or over a substance, as in acting on large quantities of naphthaline in Laurent's process for preparing the bichloride, or in making considerable quantities of pentachloride of phosphorus, &c., the oxide of manganese in very fine powder should be placed in a six-gallon stone bottle, provided with a cork, through which two tubes pass. One of these is merely for the exit of the gas, the other is a safety-funnel, by which the

hydrochloric acid is to be added. The stone bottle is to be placed in a water-bath, all the joints of the tubes being made with rather long pieces of vulcanized tubing, in order that the various parts of the apparatus may be susceptible of considerable movement without deranging the rest. The chlorine first passes into an empty bottle kept cold in order to allow the greater part of the moisture to deposit, and then two flasks of concentrated sulphuric acid, one after the other, to ensure perfect dryness. The gas then, by means of a tolerably wide tube, enters the flask in which the naphthaline, phosphorus, or other matter is contained, care being taken that if at any stage of the operation the substance acted on thickens under the influence of the gas, the tube by which it enters does not quite touch the matter acted on. Another tube from the flask is allowed to pass out of the window, to get rid of the excess of chlorine and other gases and vapours generally evolved under such circum- stances. If it is suspected that volatile products of decompo- sition are evolved, as not unfrequently happens in operations of this class, the gases before passing out of the window may be made to traverse a bulbed tube immersed in a good freezing mixture. This will generally be found to retain any products that may be formed. The method above described must of course be modified to meet the varying circumstances of the experiment.

485. *Sulphurous acid.*—Where a considerable quantity is required, the iron pot with the tube screwed on, fig. 198, is perhaps the most convenient apparatus. In this case it is evolved from a mixture of bruised charcoal and concentrated sulphuric acid. The pasty mass is gently heated, the gas being copiously evolved. The mixture is almost without action upon iron. It is also sometimes procured by the action of sulphuric acid upon mercury or copper, but this process is only adopted upon the small scale, where a pure product is required. As a very effective condensation is necessary, where the gas is to be condensed by itself, the methods of effecting condensation described in §§ 352 and 383, may be employed. It is proper

to have the exit-pipe immersed a short distance under the sur-
face of mercury, so as to assist the condensation by slight pressure.
The product must be kept either in thin stoppered flasks, which
are to be retained at as low a temperature as possible, or, which
is preferable, sealed tubes. It is seldom used in this condition,
except, perhaps, for demonstrating the spheroidal state of water,
by the conversion of it into ice in a red-hot crucible, as in
Boutigny's remarkable experiment. Sulphurous acid very much
diluted, as prepared by passing the gas produced by the mutual
action of charcoal and sulphuric acid into water, is used to re-
duce arsenic acid to arsenious acid, previous to precipitating the
fluid by a stream of sulphuretted hydrogen.

486. On the large scale, sulphite of soda is prepared by pass-
ing the gas, produced as last mentioned, into a strong solution of
carbonate of soda. The sulphite of soda, thus prepared, is one of
the ingredients used in making hyposulphite of soda according
to Berzelius's method. A strong solution of sulphide of sodium,
procured by boiling caustic soda with excess of flowers of sulphur,
has the sulphite of soda added to it until the dark colour of the
sulphide disappears; a little more of the latter is then added,
until the fluid assumes a pale but distinct straw tint. On eva-
poration, crystals of hyposulphite of soda, slightly yellow, are
obtained, which by recrystallization may be procured colourless
and very pure. The bisulphites of soda and ammonia are inva-
luable in organic research, from the powerful tendency which
they evince to combine with the aldehydes, and some other
bodies.

487. *Cyanogen.*—This gas has lately been used with great
success as a reagent, more especially by Hofmann, in his ex-
tremely beautiful researches on aniline, an investigation which,
from the completeness with which all the analogies which the
base alluded to presents with ammonia, have been followed out,
has probably never been surpassed.

The gas is evolved in a test-tube by the action of heat upon
cyanide of mercury, and is conveyed into another, where any
aqueous or mercurial vapour is condensed, the pure gas passing

into a third, where it exerts its action upon the fluid submitted
to it. For details connected with the action of cyanogen and
the chloride of that radical upon organic bases, the reader is
referred to the original papers of Hofmann in the Quarterly
Journal of the Chemical Society of London.

488. *Nitrous acid.*—The action of this gas upon oils and other
matters has been studied of late to a sufficient extent to make its
mention here not improper. If nitric acid moderately diluted
is placed in a flask with a bent tube to convey the produced gas
into the solution to be acted on, and a few pieces of starch are
added, and the whole is gently warmed, a mixture of nitrous
and hyponitric acids is given off with extreme regularity; and
by removing the flask from the source of heat, may be passed
through the oil or other matter to be examined in a slow steady
stream, excellently adapted for producing the intended effect.

489. *Muriatic acid gas.*—When it is desired to submit any
fluid to the action of muriatic acid, as in the preparation of the
ethers, the production of the muriate of camphene, &c., several
ways may be adopted. The gas may be procured by merely
heating hydrochloric acid, and passing the evolved gas first through
sulphuric acid and then into the fluid, or by adding concentrated
sulphuric gently through a safety-tube into strong muriatic acid,
in a flask provided with a bent tube, to convey the gas to the
place where it is to exert its action: or the action of sulphuric
acid upon common salt may be resorted to as being the more eco-
nomical method of procedure. In most cases, no matter in what
way the gas is procured, the matter to be acted on should be kept
very cold, to prevent the vapour from escaping before it has had
time to produce the desired reaction.

490. There are other gases often required in the laboratory for
purposes either of demonstration or research, but the methods of
manipulation in the following pages will be found amply sufficient
to indicate the mode of procedure to be adopted, and the apparatus
to be made use of.

491. *Collection and retention of gas.*—The way in which che-
mists at the present day collect elastic fluids is pretty much the

same as it was in the time of Priestley, the differences being only in the arrangement of the apparatus, not in the principle.

The method depends upon the displacement of water or mercury by the gas as it is evolved from any of the instruments either to be alluded to or those already given. If a bottle be immersed in a vessel of water, so that it becomes filled, and it is then raised, bottom upwards, out of the liquid, the latter will not escape so long as the mouth of the vessel is under the water ; the same thing happens with mercury. The older chemists were in the habit of suspending the jars to be filled with gas by means of strings, in the pneumatic trough as it is termed, but the method shown in fig. 224 is that now generally adopted.

It will be seen that two jars stand upon the shelves of the

Fig. 224.
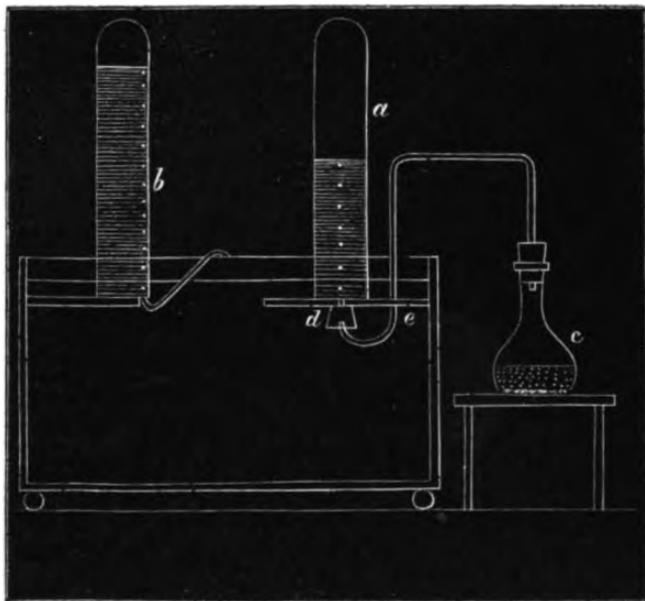
trough, in both of which the water has been partially displaced, that in *a* by the gas evolved from the flask, *c*, the tube of which passes through a slit cut in the shelf at *e*.

492. When an inverted jar of water has the end of a pipe delivering gas passed under it, the water is displaced, descending into the trough, the level of the fluid in which of course rises, the gas supplying the place in the jar. At *d* is a small funnel placed immediately beneath the aperture in the shelf, by which the gas ascends. Sometimes, instead of this arrangement, the jars are so placed upon a plain shelf that they project over it sufficiently to allow of the delivery-tube being placed under it, as at *b*, in the figure. Another method is to have notches cut in the shelf to permit the tube to pass under the jar without any danger of the latter falling, as may take place where they are allowed to project over the shelf. But by far the most convenient and portable method is that seen in fig. 225, where what is termed a bee-hive shelf is used. The last-named piece of apparatus consists of a vessel shaped like a bee-hive, only flat at the top, so as to support a gas-jar. An aperture in the side permits the passage of a delivery-tube. The use of this little contrivance (the invention, it is believed, of Mr. J. J. Griffin) almost dispenses

Fig. 225.
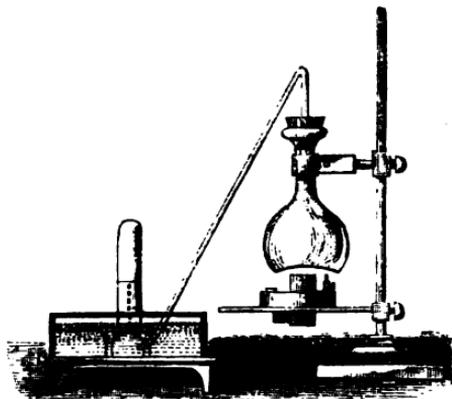
with the use of the cumbrous pneumatic trough, any basin or water-tight box answering the purpose. The water should be poured in until it covers the shelf for about an inch, when the jar, full of water and inverted, may be placed upon it, and supported, if necessary, by a ring of the retort-stand, or by Galin's cylinder-holder, described at p. 161.

493. Pneumatic troughs of large size adapted for class illustration and lecturing, are frequently made of japanned tinned-iron or wood. Their construction and use will be obvious from what

has already been said.   Where it is necessary to fill several jars
with gas one after another, they may all be arranged in a row
upon the shelf of the large trough, and the delivery-tube may be
brought in succession under each until it has become full of the
gas.   In this latter case, however, as the quantity of water dis-
placed gradually accumulates, the trough soon becomes filled with
water to an inconvenient height, and may easily overflow.   The
undue rise of water is to be carefully avoided, because the jars,
when full of gas, are easily upset as the water rises, their buoy-
ancy being considerable.   It is best to have a siphon, with its
longer leg closed with a cork or tap, hanging over the side of the
trough, so that any quantity of water required may be drawn off.
Where very small troughs, such as that seen in use with the bee-
hive shelf in fig. 225, are employed, it is of course impossible to
fill the gas-jars by immersion in the troughs, and then inverting
them ; in this case one of two methods may be employed, de-
pending upon the calibre of the jars.   If they are long and narrow,
as in figs. 226 and 232, they should be ground at the opening, and
then, being inverted, may be filled up with water, and a ground-
glass plate being placed over the aperture, they may be restored to
their proper position as used in the trough, and the mouth being
placed under water, the glass plate may be removed, and the jar
put in its place on the shelf.   Where, on the other hand, the jars
are too large to be closed with a plate, they must be filled with
water at a cistern or some other convenient vessel ; and a small tin-
tray or an evaporating-basin, or even, if nothing else be at hand, a
saucer or small cheese-plate, should be slipped under the jar be-
neath the surface of the water, where the small quantity of fluid
in the plate will be quite sufficient to retain the water in the jar
on lifting it out.   In the same manner a jar full of gas may be
taken from the trough and put aside until wanted.

494. The jars used at the pneumatic trough vary in size and
capacity according to the purposes for which they may be required.

Fig. 226 shows a form of gas-jar of very frequent use in the
laboratory in various researches, especially at the mercurial trough.
It is made very thick in the glass, to enable it to bear the great

weight of the metal; it is also ground at the bottom, to facilitate the removal of the jar and contents by closing it with a glass plate, in the manner described further on.

Fig. 227 is chiefly used in experiments involving the transference of a gas to a globe or bladder, by the method the details of which will be found further on.

Fig. 228 represents a form of jar much used in demonstrative

Fig. 226.　Fig. 227.
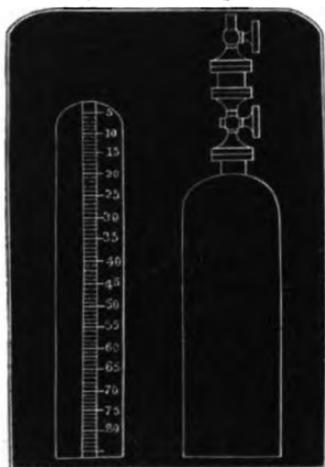
Fig. 228.
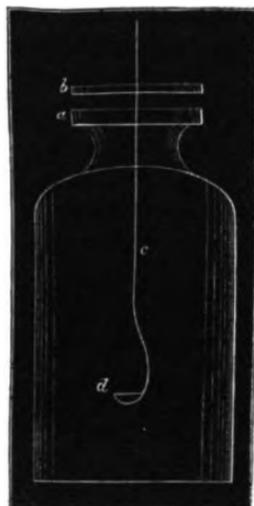
experiments; it consists of a wide-mouthed bottle open above and below, the outside of the neck being ground smooth at *a*, to admit of its being accurately closed by a glass plate, or by the air-tight collar, *b*, through which passes a wire, having a small spoon, *d*, at the lower end.　To use this jar for deflagrations, as, for example, to show the combustion of sulphur in oxygen, the mouth is closed with a glass plate, slightly greased to ensure complete adhesion, and the bottle being filled with water, is to be inverted in the pneumatic trough, and the gas passed in until full.　When this is the case, the collar and wire being at hand, the matter to be burnt is placed in the spoon and ignited, and the plate of

glass being quickly removed, the spoon, with its lighted charge, is to be quickly and steadily inserted, the collar, *b*, resting on *a*.

Fig. 229 is a form of jar equally adapted to lecture experiments, and, when graduated, to researches. It is, however, not used where ignitions are to be performed in gases, except for the combustion of antimony or copper in chlorine, where the gas is inserted by displacement instead of over the water-trough, as described at p. 302, and in this case the round top is very inconvenient, and the jar seen in fig. 231 is almost always substituted. Fig. 230 is used in lecture experiments, to show the combustion of phosphorus in air or oxygen gas. In using this apparatus, the globe previously filled at the trough with gas, where oxygen is used, is, after the phosphorus has been ignited, steadily placed over the deflagrating spoon, *a*, supported on the stand, *b*. Figs. 231 and 232 show two forms of plain gas-jars much used in experiments at the lecture-table; the first is well adapted for showing the effect of oxygen upon the gas produced by the action

Fig. 229.

Fig. 230.
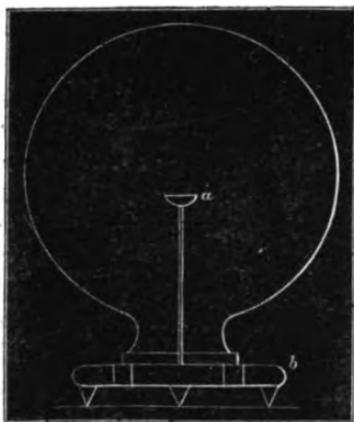
Fig. 231.

of nitric acid upon copper, the binoxide of nitrogen being converted

Fig. 232.

into the red fumes of hyponitric acid. It is equally
well adapted, from its flat top, for experiments with
chlorine, carbonic acid, &c., where it is filled by dis-
placing the air with the heavy gas. The tall tube,
fig. 232, is useful for showing the decomposition of
water by sodium. The vessel, the mouth of which is
ground, so as to enable it to be closed with a glass plate,
is filled with water, by pouring the latter in from a
jug; the plate being then placed over the mouth, it
is inverted in the pneumatic trough, and the plate is
removed. If, now, a pellet of sodium is wrapped in
paper and dexterously inserted under the edge, it
ascends to the top, and as soon as the fluid has pene-
trated the paper, the decomposition of the water takes
place, with evolution of hydrogen gas, the liquid be-
coming of course depressed; if, now, the plate is
placed under the jar, and the latter being raised
mouth upwards, the plate is removed, a light being
at the same time brought close to the aperture, the
inflammability of the gas will be shown. It is better
in this experiment not to use sufficient sodium to
expel all the water, as a little oxygen, or even atmo-
spheric air, may be introduced, and, on the approach
of the light, an explosion will take place, the experi-
ment thus becoming more perceptible to those at
some distance from the lecture-table. The reason that sodium is
used, is because it is more manageable than potassium, from being
not quite so rapidly oxidized by water, so that less heat being
developed, there is little danger of fracturing the jar. The jar,
fig. 227, has a cap cemented to it to allow of stopcocks or other
pieces of apparatus being attached, to enable the gas to be trans-
ferred to bladders or other receptacles. A convenient form of
cap is that given in fig. 233, where it appears attached to the
neck of a glass balloon; the female screw allows of the stopcock
of the bladder or gas-bag being attached or removed. To ascer-
tain the tightness of a gas-jar with the stopcocks and cap attached,

it is to be placed upon the shelf of the pneumatic trough, and, applying the mouth to the opening, air is to be drawn out so as to cause the water to stand several inches inside the jar, above the level of that in the trough. The stopcock is now to be turned off, and the height of the water is to be marked with a piece of gum-

Fig. 233.

med paper. If at the end of an hour or so the water has not fallen, the cap and its adjuncts are perfect.
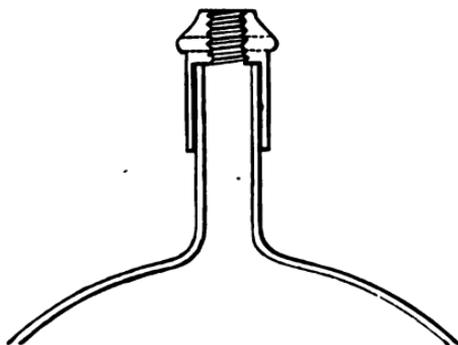
495. Heavy gases, such as chlorine and carbonic acid, are frequently collected very conveniently by the method of displacement, the arrangement of the apparatus being evident from fig. 234,

Fig. 234.
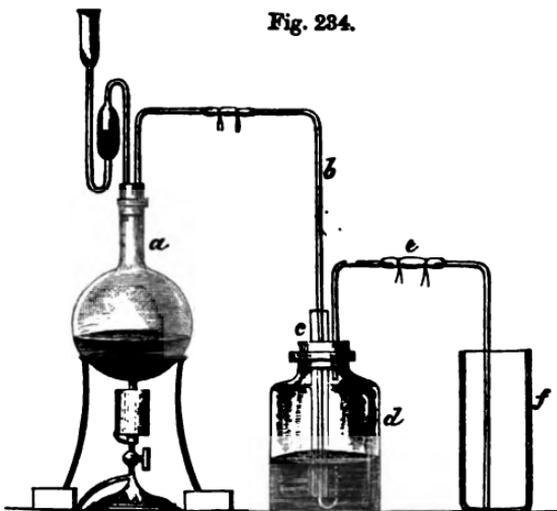
where *a* represents a flask in which the gas is prepared, which

passes through *b*, down the large tube *c*, into the washing-bottle, *d*. The washed gas passes from *d*, through the tube *e*, to the bottom of the cylinder, *f*, which is the same as figure 231 inverted. The heavy gas gradually accumulates in *f*, rising higher and higher until the atmospheric air is expelled; when this is the case, the mouth is covered with a glass plate ground to fit it, and the vessel is ready for the lecture-table. In the case of chlorine, it is easy to know when the cylinder is full from the colour of the gas, but with carbonic acid it is proper to continue the stream until an ignited splinter held close to the side at *f* is extinguished by the gas, which, having filled the vessel, flows over the sides owing to its high density, and then extinguishes a burning body as effectually as water.

496. Ammonia may be conveniently obtained in jars for the lecture-table by an inversion of the latter process as shown in fig. 235, where the ammoniacal gas libe-rated from the flask, *a*, is carried by the bent tube, *b*, to the top of the cylinder, *c*, until a piece of turmeric paper is turned red the instant it is held near the mouth of the cylinder, as at *d*.

Fig. 235.

497. Where very small quantities of gases are being examined as to their solubility or any other physical or chemi-cal character, it is sometimes convenient to dispense with the pneumatic trough altogether, and several contrivances have been adopted to meet this require-ment. One of these, Kerr's tube-receiver, fig. 236, although less used than it deserves to be, will be described from its great convenience in many experiments of research where the quantities are very limited. It consists of a V-tube, so constructed that the lowest part, *b*, is not exactly in the centre, but rather towards
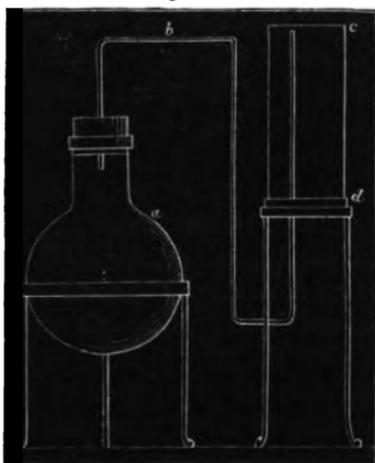
the side, c, so that if the apparatus be filled with the acid to d, and a fragment of carbonate of lime, for example, be dropped in, it will occupy the position seen in the figure, and the bubbles of gas will ascend in the limb, b c. If it is desired to replace the acid by water in order to examine the behaviour of the gas towards reagents, it may easily be effected by plunging the apparatus into
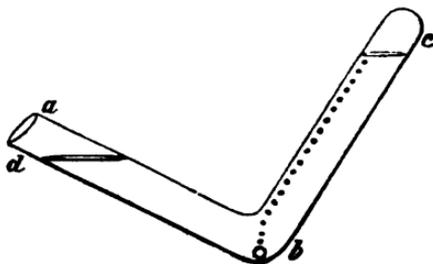
Fig. 236.

water, keeping the end, c, uppermost, when the acid will flow out and its place be occupied by the water. The tube being filled with water, except that portion of b c occupied by gas, it is easy, by closing the end, a, with the thumb and depressing c, to obtain any quantity between the thumb and the surface of the water in the limb, b a, so as to try the effect of flame, &c. upon it. The method of performing these experiments will, however, be made more evident by consulting the description of Cooper's mercurial receiver.

498. In most instances where a gas is to be collected for experiments to be made upon it, it is essential to allow all the air contained in the delivery-tubes, and in that portion of the generating flask above the materials, to be expelled before collecting the remainder; where this precaution is necessary, it is improper to allow the gas and air to stream from the end of the delivery-tube into the apartment, even in cases where no immediate inconvenience would result from such a procedure, because by this means it is impossible to ascertain with accuracy the point at which it is necessary to stop; but if, on the other hand, the first portions which come over are received at the pneumatic or mercurial trough in small tubes, it is easy to ascertain by appropriate tests when the air is sufficiently expelled to make it proper to receive the remainder in the regular manner. On other occasions, however, as, for example, in one of the older and least-used

methods of determining nitrogen, the whole of the gas is received from the commencement.

499. *Solution of gases.*—Where gases are to be dissolved in fluids, the simplest method of proceeding consists in passing the former into the latter contained in a test-glass; the manipulation necessary in a case of this kind having already been described, will not be repeated. But if, on the other hand, the gas is extremely soluble in the absorptive media employed, there is considerable tendency in the fluid to rush back into the generating bottle. As the ordinary routine of laboratory-work presents numerous examples of this kind, and as it is very necessary for the student to be familiar with all the precautions requisite to ensure freedom from accident, the operation will be described somewhat minutely. If, for example, it is desired to obtain a saturated solution of ammonia in water, by the reaction of slacked lime and chloride of ammonium, the materials are mixed in the flask, to which is

Fig. 237.
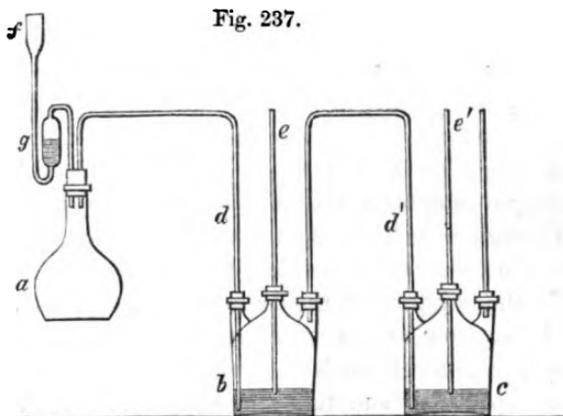
fitted a perforated cork; a tube passes from this into a little water contained in the first bottle, *b*, intended to wash the gas and retain any impurities mechanically carried over; from this another tube proceeds into *c*, which contains the water to be saturated, and thence, if necessary, into one or two more bottles. The

delivery-tubes proceed to the bottom of the water, and it is to be observed that when contraction takes place in a or b, which frequently happens, there is a tendency in the fluid to rush up the tubes, $d\,d'$, the fluid in c going back into b, and that in the latter into the flask, a; but this is prevented by the safety tubes, $e\,e'$ and f; the two former dip only just below the surface of the water in the bottles, and therefore when contraction takes place, air enters by them and restores the equilibrium of pressure. But as there is no fluid in the flask for a tube to dip into, the Welter's tube, f, is used, a little water, or sometimes mercury occupying the bend. As mercury is nearly fourteen times denser than water, it is necessary that the delivery-tube, d, should be fourteen times longer than the distance that exists from the bottom of the curve in f to the surface, g, of the metal in the tube and arm of the safety-tube: if this is so managed, air will preferably enter by bubbling up through the mercury, than by forcing the column of water from b through d into a*.

500. If, on the other hand, alcohol is to be saturated with ammoniacal gas, liquor ammoniæ may be gently heated in a retort, in contact with fragments of quartz, to facilitate escape of the gas, which, after passing through a U-tube filled with fragments of quicklime, may be passed into alcohol kept cold by immersing the flask containing it in water or otherwise. In this case it is unnecessary to employ a Welter's tube, because, if a glass tube passes through a cork in the tubulature of the retort and just dips into the fluid, air will enter by it, if any contraction takes place, and thereby prevent the recession of the alcohol.

501. It has been said in the section on Distillation, that it is often required to add a portion of fluid to the contents of a retort during an operation, and this may be effected easily by a tube often used in experiments with gases. It also acts as a safety-tube. It is seen at several places in this volume, among others in fig. 237. When the fluid poured in at f rises above the bend of the tube over the bulb, it begins to flow over into the retort,

* A very simple method of constructing a Welter's safety-tube will be found in the section on Glass-working.

and thus any desired quantity may be added, and if contraction occurs, air enters through the liquid into the retort. The length of the column of fluid in the limb, *f*, must be sufficient to prevent any outward pressure from ejecting it and thus allowing escape of gas.

502. A very neat safety-tube, which is especially convenient in cases where the retort has no tubulature, is seen in fig. 238.

Fig. 238.
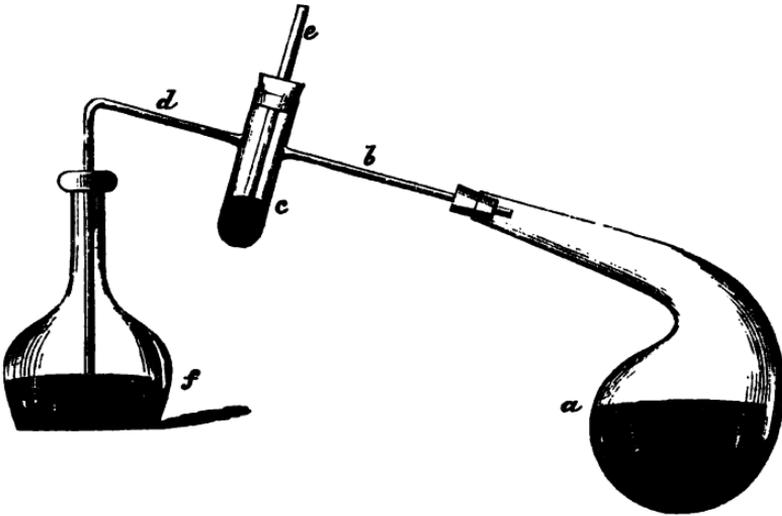
Muriatic acid gas is formed in *a* by the reaction of salt and sulphuric acid; the gas passes through *b* into a tube containing a little mercury, and thence through *d* into water contained in the bottle, *f*. The tube, *c*, is closed with a cork, through which passes a tube, *e*, dipping a short distance (about ½ an inch) into the metal. On contraction taking place in *a*, air enters by *e* through the mercury and prevents the regurgitation of the acid in *f*. Another, but more expensive safety-tube, equally adapted with the last described to retorts which have no tubulature, is seen in fig. 239. One very important use of these safety-tubes is, that in the event of the exit of the apparatus becoming choked, the

retort is saved from bursting by the gas escaping in the direction
of the arrows.

503. Two more
forms of safety-
tubes are seen in
figs. 240 and 241.
The former is con-
structed with glass
valves, one of which
opens inwards and
the other out-
wards; they re-
quire, however, to
be finished with
extreme care to
answer the in-
tended purpose,
and are certainly
not more conve-
nient than the
common form. The
other is intended,

Fig. 239.

Fig. 240.

in the event of sudden condensation taking place in the retort,
to prevent the fluid from finding its way in, and thus by mixing
with the contents, spoil the result. It also has other and better
uses, which will be seen by inspecting d, fig. 100.

504. A very convenient method of obtaining the most intimate
contact of a gas with a fluid on which it is to exert a reaction,
especially where the gas is valuable or the quantity at the opera-
tor's disposal is small, consists in passing it through the fluid
contained in a potash-tube, as in fig. 242. The apparatus should
be inclined by means of a cork, as is described in the chapter on
the manipulation connected with organic analysis. This is par-
ticularly useful in experiments on the action of heat upon some
organic bodies. On exposing the hydrochlorate of camphene to a
high temperature in contact with lime, by passing it over frag-

ments of the latter in a long glass tube, both fluid and gaseous products are evolved. As they pass from the tube into a Woulfe's bottle protected by a screen of tin plate from the heat, and also immersed in cold water, the greater portion of the products obtained are condensed, only a few drops of an excessively volatile fluid being found in the U-tube cooled by a powerful freezing mixture, but a very considerable quantity of the gas is retained in the potash-tube filled with alcohol.
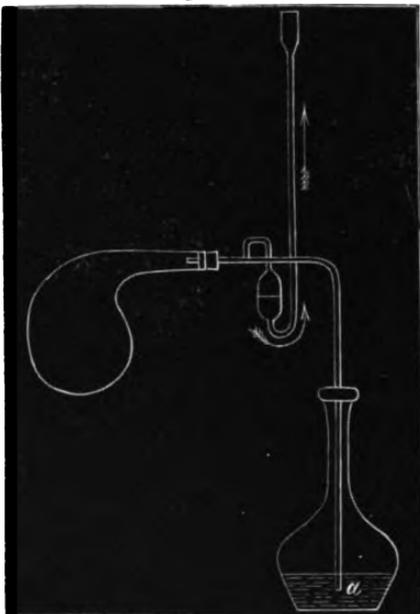
A similar method of condensing easily dissipated products should be adopted in submitting volatile acids to the action of the pile. Kolbe found that valyl (butyl) vapour was carried away with the gas formed by the electrolysis of valerianic acid, and I observed in electrolysing butyric acid the same to happen to a still greater extent in consequence of the superior volatility of propyl.

505. *The Gasometer.*—This is an indispensable piece of apparatus in all laboratories of research; and in consequence of the very general adoption of Hofmann's method of performing organic analysis, finds its way into places where otherwise its presence would not be required.

Fig. 241.

506. The gasometer, as modified for the last-named purpose, will be described in its place, under the head of Manipulation connected with Organic Analysis. The method of using the ordinary gasometer will be evident from the following description of fig. 243. The vessel, *a, b, c, d,* is a cylinder of copper or zinc, made air-tight, and surmounted by another much shorter one, *h, i, k, l.* These two are connected with each other by the tubes *e* and *f,* which also perform the office of supports

for the upper cylinder. The tube, *e*, descends to the bottom of the lower cylinder, and serves to allow the water in *h, i, k, l* to

Fig. 242.
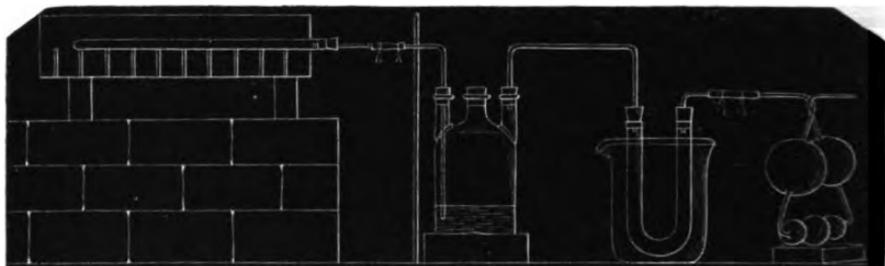
descend to displace the gas which escapes by the cock, *b*, to the place where it is desired to be sent. The tube, *f*, on the other

Fig. 243.
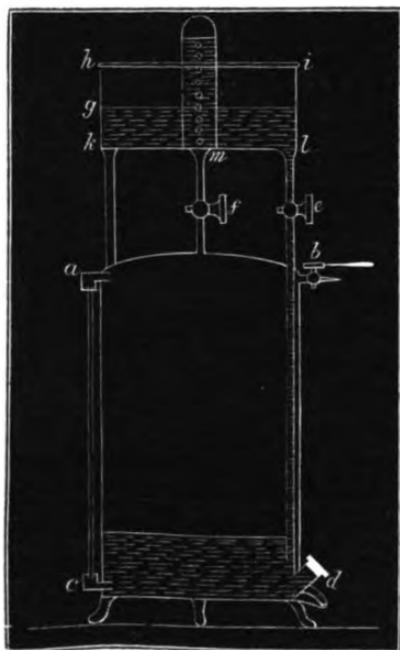
Fig. 244.

hand, only connects the upper with the lower cylinder, and does not descend into the latter ; it is used to supply gas-jars, which for

this purpose are filled with water at a cistern or other convenient place, conveyed to the water-tank, *h*, *i*, *k*, *l*, and placed immediately over the aperture, *m*. The glass tube, *a*, *c*, is used as a gauge to indicate the amount of gas, and for this purpose opens into the lower cylinder at the top and bottom, where it is fastened in with cement. In the figure, it is represented as standing out from the gas-holder; in general, however, it is better to have it sunk in, so as to incur less danger of fracture. The pipe with a cap, seen at *d*, is intended to introduce the gas from the apparatus where it is generated, and will be described further on.

To illustrate the method of using the instrument, let it be supposed that all the cocks are closed, and that the upper cylinder is half-filled with water. If, now, the tap, *e*, is turned so as to open a communication between the two, water will, it is true, descend for a short time; but *b* and *f* being closed, so that the air cannot escape, no result takes place, with the exception of a slight condensation, proportional to the height of the column of water. If, now, *f* is turned so as to open a passage between the vessels, bubbles of air will rise into the bell-jar placed to receive them. If *f* is shut off and *b* opened, the air will escape by the latter, and may by suitable connexions be carried to any desired spot. In some gasometers the part represented at *b* is of a somewhat more complex structure than appears by fig. 243. This part is seen in plan in fig. 244, as observed on looking downwards. The circle indicates the body of the gas-holder shown at *a*, *b*, *c*, *d*, in the previous engraving. In fig. 244, *a*, *b* represents a brass tube, connected by a rectangular bend, at *a*, with the body of the gasometer, and capable of being opened or closed against the passage of the gas by the stopcock, *c*. This latter has a lever, *f*, 7 or 8 inches long, attached to it, which moves over a small divided segment of a circle, *g*, enabling the operator not only to make smaller movements of the handle than could be done without it, but also to place it in exactly the same positions on several occasions, which would be impossible without some guide of this kind. It must be remembered, however, that the flow of gas will not always be of equal rapidity when

the handle is in the same position on the scale, unless the pres-
sure in the chamber, a, b, c, d (fig. 243), is the same.   The cross
piece, fig. 244, e, parallel to c, is merely a support to assist in
keeping the tube, a, b, immoveable.   The aperture, b, which is
capable of being closed with a stopcock, h, is intended to enable
another gasometer, containing a different gas, to be connected
with the first when necessary.   The pipe, d, is the outlet for
the gas, and is the part to which a flexible tube is generally
attached, to direct the gas to its destination.   The direction of
the current is shown by arrows.

507. Fig. 245 is an enlarged view of d in fig. 243.   It con-
sists of a short wide tube, soldered into the side of the gaso-

Fig. 245.
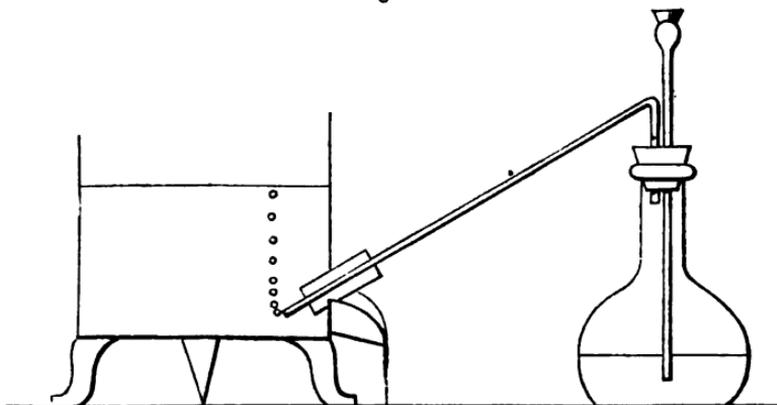
meter, and so arranged that the lowest portion of the outer rim
is higher than the highest portion of the inner rim.   The tube
is seen delivering gas into the gasometer, which has been filled
with water by means of the upper cistern, until it escaped by b,
fig. 243, the cap, d, being previously screwed on.   The taps, f
and e, being then closed, the cap, d, may be removed, and the
gas-delivering tube inserted, when the water will escape by d
as the vessel becomes filled with gas.   When it is seen by the
gauge that the lower chamber is filled with gas, or bubbles of
the latter escape by d, fig. 243, the delivery-tube is withdrawn,

and the cap, *d*, screwed in its place : the further manipulations will be evident from what has been already said.

508. The operator, by the exercise of a little ingenuity, will easily be able to form a gas-holder out of a tin oil-can or even a glass carboy, for purposes which do not require any great amount of accuracy in workmanship.

In order to ascertain the tightness of the joints in the gasometer described, it is merely necessary to close the lower aperture, and pour water into the upper cylinder, at the same time opening *f, e* and *b*, and continuing the addition of water until, the gasometer being full, the water escapes at *b* ; the cocks are then to be closed, and the cap, *d*, being removed, the apparatus is allowed to stand for some time, when if no leaks exist, the water will not escape ; but if, on the contrary, the gauge indicates the descent of the water, some deficiency will be found either in the stopcocks or seams, which must be made good before using the apparatus.

509. Where a very considerable pressure has to be met by the gas, as, for instance, in cases in which the delivery-tube dips deeply into mercury, the column of water in the gasometer may not be sufficient to overcome the resistance ; to do away with this difficulty is easy: it is sufficient to fasten a long pipe with a funnel at the top, into the aperture at *l*, fig. 243, through which the water is to be introduced, and by increasing the length according to the amount of resistance, the gas may be conveyed into any required position.

510. The gas, as thus obtained, is saturated with moisture, and therefore in an unfit state to be used in some experiments. When it is suspected that the presence of water might prove injurious, it may be removed by passing the gas through a washing-bottle, or a Liebig's potash apparatus filled with sulphuric acid, or through a U-tube filled with fragments of pumice-stone moistened with sulphuric acid.

511. A very elegant, and at the same time convenient gasometer, particularly adapted for use in organic analysis, where it is desired to complete the combustion with a current of oxygen, is seen in fig. 246. It is constructed out of a large Woulfe's bottle, through the middle tubulature of which passes a tube to

P

which a stopcock, surmounted by a funnel, is cemented; this is intended to regulate the flow of the water which expels the gas. Another tubulature permits the passage of two tubes, one of which

Fig. 246.
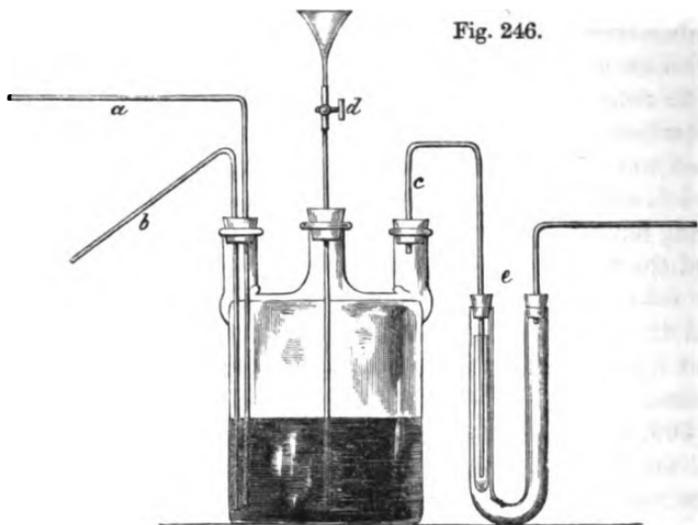
passes to the bottom of the bottle and serves to admit the gas, the other, *b*, allows of the exit of the water as the oxygen enters. The gas as it escapes by *c*, on opening the stopcock, *d*, is dried by passing through the U-tube, *e*, in which is placed a small tube to retain water carried over mechanically, in order to prevent the too rapid moistening of the chloride of calcium contained in the other limb; it is necessary, when used in organic analyses, to pass the gas through a bottle containing sulphuric acid, so as to partially desiccate it before entering the chloride-of-calcium-tube, and also to allow of the rapidity of the flow of gas being made evident to the eye.   In ordinary operations this may be dispensed with.

512. *Transference of gases at the pneumatic trough.*—To transfer a gas from one jar to another at the water-trough is an operation of ease or difficulty, according to the relative shapes and sizes of the vessels used.   If it is merely required to transfer

from a plain to a graduated jar for the purpose of measurement,
or to instance an equally common case, where it is required to
add a certain quantity of one gas to a portion of another kind
standing in a jar over water, and if the jars are tolerably large,
it is necessary to advance that which is to receive the contents of
the other about half its diameter over the shelf with the left-hand,
while that which is to be *poured upwards* into it is to be steadily
depressed with the right hand until its mouth is a short distance
below the edge of the other.   The jar in the right hand is then
to be inclined in such a manner that it shall lean with its top
away from the other, while the upper edge of its lower extremity
projects a short distance under the bottom of that which is sup-
ported by the left hand.   The decanting jar is then to have its
highest portion steadily and slowly lowered, in such a manner
that the contents flow upwards into the other in bubbles not too
large, as in the latter case it is difficult to prevent them from
escaping.   It happens, somewhat unfortunately, that small tubes,
which in experimental research are constantly used, are ra-
ther troublesome to transfer in this manner, as the ascending
bubbles interfere with the descent of the water at the same time.
This difficulty may be obviated by the use of funnels to direct the
ascending gas, or by having the decanting tubes made with a lip.
Or where it is merely desired to make gaseous mixtures of only
approximative accuracy, as in lecture experiments, one of the
lipped measures holding 3 or 4 ounces may be used.

513. Instances of transference of gases from the apparatus in
which they were generated to the places where their action is to
be exerted, have already been given.

514. When a gas standing over water is to be made to enter
a bladder or gas-bag, a jar provided with a cap and stopcock must
be used; a bladder is to be selected, closed with a brass piece in
which a stopcock is inserted, capable of being joined to that in
the gas-jar by means of the connectors described further on.
Before allowing the gas to pass from the jar to the bladder, the
latter must be moistened, and so squeezed that all the air is ex-
pelled; it should then have the connecting piece joined to it, and

P 2

the latter to the stopcock on the air-jar; the tap is now to be turned in such a manner as to open communication between the two; and the bell-jar being steadily and slowly depressed, the gas will be forced into the bladder; the taps may then be turned off, and the bladder, with its contents, be removed.

In all cases where a gas standing over water or mercury is to be made to enter a globe or bladder, care must be taken to stop the depression of the jar in time to prevent the fluid from being forced into the bladder.

To fill a jar, fitted with a stopcock, with water at the pneumatic trough, it is merely necessary to open the stopcock and depress the jar, exactly as in the last process, until all the air is expelled, and the water just reaches the brass-work of the cap, but no further; the tap is then to be turned off, and the jar raised full of water and placed on the shelf of the trough, ready to receive the gas from the delivery-tube.

515. *Manipulation with gases over mercury.*—The chief difference in the modes of operating with jars at the mercurial and pneumatic trough, is caused by the great weight of the mercury. If a jar of moderate size, say holding 200 cubic centimetres, be filled with water from a jug or other convenient vessel, and its mouth is then covered with a glass plate, nothing can be easier than to invert the jar in the trough, and, by removing the plate, to leave the jar in a fit condition to receive the gas. But if mercury be used, the inexperienced operator will find that great care is required to keep the glass plate so tightly in its place as to prevent some of the metal escaping at the moment of inversion.

516. The operation may, however, be easily managed after a little practice, and taking care to press firmly with the two first fingers of the left hand upon the plate, while the right hand assists in raising up the other end of the jar. It must not be forgotten, that, from the great weight of the metal, a very slight blow will be sufficient to cause a fracture to a jar filled with it, and therefore it is necessary to have mercurial jars made stouter than those used at the water-trough. Whenever a jar has been filled with mercury, it is necessary to insert a glass rod, and with

it to bring to the surface any air-bubbles which may be seen be-
tween the metal and the glass, as they are liable to cause con-
siderable errors in delicate experiments if allowed to remain.

517. The expense of mercury being considerable when required
in large quantities, mercurial troughs are generally made as small
as possible, and it is necessary therefore, in almost all cases, to
fill the jar from some convenient vessel, and to transfer it to the
trough. Stoneware mercurial troughs are in common use, and,
if carefully used, very convenient; but it must not be forgot-
ten that their hardness somewhat endangers the safety of any
jars that may be allowed to strike the side with even a slight
blow. The kind of porcelain trough in most common use is repre-
sented in figs. 247 and 248, where the first shows a plan, and the

Fig. 247.
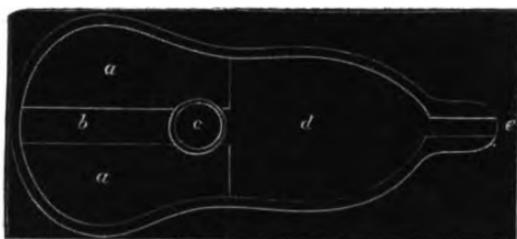
second, fig. 248, a section of it, with the position occupied by a
jar. In fig. 247, *a a* represent two projections, one on each side
of the interior of the trough, which serve to support the tube, *c.*
The hollow space between these two solid portions shown at *b,*
is intended to admit the delivery-tube; *d* shows the body of the
trough, and *e,* a spout by which the mercury may be poured off
when the instrument is done with. As the same letters refer to
the same portions of fig. 248, no further description is necessary.

518. Mr. Griffin has constructed a stoneware trough for minute
experiments, capable of being worked with only four pounds of
mercury, and yet allowing tubes 6 inches in length, and nearly
1 inch in diameter, to be inverted, when full, with safety. It is
seen in plan and section in figs. 249 and 250. The part at *a* is
on the principle of the bee-hive shelf, which latter is a contri-

vance of the same person.　Between b and c there is a cavity

Fig. 248.
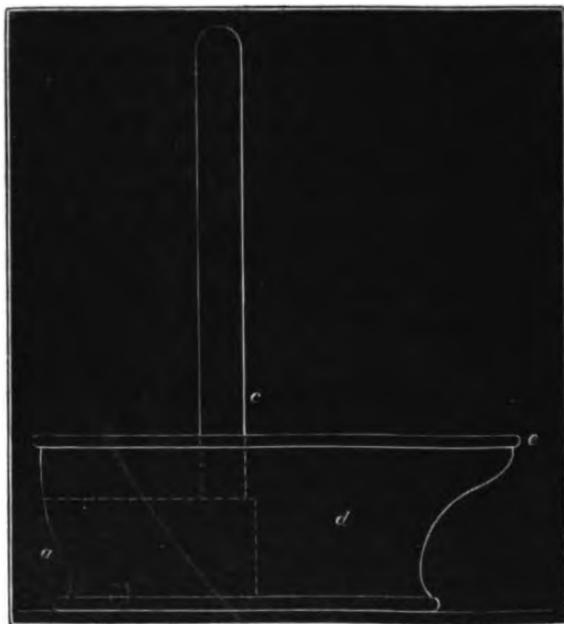
capable of admitting a glass tube 2 inches long by $\frac{1}{2}$ an inch wide, to enable caustic potash or any other substance required to

Fig. 249.
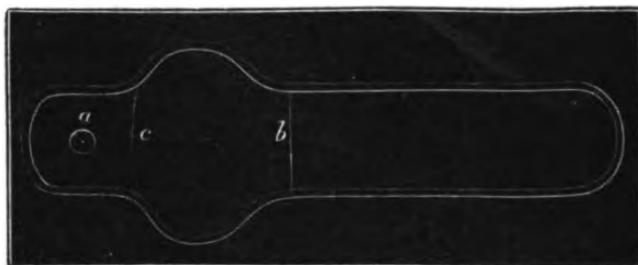
be passed into the gas-jar.　There are also two recesses, to enable the thumb and finger to enter the trough, to manage the tube used to introduce the reagents alluded to.

519. It is essential to use these troughs upon a tray, in order

Fig. 250.
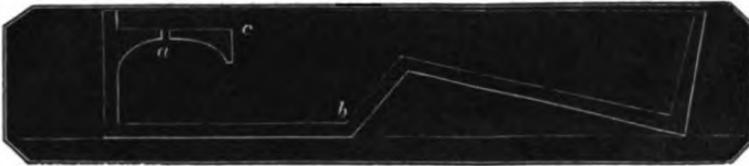
that the mercury, small portions of which will inevitably be
spilled, may be gathered up with facility.   As soon as the metal
is done with, it should be poured away into an iron bottle kept
for the purpose.

520. Fig. 251 represents Bunsen's wooden mercurial trough,

Fig. 251.
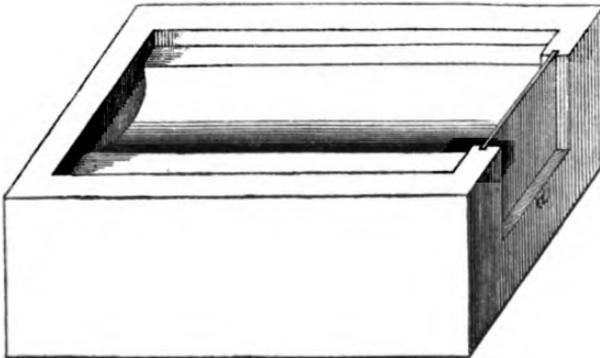
which is exceedingly well adapted for eudiometrical experiments.
It is made of wood, and has a piece of plate-glass inserted at *a*,
by slipping between two grooves.   It does not require so much
mercury as would appear from its size.

521. A most excellent substitute for a mercurial, and even
for a water-trough in many experiments, is the instrument shown
in fig. 252, and known as Cooper's mercurial receiver.   It con-
sists of a glass tube, *a b*, closed at one end, and bent upwards, as
seen in the figure.   It is filled with the metal by inverting and

pouring it in at *b*. On again inverting it cannot fall out, in consequence of the pressure of the atmosphere being unable to act upon the end, *a*. If, now, the delivery-tube, as seen in the engraving, is made to enter, and gas is sent in, the mercury descends and escapes by *b*; but the operation is concluded when the gas occupies from *a* to the bend of the tube. One of the great advantages of this contrivance, is the facility which it affords for making a great number of experiments upon a small quantity of gas; for if the thumb be placed upon the end, *b*,
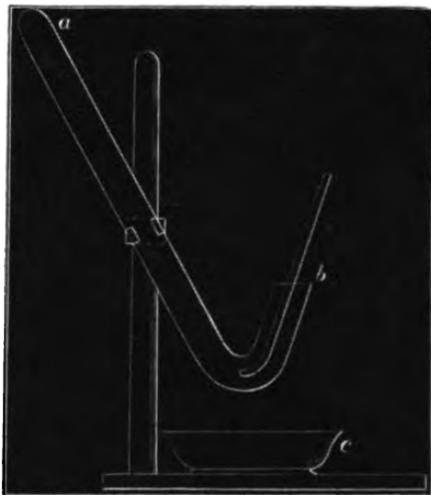
Fig. 252.

and the tube is so inclined as to permit a little of the gas to flow round the bend into the part *b*, so as to occupy a space of from $\frac{1}{2}$ to 1 inch between the mercury and the thumb, it may be examined as to its chemical or physical characters, such as smell or inflammability. And by filling up the vacant space with mercury, another portion may be made to occupy the same position, and may also be examined, and so on until all the gas has been used. The basin, *c*, fig. 252, is placed to catch the mercury which falls on the admission of the gas.

522. It is necessary in all cases to guard against the great pressure exercised by mercury as compared with water, a pressure which is as their respective densities; and as mercury is 13·5 times heavier than an equal bulk of water, it is evident that a tube dipping 1 inch into mercury will exercise as great a pressure as if it dipped into 13·5 inches of water; this pressure must be provided against by increased security of all the joints of the apparatus; and for the same reason it is essential not to allow

the tube delivering a gas to dip to an unnecessary extent under the surface of the metal.

523. It is advisable in all cases where a gas is to be passed into a tube over mercury, to make it turn up at the end, in order to throw the gas up at once, and prevent that tendency to escape, by returning along the outside of the tube, which is sometimes perceived in experiments at the mercurial trough.

524. When a dish is placed under a jar of mercury in order to remove it to the mercurial trough, care must be taken that it is not too thin, for as more force is applied in lifting such a weight than when water is used, there is some danger of breaking the basin unless it is tolerably stout.

525. *Transference of gases.*—One of the most common operations in experiments upon gases, is to remove a portion from a quantity standing over water or mercury for the purpose of submitting it to further examination, such, for instance, as ascertaining its behaviour towards various reagents. Sometimes, however, it is desired to remove a portion of a gas standing over water to a tube at the mercurial trough, and yet it is necessary to avoid the presence of water in the latter vessel. The late Dr. Henry describes, in his 'Elements of Chemistry,' a transferrer which was invented by Cavendish:—"A tube, 8 or 10 inches long, and of very small diameter, is drawn out to a fine bore, and bent at the end, so as to resemble the italic letter *l*. The point is then immersed in quicksilver, which is drawn into the tube till it is filled by the action of the mouth. Placing the finger over the aperture at the straight end, the tube filled with quicksilver is next conveyed through the water, with the bent end uppermost, into an inverted jar of gas. When the finger is removed, the quicksilver falls from the tube into the trough, or into a cup placed to receive it, and the tube is filled with the gas. The whole of the quicksilver, however, must not be allowed to escape, but a column is to be left a few inches long, and kept in its place by the finger. The tube is to be removed from the water and dried by an assistant with a towel or with blotting-paper; the point of the bent tube is then to be introduced into the aperture

P 5

of the tube standing over quicksilver, and on withdrawing the finger from that aperture, which is now uppermost, the pressure of the column of quicksilver, added to the weight of the atmosphere, will force the gas from the bent tube into the one standing in the mercurial trough." But since the time when Cavendish contrived the transferrer last described, many instruments have been invented for the same purpose, some of which serve also to enable gases to be treated with reagents away from the measuring-tube. The annexed cut, fig. 253, represents one of the most convenient of them; it illustrates the shape most commonly employed, but several modifications are adopted in special cases of research. For the double purpose of transferring a gas and treating it with a reagent, the tube, a, is partly filled with mercury and partly with the liquid, to the action of which the gas is to be subjected. The tube, $b c f$, is also filled with the metal. The portion $b c$ is introduced under, and then up into the jar containing the gas to be experimented upon, and the lips being applied at e, the mercury is drawn from a into g, and of course at
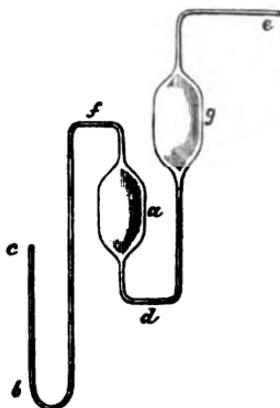
Fig. 253.

the same time the gas passes through $c b$ and f into a. As it is now essential that the tube, $b c$, should be closed, that is done, if the gas alluded to stands over mercury, by merely depressing the aperture, c, beneath the surface of the metal, and applying a slight suction to e.

As soon as the action of the absorbent is completed, which may be facilitated by agitation, and it is desired to pass the gas into the measuring-jar, or into one where it may be intended to act upon it with some other reagent, the aperture, c, being again depressed below the mercury, the metal is to be drawn in by the same method as before, until it stands higher in $d g e$; the tongue for a second closes e, and then a moistened finger is dexterously

substituted for the tongue.   To cause the passage of the gas into the jar, it is merely necessary to gently withdraw the finger from covering the orifice, when the pressure of the mercury in *g* will force the gas into the vessel.

A tranferring pipette, which is extremely easy to use, has been devised by Dr. W. A. Miller.   It consists of a system of glass tubes, having at the centre a bulb, *d*, fig. 254, with a capacity of about a cubic inch.   A funnel, *c*, holding enough mercury to fill the bulb and all the tubes, is joined to a steel stopcock*, *b*, which at its inferior extremity is cemented to a long tube communicating with the bulb.   From the latter proceed two tubes, the lower of which descends and is cemented into a second steel stopcock, *a*, while the upper tube is bent four times at right angles, and terminates in a fine orifice, *e*.   To use the instrument, the stopcock, *a*, is opened, and mercury poured in at *c* until it descends and fills the tube, *f*, escaping by *a*; the latter is then closed; the metal still running in gradually fills the bulb, *d*, and escapes by *e*; the stopcock, *b*, is then shut.   If the gas to be transferred is in a tube over mercury or water contained in a tall cylinder, *e* must first be depressed beneath the surface of the fluid, and then raised inside the cylinder of gas; *a* is now to be opened so as to allow the mercury to escape, which will cause the gas to enter by *e* and fill *d*; the orifice, *e*, is then to be depressed beneath the metal, and a little allowed to enter, so as to close the aperture.   After this, the pipette may be removed, any communication between the gas in *d* and the external air being shut off by the mercury in *e*.   In order to transfer the gas to another tube over mercury or water, it is necessary to fill the funnel, *c*, with mercury, and introduce *e* into the tube as before.   On opening *b*, the metal will enter *d*, dis-

Fig. 254.

* I have constructed this pipette with the stopcocks of vulcanized caout-chouc, on the principle represented in fig. 189, p. 221, and have found them to answer excellently.

placing the gas, which may then be measured, due attention being given to the pressure, temperature, &c., after which it may be subjected to any desired treatment. The whole apparatus is fastened to a board to prevent fracture.

526. The analysis of gases having now become a problem which the chemist has frequently to solve, it is necessary to describe the instruments which have been found to yield the most accurate results. These are undoubtedly those of Regnault and Messrs. Frankland and Ward. The latter gentlemen's apparatus is a modification of Regnault's, and possesses certain advantages over it in practice. For anything more than the descriptions following, the student is referred to Regnault's ' Elements of Chemistry,' an excellent translation of which has been made in America by Dr. Betton, edited by Messrs. Booth and Faber; and also to the paper of Messrs. Frankland and Ward in the ' Quarterly Journal of the Chemical Society.'

527. The apparatus of M. Regnault is seen by reference to figs. 255 and 256. The former represents a geometrical projection of the anterior surface, and fig. 256 gives a vertical section made through a plane perpendicular to this face.

528. " The apparatus is composed of two parts, which may be separated and united at pleasure; and while the first, or *the measurer*, serves to measure the gas under given conditions of temperature and moisture, in the second the gas is subjected to various absorbent reagents, on which account we shall call it the *absorption-tube*.

" The measurer is composed of a tube, ab, of 15 to 20 millimetres diameter internally, divided into millimetres, and terminating above by a curved capillary tube, $b\,e\,r'$, while the lower end is luted into a cast-iron piece, $p'\,q'$, having two tubulures, a, i, and a stopcock, R.

529. " To the second tubulure, i, is luted a straight tube, $i\,h$, open at both ends, of the same diameter as the tube, $a\,b$, and also divided into millimetres." The stopcock, R, is somewhat peculiar, and will be found fully described in a subsequent por-

tion of this volume*, where it is seen in the three principal positions in which the key may be turned. " A communication can
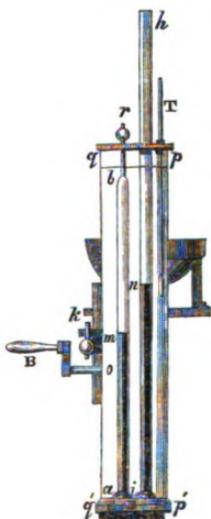
Fig. 255.   Fig. 256.
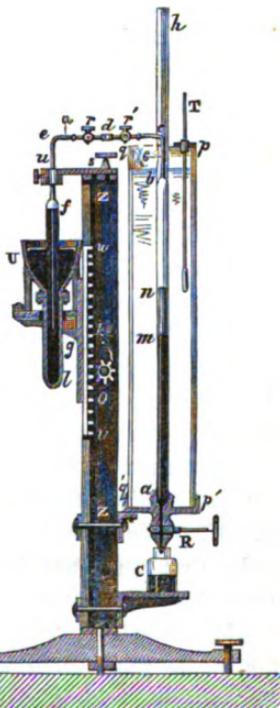
therefore be established at will between the tubes $a\,b$, $i\,h$, or one or other of these tubes only may be opened to the external air.

" The two vertical tubes and the cast-iron piece form a manometric apparatus contained in a glass cylinder, $p\,q\,p'\,q'$, filled with water, which is maintained at a constant temperature, marked by the thermometer, T, during the whole time of the analysis. The manometric apparatus is fixed on a cast-iron stand, Z Z', furnished with adjusting screws.

530. " The absorption-tube is composed of a bell-glass, $g\,f$, open

* On the analysis of certain gases by the method of ultimate organic analysis.

at the bottom, and terminated above by a curved capillary tube, *f e r*. The bell-glass dips into a small mercurial bath, U, of cast-iron, exactly represented in figure 257, while the basin, U, is fixed on a plate which can be raised at will along the vertical support, Z Z', by means of the toothed rack, *v w*, which works with a toothed pinion, *o*, set in motion by the crank, B. The ratchet, *r*, arrests the toothed racks, and consequently keeps the basin, U, in any given position. A counterpoise affixed to the ratchet facilitates its working, and as it is turned to one side or the other, the ratchet is thrown in or out of gear with the pinion. The ends of the capillary tubes, which terminate the absorption-tube and measurer, are luted to two small steel stopcocks, *r, r'*, the ends of which exactly fit each other, and have the same shape as those represented in figures 258 and 259 in section*. Fig. 258

Fig. 257.

represents a section of stop-cocks, *r r'*. It will be seen that the first tubulure is terminated by a plane surface, *a b*, and a projecting cone, *c*, while the second has also a plane surface, *a' b'*, and a hollow cone, *c'*, which exactly fits the plane surface and projecting cone of the other. In order to close them hermetically, it is sufficient to press the two parts against each other by means of the clamp (fig. 260, and in section, fig. 261), which is to be tightened with screws, after having poured in a small quantity of melted caoutchouc.
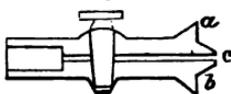
Fig. 258.   Fig. 259.
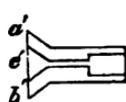
" The absorption-tube is maintained in a vertical position by means of pincers, *u,* lined with cork, which are easily
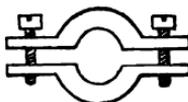
Fig. 260.   Fig. 261.

* This description is introduced for completeness here, although in Regnault it is placed in a different part of the work.

opened or closed when the tube is to be removed or replaced. The measurer, $a\,b$, is traversed at b by two platinum wires opposite to each other, the ends of which approach to the distance of a few millimetres from the inside of the bell-glass, and of which the other ends are fastened with wax to the lower edge of the large cylinder. The electric spark is passed into the bell-glass by means of these wires, and the water in the cylinder is no obstacle if the spark be furnished by a Leyden jar.

531. " Let us suppose that in this apparatus a mixture of atmospheric air and carbonic acid is to be analysed.

532. " Through the tube, $i\,h$, the measurer, $a\,b$, is filled with mercury, until the latter escapes through the stopcock, r, which is then closed, and at the same time the absorption-tube, $g\,f$, is filled with mercury, to effect which the tube, $g\,f$, is detached from the pincers, u, and plunged into the bath, U, the stopcock, r, being opened; and the operator sucks with a glass tube furnished with a caoutchouc tubulure, the edge of which is applied to the plane part of the tubulure, r. When the mercury begins to escape, the stopcock, r, is closed.

" The gas to be analysed, which has been collected under a small bell-glass, is then introduced into the absorption-tube, and the extravasation is easily performed in the bath, U, on account of the shape given to the latter. The absorption-tube being then replaced by the pincers, u, the two tubulures, r, r', are fitted to each other; then, elevating one end of the bath, U, and allowing the mercury of the measurer to flow from the other through the cock, R, and lastly, opening the stopcocks, r, r', the gas is caused to pass from the absorption-tube into the measurer. When the mercury begins to rise in the capillary tube, $f\,e$, its escape through the stopcock, R, is slackened, so as to cause the mercury to rise very gently in the tube, $f\,e\,r$, and the cock, r, is closed when the mercurial column reaches a mark, a, on the horizontal leg, $e\,r$, at a small distance from the tubulure, r. The level of the mercury is then brought to a given division, m, of the tube, $a\,b$, and the difference in height of the two columns can immediately be read on the scale of the tube, $i\,h$. The water in the cylinder has been

several times agitated throughout by blowing air into it by means of a tube which descends to the bottom.

533. "Let t be the temperature of the water, which is to be stationary during the analysis; f the elastic force of the aqueous vapour saturated at this temperature; V the volume of the gas; H the height of the barometer; and lastly, h the height of the mercury elevated: then will $H + h - f$ be the elastic force of the gas when supposed dry. The temperature of the water in the cylinder should be nearly that of the surrounding air, which does not vary sensibly during the short duration of the experiment; and it is unnecessary therefore to reduce to 32°, by calculation, the height of the barometer, and that of the mercury elevated in the manometric apparatus, $a\ b\ i\ h$. The gas collected in the measurer is, moreover, always saturated with moisture, because the sides of the tube, $a\ b$, are moistened with a small quantity of water; and this is constantly the same, since it is that which the mercury does not remove when the tube is filled with it.

534. "When this is done, the mercury is again allowed to flow through the stopcock, R, and the cock, r, is opened, in order to allow all the gas, as well as a column of mercury, to pass into the tube, $r\ c\ b$, after which the stopcock, r', is closed. The absorption-tube is then detached, and a drop of a concentrated solution of potassa is passed up by means of a curved pipette, when the absorption-tube is again fitted to the measurer, and the bath, U, allowed to fall to its full extent; and then, after having poured a large quantity of mercury into the tube, $h\ i$, the stopcocks, r, r', are successively opened. The gas thus passes from the measurer into the absorption-tube, and the small quantity of solution of potassa completely moistens the sides of the bell-glass. The cock, r, is closed when the mercury begins to fall in from the measurer into the vertical leg, $e\ f$, of the absorption-tube; and, after waiting for a few moments, in order to give time for the absorbing action of the potassa, the gas is passed from the absorption-tube back into the measurer, by causing the bath, U, to ascend, and the mercury to flow through

the cock, R.   As soon as the alkaline solution begins to rise in the tube, $f\,e$, an inverse movement is caused by closing the stopcock, r; that is, the gas is again passed from the measurer into the absorption-tube, by lowering the bath, U, and again pouring mercury into the tube, $i\,h$.   The intention of this operation is to again moisten the sides of the bell-glass, $f\,g$, with the solution of potassa, and subject the gas to the absorbing action of the new layer of potassa.

535. "If it be deemed necessary, these operations may be repeated several times; although, after the second, the whole of the carbonic acid is generally absorbed.   The gas is then passed for the last time from the absorption-tube into the measurer, and the cock, r, is closed when the top of the alkaline column reaches the mark a.   The level of the mercury in the tube, $a\,b$, being brought to m, the difference of height, h', of the mercury in the two legs, $a\,b$ and $i\,h$, is measured, and the height, H', of the barometer is noted down.   We shall suppose that the temperature of the water in the cylinder has not changed; if otherwise, it must be restored to the temperature, t, by the addition of hot or cold water.

536. " The elastic force of the gas, dry and deprived of carbonic acid, is therefore $(H' + h' - f)$; and consequently $(H + h - f) - (H' + h' - f) = H - H' + h - h'$ is the diminution of elastic force caused by the absorption of the carbonic acid; and

$$\frac{H - H' + h - h'}{H + h - f}$$

represents the proportion of carbonic acid in the gas when supposed dry.

537. " The proportion of oxygen which exists in the gas remaining must now be determined; for which purpose the absorption-tube is detached, and washed several times with water.   It is dried first with tissue-paper, and then by bringing it into connexion with an air-pump; and, lastly, after having filled it with mercury, it is fitted to the measurer.   The bath, U, being raised as high as possible, the mercury is allowed to run

through the stopcock, R; then opening carefully the cocks, r and r', the mercury of the absorption-tube is passed into the tube, $a\ r'$, of the measurer, taking care to close the cock, r', when the extremity of the mercurial column reaches a second mark, ς, on the vertical leg, $b\ c$. The mercury in the measurer is again brought to the level, m, and the difference of level, h'', and the height, H'', of the barometer is ascertained. $H'' + h'' - f$ is therefore the elastic force of the dry gas, the quantity of which is somewhat smaller than in the measure made immediately after the absorption of the carbonic acid, because a small quantity (about $\frac{1}{3000}$) has been lost by detaching the absorption-tube from the measurer.

" This small loss does not affect the result of the analysis, because the gas is again measured.

538. " The absorption-tube being once more detached from the measurer, the hydrogen gas intended to burn the oxygen is now introduced into the latter, by arresting the ascending mercury at the mark ς. The mercury is again levelled to m, the difference of height, h''', of the two columns of mercury measured, and the height, H''', of the barometer observed. $H''' + h''' - f$ is therefore the elastic force of the mixture of hydrogen and oxygen to be analysed. As sometimes required for the perfect admixture of the gases, combustion by the electric spark cannot be immediately effected. The gas must again be passed from the measurer into the absorption-tube, and a small quantity of mercury, which produces an agitation in the gas, allowed to flow through the tube, $c\ d\ e\ f$; and, lastly, the mixture is passed back into the measurer, this time allowing the mercury to entirely fill the tube, $r'\ c\ b$, in order that the whole volume of gas may be subjected to combustion.

539. " The electric spark is then applied, and after having established an excess of pressure in the measurer, $a\ b$, the stopcocks, r, r', are carefully opened, in order to allow the mercurial column to retrograde into the tube, $b\ c\ r'$; and it is stopped when it reaches the mark ς. The elastic force of the gas re-

maining is again measured, after having levelled the mercury to
m; and $H'''' + h'''' - f$ is then the elastic force. Consequently,
$(H''' + h''' - f) - (H'''' + h'''' - f) = H''' - H'''' + h''' - h''''$ is
the elastic force of the gaseous mixture which disappeared during
the combustion; $\frac{1}{3}$ $(H''' - H'''' + h'''')$ is the elastic force of
the oxygen contained in the dry gas, of which the elastic force
is $(H'' + h'' - f)$, and

$$\frac{1}{3} \frac{H''' - H'''' + h''' - h''''}{H'' + h'' - f}$$

is the proportion of oxygen contained in the gas when freed from
carbonic acid; whence the proportion of oxygen in the original
mixture may be easily deduced.

540. "The example chosen shows the mode of operating with
the apparatus; the manipulations are of such a simple cha-
racter, that the operator requires no assistant; and, lastly,
the operation is so rapid, that less than three quarters of
an hour is required for that just described; the greater por-
tion of which time is consumed by the absorption of the car-
bonic acid and the cleansing of the bell-glass after the experi-
ment. Air freed from carbonic acid can be analysed in less than
twenty minutes."

541. The above will, it is hoped, sufficiently illustrate the
nature and mode of using this admirable instrument, but for any
other points which may require elucidation, the reader is referred
to the work cited.

542. Messrs. Frankland and Ward, the first of whom has
long been well known for his dexterity in the manipulation
connected with gas analysis, while admitting the advantages
which the apparatus just described possesses over even the very
accurate method of Bunsen, the latter requiring the use of a room
capable of being maintained at a standard temperature, take
exception to M. Regnault's method of determining volumes by
ascertaining the pressure of a constant volume greater or less
than that of the atmosphere as expressed in millimetres of mer-
cury, as having the disadvantage of expressing large variations in

bulk by small numbers, as compared with Bunsen's method. They illustrate the force of their remarks by analyses made on a mixture of air with a very small portion of carbonic acid, where they show that an error of observation equal to $\frac{1}{10}$th of a milli-metre had an effect seven times greater with Regnault's method, than when that of Bunsen was adopted. They commence the description of their process, which is intended to combine the advantages of both methods, by stating the requisites of a perfect instrument; these are,—

543. "1. The determinations of the gaseous volumes should be made in a manner entirely independent of the pressure and temperature of the external atmosphere.

" 2. Such determinations of volume should also be self-correct-ing, as regards the tension of aqueous vapour and the variations in the density of mercury.

" 3. Each change of volume should be expressed by a numerical difference as large as possible.

" 4. In order to avoid the inconvenience and loss of time occasioned by tedious calculations, references to tables, &c., the numerical expression of each volume actually read off should either be the true and corrected volume, or a number from which such volume can be at once obtained by the most simple arith-metical process.

" The advantage of securing the first and second of these qua-lifications is sufficiently obvious; for whilst we can then carry on the operations of gaseous analysis without an apartment of nearly constant temperature set apart for the purpose, the accuracy of our results is also not liable to be affected by any errors that may have been made in the determination of the expansion of gases by heat, the tension of aqueous vapour, and the expansion co-efficient of mercury.

" The third and fourth qualifications are also scarcely of in-ferior importance, the one for securing delicacy in the read-ings, and the other for economizing time, and enabling the operator to see the corrected results of his experiments during their progress, an advantage which can best be appreciated by

those who have had to make large numbers of consecutive gas analyses.

" In constructing an apparatus to combine the foregoing qualifications, we have taken as a model the ingenious and very convenient arrangement of MM. Regnault and Reiset, with the mechanical arrangement of which our apparatus, though different in principle, has much in common.

544. " Our instrument, which is represented by the accompanying figure, consists of the tripod A, furnished with the usual levelling screws, and carrying the vertical pillar, B B, to which is attached on the one side the moveable mercury-trough, C*, with its rack and pinion, a a, and on the other the glass cylinder, D D, with its contents. This cylinder is 36 inches long and 4 inches internal diameter; its lower extremity is firmly cemented into an iron collar, c, the under surface of which can be screwed perfectly water-tight upon the bracket plate, d, by the interposition of a vulcanized caoutchouc ring. The circular iron plate, d, is perforated with three apertures, into which the caps, e e e, are screwed, and which communicate below the plate with the T-piece, E E. This latter is furnished with a double-way cock, f, and a single-way cock, g, by means of which the tubes cemented into the sockets, e e e, can be made to communicate with each other, or with the exit-pipe, h, at pleasure.

Fig. 262.

* The mercury-trough, including its tubular well, b, may be conveniently constructed of gutta percha.
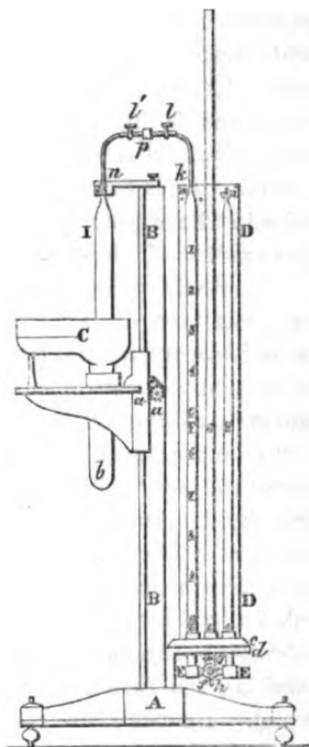
" F G H are three glass tubes, which are firmly cemented into the caps, *e e e*. F and H, which are only slightly shorter than the glass cylinder, are each from 15 to 20 millimetres internal diameter, and are selected of as nearly the same bore as possible, to avoid a difference of capillary action. The tube, G, is somewhat wider, and may be continued to any convenient height above the cylinder. H is accurately graduated with a millimetre scale, and is furnished at top with a small funnel, *i*, into the neck of which a glass stopper, about 2 millimetres diameter, is carefully ground. The tube, F, terminates at its upper extremity in the capillary tube, *k*, which is carefully cemented into the small steel stopcock, *l*. F has also fused into it, at *m*, two platinum wires, for the passage of the electric spark. After this tube has been firmly cemented into the cap, *e*, its internal volume is accurately divided into ten perfectly equal parts, which is effected without difficulty by first filling it with mercury from the supply-tube, G, up to its junction with the capillary attachment, and then allowing the mercury to run off through the nozzle, *h*, until the highest point of its convex surface stands at the division 10, previously made, so as exactly to coincide with the zero of the millimetre scale on H ; the weight of the mercury thus run off is carefully determined, and the tube is again filled as before, and divided into ten equal parts, by allowing the mercury to run off in successive tenths of the entire weight, and marking the height of the convexity after each abstraction of metal. By using the proper precautions with regard to temperature, &c., an exceedingly accurate calibration can in this way be accomplished.

545. " The absorption-tube, I, is supported by the clamp, *n*, and connected with the capillary tube, *k*, by the stopcock and junction-piece, *l' p*, in exactly the same manner as in Regnault's apparatus.

546. " When the instrument is thus far complete, it is requisite to ascertain the height of each of the nine upper divisions on the tube above the lowest or tenth division. This is very accurately effected in a few minutes, by carefully levelling the instrument,

filling the tube, G, with mercury, opening the cock, *l*, and the stoppered funnel, *i*, and placing the cock, *f*, in such a position as to cause the tubes, F H, to communicate with the supply-tube, G. On now slightly turning the cock, *g*, the mercury will slowly rise in each of the tubes, F and H; when its convex surface exactly coincides with the ninth division on F, the influx of metal is stopped, and its height in H accurately observed; as the tenth division on F corresponds with the zero of the scale upon H, it is obvious that the number thus read off is the height of the ninth division above that zero-point. A similar observation for each of the other divisions upon F completes the instrument.

547. " Before using the apparatus, the large cylinder, D D, is filled with water, and the internal walls of the tubes, F and H, are once for all moistened with distilled water by the introduction of a few drops into each through the stopcock, *l*, and the stoppered funnel, *i*.   The three tubes being then placed in communication with each other, mercury is poured into G, until it rises into the cup, *i*, the stopper of which is then firmly closed. When the mercury begins to flow from *l*, that cock is also closed. The tubes, F and H, are now apparently filled with mercury, but a minute and imperceptible film of air still exists between the metal and glass; this is effectually got rid of by connecting F and H with the exit-tube, *h*, and allowing the mercury to flow out until a vacuum of several inches in length has been produced in both tubes; on allowing the instrument to remain thus for an hour, the whole of the film of air above mentioned will diffuse itself into the vacuum, and will become visible as a minute bubble in each tube, on allowing the vacuum to be filled up from the supply-tube, G.   These bubbles are, of course, easily expelled, on momentarily opening the cock, *l*, and the stopper, *i*, whilst G is full of mercury.   The absorption-tube, I, being then filled with quicksilver, and attached to *l* by the screw-clamp, the instrument is ready for use.

548. " In localities where a constant supply of water from street mains can be had, the temperature of the water in the cylinder, D D, can be maintained perfectly constant, by allowing a con-

tinuous stream direct from the main to flow into the bottom of the cylinder, and make its exit near the top. By this arrangement, it has been proved by one of us, in an extensive series of experiments, that the temperature of a cylinder supplied from the Manchester high-pressure mains, does not vary more than $0°·02$ Centigrade in twelve hours, a variation which scarcely requires correction in the most delicate experiment.

" In illustration of the manner of using our apparatus, we will take as an example an analysis of atmospheric air. A few cubic inches of air freed from carbonic acid having been introduced into the tube, I, it is transferred into F for measurement by opening the cocks, ll', and placing the tube, F, in communication with the exit-pipe, h: the transference can be assisted, if needful, by elevating the trough, C. When the air, followed by a few drops of mercury, has passed completely into F, the cock, l, is shut, and f turned, so as to connect F and H with h. Mercury is allowed to flow out until a vacuum of 2 or 3 inches in length is formed in H, and the metal in F is just below one of the divisions; the cock, f, is then reversed, and mercury very gradually admitted from G, until the highest point in F exactly corresponds with one of the divisions upon that tube: we will assume it to be the sixth division. This adjustment of mercury, and the subsequent readings, can be very accurately made by means of a small horizontal telescope placed at a distance of about 6 feet from the cylinder, and sliding upon a vertical rod. The height of the mercury in H must now be accurately determined; and if, from the number thus read off, the height of the sixth division above the zero of the scale in H be deducted, the remainder will express the true volume of the gas; but in order to compare this with subsequent readings made at other divisions upon F, the number thus obtained, which evidently represents the pressure of the gas, is reduced to what it would have been had the gas been expanded to the tenth division of F. Bearing in mind that the pressure of a gas is inversely as its volume, this reduction is very simply effected by multiplying the number as above obtained by $\frac{6}{10}$ or $0·6$; and in all cases any determination of pressure made at any division

upon F may be reduced to the pressure of the same volume when expanded to the tenth division, by the use of a fractional multiplier whose denominator is 10, and numerator the number of the division at which the determination is made.

549. " As the temperature is maintained constant during the entire analysis, no correction on that score has to be made; the atmospheric pressure being altogether excluded from exerting any influence upon the volumes or pressures, no barometrical observations are requisite; and as the tension of aqueous vapour in F is exactly balanced by that in H, the instrument is in this respect self-correcting.

550. " Hydrogen being then introduced in the same way as the original gas, and the volume determined anew, the electric spark is passed through the mixture by means of the platinum wires at *m*, and the determination of the contraction caused by the explosion terminates the analysis."

551. *Eudiometers.*—It would perhaps have been more in accordance with the ordinary modes of arrangement, to have introduced the more simple kinds of eudiometer first, and then to have proceeded to a description of the more complex; but it has been preferred to reverse this,—to give the more perfect methods the priority, and to make the others merely supplemental to them.

There are several instruments in use for the analysis of gases by the passage of the electric spark through mixtures, but before proceeding to notice these, it will be proper to call attention to a few precautions which are necessary to ensure success with all of them. The spark is obtained either from an electrophorus, the prime conductor of an electrical machine, or a Leyden jar[*]. In the case of the two former, it is essential that every facility should be given to enable the spark to pass as a bright distinct flash, and not in the feeble manner in which the electric fluid is evolved from points. It is necessary, therefore, where the source of electricity is not sufficiently powerful, that extra care should be taken to ensure roundness of the ends of the wires in the interior

[*] In the Appendix another method will be described of obtaining the spark, even in cold, damp rooms.

Q

of the eudiometer from which the spark is given off, and also that those on the exterior should have knobs, or if this is inconvenient, that the hooks should not be thin. Where a Leyden jar is used, these precautions are not so essential, as there is then much less difficulty in detonating the mixture.

552. It is moreover essential that the quantity of gas to be exploded should not be too large, as otherwise it will be difficult or impossible to prevent loss. It is not easy to give a general rule for the quantity of gaseous mixture that may be detonated with safety, because such great differences exist in the degrees with which expansion takes place on the passage of the spark; the operator must therefore be guided to a great extent by his judgment; but it is frequently proper not to explode more gas than is equal to a tenth of the internal measure of the instrument, although sometimes a third may be exploded without danger.

553. When the gas has been introduced, the exterior of the tube is to be well dried by friction with a warm cloth, as damp much
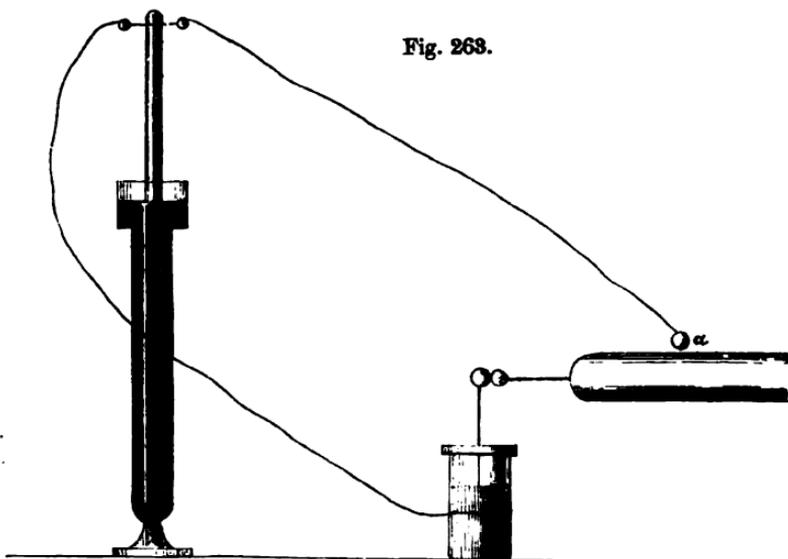
Fig. 263.

increases the difficulty of obtaining a sufficiently powerful spark.

The charge may be passed through the eudiometer in several

ways; that represented in fig. 263 is frequently convenient. One ball of the tube is attached to a copper wire in contact with the exterior of the jar, while the other ball is connected with another wire terminating in a brass ball, which is approached to within a $\frac{1}{4}$ or $\frac{1}{2}$ an inch of the conductor of an electrical machine, the knob of the conductor being in contact with the ball which communicates with the interior of the jar. The ball, a, is supported by a piece of glass tube at the proper distance from the conductor. When the preparations are complete, the electrical machine is worked, and as soon as the tension of the electricity becomes sufficiently powerful to overcome the resistance of the air between the ball, a, and the conductor, a bright spark will pass and cause inflammation of the gaseous mixture. The eudiometer figured above is of the common kind, but where it is feared that the expansion consequent on the explosion might project a portion of the contents of the vessel, the contrivance of M. Gay-Lussac, fig. 264, may be adopted. It will be seen that it is provided with a valve which descends as the mixture expands on passage of the spark, and thus closes the aperture; but on the contraction which takes place immediately afterwards, it ascends, and thus allows the mercury to enter and fill the vacuum thus produced.

Fig. 264.

Fig. 265.

554. Mitscherlich uses a eudiometer similar to fig. 265. It is closed by the glass stopper, a, until after the explosion, when it is turned to allow entrance of the mercury.

A much better way of preventing escape of gas at the moment
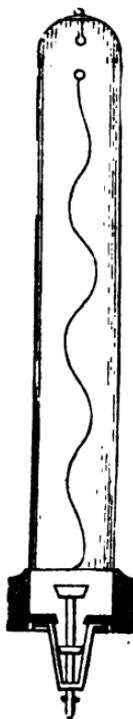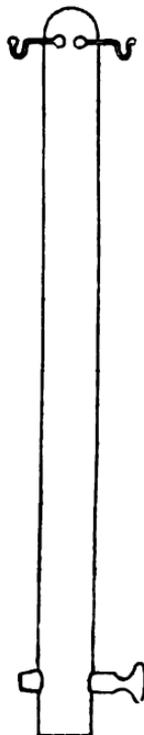
of explosion, is by pressing the lower end of the eudiometer against a piece of vulcanized caoutchouc, the latter being placed at the bottom of the mercurial trough. The caoutchouc should be moistened with solution of corrosive sublimate to remove the film of air which adheres to it, and may give rise to errors.

If the wires of the eudiometer are too thin to allow good sparks to pass, balls attached to wires may be fastened by twisting those on the exterior of the eudiometer.

555. The connexion between the interior and exterior of the jar should be always by wires in eudiometrical experiments, and not by a chain, as is frequently represented; in the latter case, there is sometimes a difficulty in obtaining perfect contact between all the links, especially when the jar is held by the hand while exploding. If inconvenience is occasioned by the rigidity of the wire, it may be divided into two or three pieces, and hooked together so as to form links, but their being so few in number prevents any danger of non-contact if they are clean and properly attached by small hooks.

Fig. 266.

556. It is seldom that any difficulty is found in selecting a copper wire of sufficient pliability; if, however, this is the case, the wire may be bent into a spiral in one or two places so as to allow freedom of motion, as is sometimes adopted with the wires from the battery in electro-depositing. In the arrangement, fig. 266, the charge passes directly from the one coating of the jar to the other through the eudiometer, and does not affect the operator.
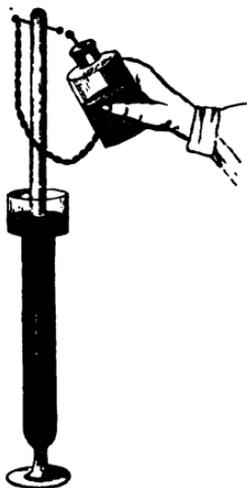
Dr. Ure's eudiometer was intended to render gas-analysis easy of performance by one person, but, from what has been previously said, it will be seen that with a little management almost all operations of eudiometry may be performed without the necessity of an assistant. Nevertheless, it has other qualities which would render its omission improper; not the least of these is the com-

paratively small amount of mercury with which it may be worked. One important feature is the manner in which the elasticity of air is made to serve as a spring, and by this means to moderate the violence of the explosion.

557. The instrument, fig. 267, may be filled with mercury by inclining it a little on one side, and, the open end being immersed in the trough, the delivery-tube from the gasometer or apparatus evolving the necessary gas is to be placed beneath the aperture, or it is more generally convenient to introduce the gas by means of a small-lipped transfer-tube; by this means a measured quantity may be readily obtained in the instrument. The leg, $a\,b$, is graduated, but before estimating the volume of gas, it is necessary to carefully level the mercury in both limbs by a pipette, or otherwise. Before

Fig. 267.

passing the spark, it must be observed that about 2 inches of the open leg are free from mercury, so that when held as in fig. 268, the portion included between the thumb and the surface of the metal may serve as the spring before alluded to. The end of the thumb must touch one of the balls, while with the other the spark is taken from the conductor or electrophorus-plate. On allowing the spark to pass, a slight sensation is perceived as if the finger was pressed outwards, and directly after, as soon as the diminution of volume has occurred, the reverse sensation is perceived, the thumb being drawn in by the pressure of the atmosphere; it must now be removed slightly to one side, so as to permit ingress of air, not too rapidly, and the metal will ascend in the closed limb; mercury is now to be poured into the other limb until it occupies exactly the same height in both legs, when the volume may be read off and the amount of contraction observed. When, from the reasons before detailed, a spark from
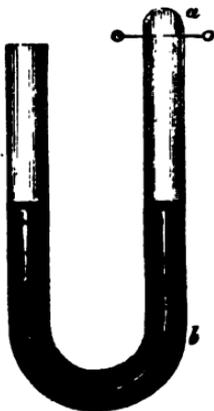
the prime conductor of a machine, or that of a good electrophorus, is insufficient to cause the inflammation of the gas, the arrangement must be modified so as to prevent the unpleasant effects of the shock.

558. The method seen in fig. 268 is then to be employed. It will now be seen that the thumb does not touch the knob nearest to it, but that the latter is in connexion with the outer coating of

Fig. 269.

Fig. 268.
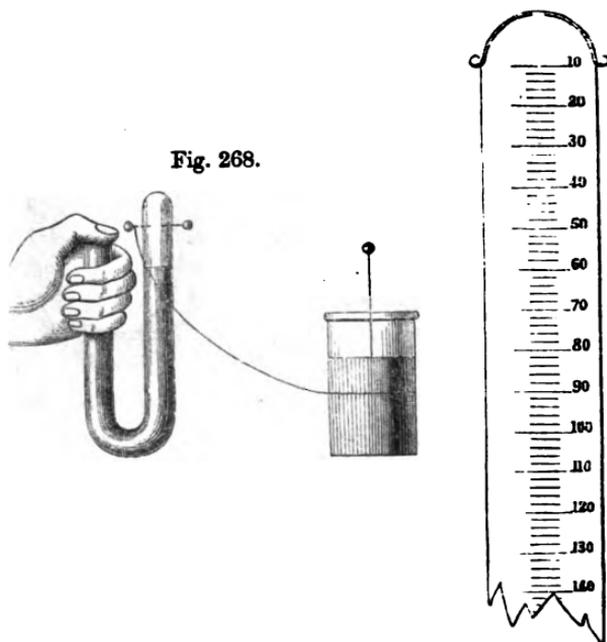
the jar.   On bringing the other wire of the eudiometer in communication with the interior coating of the jar, by means of the knob of the latter the spark passes and inflames the mixture.

Bunsen's Eudiometer.—This is constructed of the form shown in fig. 269; it is from 60 to 70 centimetres long, and 19 millimetres in internal diameter, and 1½ in thickness of glass.   The wires, which are bent upwards and along the top, are 3 millimetres apart at their extremities.   The graduations of the tube are arbi-

trary, the value of them being determined by experiment after the instrument is finished.

559. *Reading off volumes.*—In ascertaining the volume which a gas occupies in a jar over mercury or water, it is essential that the vessel should be perfectly upright. The plain surface of the mercury is to be considered as the line indicating the volume. The eye must be brought accurately to a level with this surface before reading off, for if it be either above or below, the error of observation becomes so great as to render the result of no value. A very simple but accurate method of estimating the height of a surface of mercury or water in a jar is by placing a mirror behind the jar while reading off, the eye being lowered until one-half of the pupil is seen by the mirror to cut the level of the fluid; the line on the eudiometer or gas-jar which crosses the reflexion of the centre of the pupil is to be taken as the true level. In reading off volumes over water, it is best to take the centre of the dark ring of fluid, formed by the attraction of the sides of the tube, as the true level.

The error of the meniscus of a tube may be determined thus:— A quantity of mercury is put into it, and the level of the convex surface read off; the convexity is then destroyed by the addition of a few drops of solution of corrosive sublimate and the height is again read off: the difference between the two readings is the error sought. When the mercury or water stands above the general level in the trough, the height must be carefully measured with a pair of compasses and the necessary correction made; of course in the case of mercury this correction has far greater influence upon the result than where water is the fluid used to confine the gas. In the former case, the height of the metal in the jar is to be deducted from that of the barometer in making the correction for pressure. Where differences of level are to be estimated with great precision, it is necessary to make use of a cathetometer.

560. But there is another source of error which must not be lost sight of, when an accurate result is to be obtained. When tubes are graduated by pouring equal quantities of mercury into

them, their position is exactly the reverse of that in which the volume of a gas is observed; it is necessary, therefore, when the volume of the gas has been ascertained by reading off over the surface of the metal by means of a mirror (§ 559), to add to the number so obtained double the error of meniscus of the tube previously ascertained.

It is a good plan to mark on each gas-jar its own error of meniscus with a writing diamond, in some part where it does not interfere with the graduations.

561. *Estimation of carbonic acid in carbonates by weight.*—Several ingenious pieces of apparatus have been invented for this purpose ; most of them are extremely easy to construct, and, when used carefully, afford accurate results.   For the estimation of the amount of available alkali in the pearl and soda ashes of commerce they answer well, but certainly do not surpass, if they even equal in accuracy, the process by means of a test acid, either by weighing or the volumetrical method.

562. The most simple arrangement is, perhaps, that of Parnell, seen in fig. 270, and, in careful hands, it yields equally accurate results with the more complex arrangement of Fresenius and Will ; and has, moreover, the advantage of being less weighty, and therefore better adapted for deli-cate balances.   It consists of a glass flask, fig. 270, of about two ounces capacity, fitted with a sound cork through which two tubes pass, one serving to connect the chloride-of-calcium-tube, *a*, while the other, *b*, will be described presently.   A small test-tube, *c*, is so placed in the flask, and is of such a size, that it cannot fall down, but its contents may be made to flow out by inclining the apparatus to one side.   To per-form the experiment, a weighed

Fig. 270.
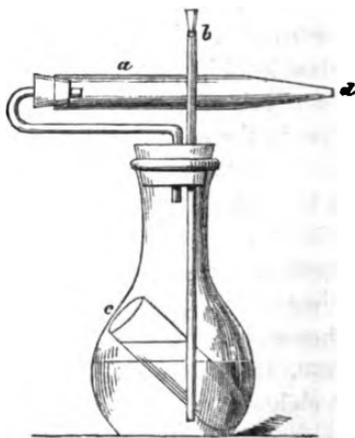
quantity of the carbonate is placed in the flask, and water added up to the level seen in the figure; the test-tube is then filled nearly to the top with concentrated sulphuric acid, and is carefully lowered into the flask; the cork with the tubes attached is then affixed, the aperture, b, being closed with a small cork. The little cylinders which are procured by perforating corks with Mohr's borers, are well adapted for this purpose. The whole · apparatus is now carefully weighed; the flask is then to be inclined so as to allow some of the acid to flow out, and, when the effervescence has subsided, a little more, and so on until no more carbonic acid is evolved; the flask is now to be so inclined as to cause the whole of the acid to mingle with the aqueous fluid, and thus cause a considerable rise of temperature; this expels the carbonic acid from the liquid; but as an atmosphere of the latter gas fills the flask, it must be removed and replaced by air, as the difference in density of the two is very considerable. For this purpose, the cork, b, is removed and air is sucked out at d, until it no longer tastes of carbonic acid; the flask is then allowed to become perfectly cold, and the little cork being replaced, it is then reweighed: the difference in the two weighings is the amount of carbonic acid in the specimen. On drawing air for some time through the apparatus, it begins slowly to acquire weight, arising from the moisture in the atmosphere being absorbed by the chloride of calcium; and although the error introduced by this means is too minute to affect ordinary experiments, it must not be neglected where, from the quantity of material in the flask being limited, or other causes, a small difference has an important bearing on the result. In this latter case another chloride-of-calcium-tube is to be attached to the aperture, b, and the air must be drawn through by means of a suction-tube applied at d, as will be mentioned in describing the apparatus of Fresenius and Will.

563. The latter consists of two flasks, a and b, fig. 271 : a has a capacity of two, and b two and a half fluid ounces of water; each is closed with a cork, through which pass two tubes; one of these, c, is a siphon, the short leg just passing through the cork in b, and the longer reaching nearly to the bottom of a. Another

Q 5

tube, *d*, reaches to the bottom of *b*, and a third, *e*, enters *a*.
A small cork stopper is fitted to *d* at the commencement of
the analysis. This cork is obtained in the same manner as
that used to close *b* in the Parnell's apparatus previously
described, and is preferable to the piece of wax generally used
for this purpose.

Fig. 271.   Fig. 272.   Fig. 273.
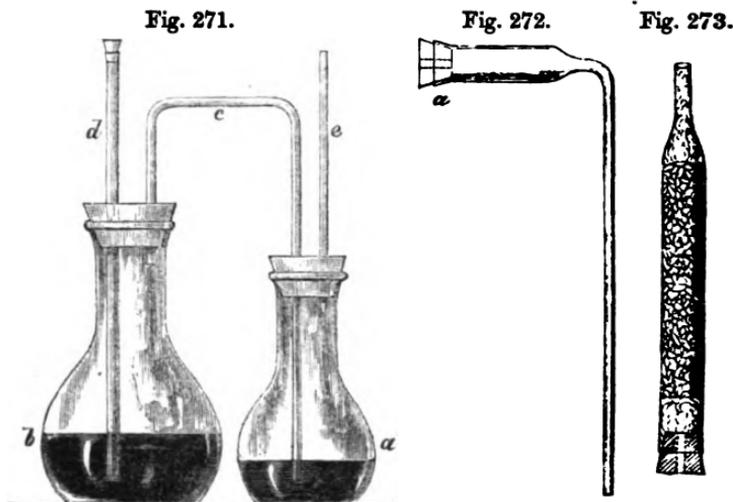
564. The carbonate to be examined is weighed out and projected
into *b*, the capsule in which it has been ignited being rinsed
with distilled water into the same, the rinsings, &c. filling the
flask to about one-third its bulk. Enough strong sulphuric acid
is then poured into *a* (without soiling the neck) to cover the exit
of the tube, *c*, to about ¾ths of an inch. The aperture of *d* is
then closed with its cork, and after weighing the apparatus, the
suction-tube, fig. 272, is applied to *e*, and a little air is drawn out,
which has the effect of creating a partial vacuum in *b*, the air
escaping in bubbles through the acid in *a*. On removing the lips,
the sulphuric acid recedes by the tube, *c*, into *b*, and a rapid
effervescence instantly takes place, the carbonic acid escaping
through *e*; but it becomes perfectly dried by its passage through
the sulphuric acid; the mixture of the acid with the water in *b*

causes a rise of temperature, and when this falls, and the air contracts, more acid enters; and this is continued (assisted, if required, by suction, as before) until the carbonate is completely decomposed; when this is accomplished, more acid is forced to enter b, so as to cause sufficient rise of temperature to expel all the carbonic acid; the cork is now removed from d, and the chloride-of-calcium-tube, fig. 273, is attached by means of the perforated cork; the suction-tube being applied to e, air is drawn through until no more taste of carbonic acid is perceived; the two last-mentioned tubes are then removed, the cork is replaced in the aperture of d, and as soon as the flasks have become perfectly cold, they are wiped with a clean dry cloth, and weighed; the difference between the first and second weighings gives the amount of carbonic acid in the specimen. For the precautions necessary where hyposulphites, &c. are present, the student is referred to works on quantitative analysis. As showing the accuracy of the method, the two examples following may be quoted. They were made some years ago, to ascertain the purity of a sample of carbonate of potash, to be used for making a test-acid, and were not originally intended for publication.

66·11 carbonate of potash gave 21·01 carbonic acid.
54·26 ,, 17·31 ,,

or, per cent.,

I.	II.	Mean.	Theory.
31·78	31·90	31·84	31·88

565. A multitide of contrivances have been described for effecting the same result as that described above; it is, however, quite unnecessary to detail them, as none possess greater accuracy, and few are more easy to use.

SECTION XXIII.

MANIPULATION CONNECTED WITH ORGANIC ANALYSIS.

566. The light which the pursuit of organic chemistry has shed upon animal and vegetable physiology, and upon agriculture, is so great, that it becomes unnecessary to insist upon the advantage, nay, absolute necessity, of a practical acquaintance with the methods of organic analysis, to all who aspire to success in those departments of science; and it may be stated with confidence, that there is no branch of natural knowledge which so richly rewards its students with discoveries. And not *merely* discoveries; for whether we regard them in their purely chemical, mathematical, stöchiometrical, or practical relations, their interest is not to be surpassed. It is also to be remembered, that so extreme is the beauty of the products produced by this method of observation, that this *alone* would far more than repay all the labour and study required in their formation.

It is remarkable that there is no class of bodies of either animal or vegetable origin, however unpromising in their superficial qualities, which may not be made to yield substances of interest, and in many instances of great value.

567. Chemists seem to have had an almost intuitive perception of this, even from the commencement of the science; for we find them always hovering near, although the key to the method of research had not yet been found. It would be unprofitable in a work of this character, however interesting the subject might be, to follow them through the steps which gradually led to the desired result. To Gay-Lussac and Thenard belongs the honour of first indicating a process by means of which the much-desired knowledge could be obtained; and the successive discoveries of Berzelius, Prout, Dumas, Bunsen, and above all, Liebig, have at last raised the process to a degree of precision not to be surpassed, and perhaps scarcely to be equalled by any other method

of physical investigation.   In fact, it is to the brilliant discoveries of the last-named chemist that the popularity of organic chemistry is chiefly owing ; and as the onward progress of the science is advancing with a rapidity doubtless unexampled in the history of knowledge, this fact should in common justice be remembered by all who avail themselves of the processes mentioned in the following pages.

568. It is frequently imagined by students in chemistry, that organic analysis requires a great amount of knowledge and dexterity on the part of the operator; but this is a fallacy.   Like most other chemical operations, it simply requires care and attention to minute precautions, it being the latter which so greatly influence the results of an experiment.   It may with safety be said, that a person possessed of a moderate knowledge of chemical processes, may in a few experiments acquire sufficient facility in organic analysis to make a failure or an abortive experiment a rare occurrence, the purity of the substance operated upon being of course presupposed.

It will not be attempted to give all the processes, or rather modifications, contrived by different individuals, such variations being in general only advantageous under the peculiar circumstances in which they were invented, but those will be indicated with which the author is practically familiar, and which have always been found to yield unexceptionable results.

First Method.

569. *Analysis of non-nitrogenous substances with chromate of lead.*—All organic substances free from nitrogen and inorganic matters, when burned in presence of a great excess of chromate of lead, are resolved into two products, which contain definite quantities of the two ingredients sought to be estimated, these two substances obtained being carbonic acid and water; and as 22 parts of the former are equivalent to 6 of carbon, and 9 of the latter to 1 of hydrogen, the calculations required are simple in the extreme.

To perform this operation, the following apparatus is required:—

570. *The potash-tube.*—This instrument, the invention of Liebig, is the chief cause of the rapid advance made by organic chemistry, from the manner in which it has removed the necessity of tedious calculations. Its form is seen by reference to fig. 67, § 107. It consists of five glass bulbs, blown upon pieces of tube, and joined together in such a manner that they may with ease be hung upon a hook attached to the balance.

It is needless to enter upon the method of making them, as such an exertion of dexterity would be a pure waste of time, where the operator had anything else to do, it being entirely unnecessary in regard to economy, as they may be procured at prices so low as to show that by practice they must be sufficiently easy to construct.

571. To render this instrument fit for use, it has to be filled with a solution of caustic potash of about specific gravity 1·25. This may be effected by immersing the tube attached to the large bulb in the liquid, and after attaching the suction-tube, fig. 272, to the other aperture, drawing with the mouth until sufficient has been introduced to nearly fill the three lower bulbs. It is unnecessary, and even improper, to introduce more than this. The exterior portion of the potash apparatus which is wetted with the caustic solution is to be wiped, and the interior is to be dried by means of a thin roll of filtering-paper. As the instrument is delicate and liable to fracture if the point of junction of the tubes is at all roughly handled, it is advisable so to connect the suspending link as to prevent the possibility of their being withdrawn from each other. The apparatus being made of German glass, free from lead, is extremely light, and when containing a proper quantity of solution of potash, should not weigh more than 800 grains at the outside; in fact, those I am accustomed to use, with the second tube attached, to be alluded to further on, do not weigh more than this.

Several other forms of potash apparatus have been contrived, one of them by Mitscherlich, but they have no advantages over

that of Liebig; they are also generally expensive, and the more complex kinds require a greater time to fill with the potash solution, and also to clean out, in addition to which they are more fragile, and, with the exception of Mitscherlich's, decidedly heavier.

In choosing a potash apparatus of the kind represented in fig. 67, § 107, there are a few points which demand attention. In the first place, it must be ascertained that the tubes by which the potash solution is introduced are sufficiently large to permit the ingress of the small roll of filtering-paper used to wipe away the superfluous moisture. It is necessary, also, that the proper proportion should exist between the two upper bulbs; this relative size may be seen by reference to fig. 67. No wrinkling must be observable where the two upper tubes cross each other, and they should approach within so short a distance that they may be bound tightly together with fine wire without fear of fracture. The hook attached to the apparatus, and by which it is suspended to the balance, is bound on by the same wire which fastens the two tubes.

572. *The chloride-of-calcium-tube.*—The water produced in the analysis is collected in a tube of the form seen in fig. 66, § 107, filled with spongy chloride of calcium, prepared as follows:— Ordinary slaked lime is dissolved in commercial hydrochloric acid, a little nitric acid is added, and the solution boiled and evaporated to dryness with constant stirring; the solid is then redissolved in plenty of cold water, a small excess of cream of lime added, and the solution allowed to remain for twenty-four hours; it is then filtered and evaporated to dryness with constant stirring. When no more water is given off, the fragments are to be passed through two sieves, one to remove the dust, and the other to separate all the pieces too large to be capable of entering with perfect ease into the tube, and at the same time lying tolerably close together. If this operation has been properly performed, a remarkably neat-looking product is the result, being in the form of white grains of nearly uniform size, perfectly dry, and excessively hygrometric. *Fused* chloride of calcium is not at all adapted for the purpose. To fill the chloride-of-cal-

cium-tube, a little loose fragment of cotton wool is made to pass into the narrow tube by means of suction; more wool is then added until it occupies about one-third of the bulb; this is much better than using less cotton, as, in the latter case, the tube soon becomes useless until refilled, owing to the solution of chloride of calcium crystallizing, whereas if done as directed, the same tube will answer for a dozen or more analyses without being refilled. The tube is then filled with the fragments of chloride of calcium to within ¾ths of an inch of the top, another portion of cotton wool is added, and then a cork containing a tube whose diameter corresponds to the tubes of the potash apparatus. The cork is cut off nearly level with the tube, but slightly conical, and is to have melted sealing-wax applied evenly, and in not too large quantity, so as to ensure tightness. The whole arrangement should not weigh more than 400 grains, and if possible less. A wire is attached by loops in such a manner as to enable it to be hung on the beam of the balance, as in fig. 66.

573. As most chloride of calcium is slightly alkaline, and if prepared by the process given, almost certain to be so, it is proper to pass a current of carbonic acid through it for half an hour before use. For this purpose, a vial containing a few fragments of white marble, and having a cork with an aperture in it of the size of the tube of the chloride-of-calcium apparatus, may be kept in the laboratory. It will be sufficient before using the chloride-of-calcium-tube for the first time, to add a little dilute hydrochloric acid to the marble, and attach the apparatus to the vial. When the acid has become saturated, the operation is finished; the gas remaining in the chloride-of-calcium-tube is then to be removed by suction, and the latter is then to be weighed.

574. *The suction-tube.*—This little instrument (fig. 272, p. 346) is used to fill the potash-tubes with solution of caustic potash, and also to draw air through the whole arrangement at the conclusion of the analysis. It is generally sold with a bulb, but the simple form given answers equally well; and in fact almost any pieces of tube may be made to answer. It is fitted with a cork at *a,*

which is perforated to admit, somewhat tightly, the end of the potash-tubes, and the exit of the second potash-tube to be mentioned further on.

575. *Tube to contain substances.*—Any small test-tube with a well-fitting cork may be used, but I prefer on some occasions a tube closed with a glass stopper. This tube, with its contents, may be enclosed in the water-bath, fig. 52, until by ceasing to lose weight it is ascertained that all the moisture has been removed.

In the place of this tube, a far more generally convenient arrangement may be adopted. It consists of the two watch-glasses previously shown in fig. 61, but without the spring. The most convenient method of desiccating the pure substance for analysis, is to expose it in watch-glasses in the water-bath until nearly dry, and then to enclose it in stoppered bottles until required.

576. When it is intended to perform the analysis, the watch-glasses having been weighed, a quantity, a few tenths of a grain more than is required (where the substance is nearly dry), is introduced into the watch-glass, and the other being put under it, they are placed in the water-bath. The weight of the substance not quite dry, is written in one corner of the note-book,

b.d. **246·86**		
(1)　246·76		
(2)　240·51		
———		
6·25		

in the manner indicated above, with b.d. attached, indicating "before drying." This is merely done to enable the operator to remember the weight, so as to save time in the subsequent weighings; when the substance has remained half an hour or more in the bath, it is taken out, and the glass which was laid undermost is placed as a cover to the other during the cooling and subsequent weighing; when no more diminution occurs, even after

considerable exposure to 212°, the weight of the glasses and substance is put as at (1); and when the substance has been removed for analysis, the weight of the watch-glasses and any remaining particles is placed beneath it, as at (2); and the weight of the latter being deducted from the former, the amount of substance used is obtained. The method of placing the weighings in the note-book will be seen a little further on.

577. It saves much trouble and time if the weight of the watch-glasses and bottles used to contain the bodies to be analysed is marked on them with a writing diamond; for although after considerable use the number scratched on may no longer be absolutely exact, yet it enables the whole number of *grains and tenths* to be put at once into the balance-pans, and then only the hundredths have to be ascertained by trial.

578. *Corks for combustions.*—No trouble should be spared in selecting the very best corks for attaching the chloride-of-calcium apparatus to the combustion-tubes; the latter should be tolerably uniform in size, in order that the same corks may be frequently used; they must be filed somewhat conical, so that when pressed into the tube a slight shoulder may rise, as at *a a*, fig. 274, which adds considerably to the tightness of the joint.

Fig. 274.
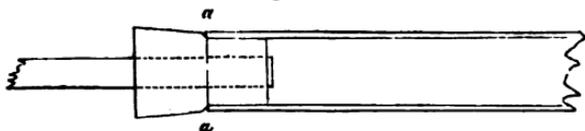
Where the corks are very bad, it is better to file them in such a manner that with considerable pressure they may be forced for about five-sixths of their whole length into the combustion-tube, as in fig. 275; for, as almost all the flaws are on the sides,

Fig. 275.
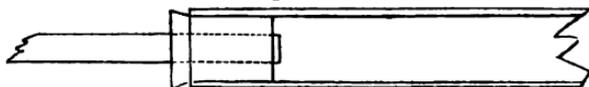
and the ends are generally free, a tight joint is almost certain to be obtained in this manner.

The chief fault of this method is, that unless the cork is well adapted to the combustion-tube, and, moreover, fits very tightly to the chloride-of-calcium apparatus, it is somewhat difficult to remove after the combustion. If the same chloride-of-calcium apparatus is always made use of, considerable trouble will be avoided, as all the corks will of course fit it. The hole for the reception of the latter is first made with a cork-borer, and afterwards finished with a rat-tail file. The tube should fit tightly into the cork throughout its whole length, and not merely in the middle with a gap appearing at the ends. Figs. 276 and 277 show, the former a well- and the latter an ill-fitting tube and
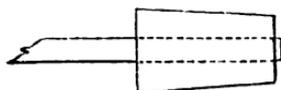
Fig. 276.	Fig. 277.
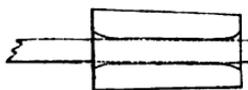
cork. It must not be considered that these details are unnecessarily minute, as much trouble and annoyance will be avoided by attending to every source of success, however trivial it may at a first glance appear.

579. Before piercing the corks, it is often advisable that they should be softened by pressure on the ends and sides, until they may be reduced to two-thirds of their length by the mere force of the finger and thumb; with the very best corks this is easily done. They are to be exposed in the water-bath *after* piercing, because by this means they dry in very much less time, and are therefore less liable to become brittle. When a cork has been used for an analysis, and therefore proved to be one which may be depended on, it should immediately be placed in a clean and dry wide-mouthed stoppered bottle kept for the purpose, as by this means, exposure for a quarter of an hour to the water-bath, when it has again come into requisition, will be amply sufficient to render it quite dry. In a laboratory where organic analyses are being constantly made, the convenience of a bottle of good combustion-corks, free from water, will not fail to be appreciated.

580. *Combustion-tubes.*—Although formerly much difficulty was experienced in procuring tubes sufficiently hard to bear the very considerable heat employed in combustions, without either blowing out or melting between the furnace-supports, no trouble is now found to arise from this source, and it is therefore scarcely ever necessary to wrap them round with a strip of sheet-brass or copper. Care should be taken in selecting combustion-tubes to procure them tolerably uniform in calibre, in order to save trouble in fitting the corks. Three sizes must, however, be procured, two for the analysis of solids, the other of liquids. The proper calibre and thickness of glass, are seen in figs. 278, 279, and 280. Fig. 278 shows the thickness and diameter of a tube
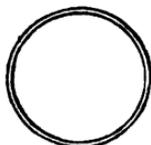
Fig. 278.	Fig. 279.	Fig. 280.

of the proper size for the combustions of fluids. Fig. 279 serves for ordinary solids; and fig. 280 is a small size, adapted for the combustion of bodies containing very little carbon, such as silver- and platinum-salts.

It is very common with beginners to use tubes far larger in diameter than is necessary; but this is improper in more ways than one. In the first place, it is much more difficult to make corks fit tightly into large than small tubes; and in the next, the former require an unnecessarily large quantity of oxide of copper or chromate of lead.

581. The ordinary length of a combustion-tube for the analysis of solid bodies which are burnt with tolerable facility, is 18 inches; but with fluids a longer tube is required, varying from 20 to 30 inches, according to their volatility; the more volatile, the longer the tube. A person accustomed to make combustions, will burn successfully with a shorter tube than an inexperienced or careless operator.

582. Beginners often have difficulty in making good combustion-tubes, but by attending to the following rules it is hoped that it will be found to be what it really is, the simplest and most easy operation imaginable. It must, however, be impressed upon the student, that in making well-shaped combustion-tubes out of the hard Bohemian glass, it is absolutely essential to have a powerful blowpipe-flame at command. Nothing answers better for this purpose than that alluded to at p. 44 as Herapath's jet. The Russian lamp may also be used, or the table-blowpipe, or any other sufficiently powerful apparatus. A tube being selected, twice the length of one combustion-tube, it is to be exposed to the flame until so soft that it yields with perfect ease to the most gentle motion of the fingers; it is then to be slightly drawn out, removed from the flame, and being grasped firmly, yet not too rigidly, with both hands, the backs of the latter being uppermost, the left-hand is then to be drawn downwards and towards the left side of the operator, while the right-hand is to be drawn upwards and a little towards the right, and rather away from him; all this must be done the instant the tube is removed from the flame, or it will become too cool for the successful performance of the operation.

By this means two tubes are made at once, of the form and in the position shown in fig. 281.

Fig. 281.
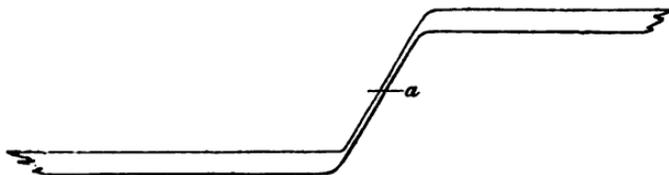
The flame is then to be directed at a for a second, to enable the tubes to be divided; the ends are then to be thickened a little, and the operation is completed. If successfully performed, the resulting instrument should approach closely in appearance to fig. 282. It is not advisable to have the tail longer than is there represented, as it renders it liable to be broken off by the slightest

carelessness, and endangers the analysis. The end which is to
receive the cork is now to
be gradually exposed to the
lamp-flame, until it has be-
come very hot; it may then
be heated at the edges with
the blowpipe until they are sufficiently rounded to prevent them
from cutting the cork when inserted, and also to lessen the chances
of fracture. If the tube has been cleaned before making the com-
bustion-tubes, it only remains to wipe it out with a wire carrying
a piece of chamois leather; a clean cork being then fitted into it,
it may be placed aside until wanted.
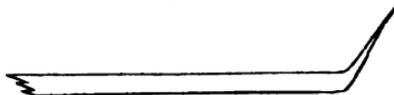
Fig. 282.

583. *Reduced copper turnings.*—In all analyses of substances
containing nitrogen, iodine, chlorine, or bromine, it is necessary to
place a few inches of bright metallic copper in the front part of the
combustion-tube. The metal may be obtained of the instrument-
makers in long thin filaments coiled into ringlets, which, when
heated to redness to remove any grease that may be on them, and
then reduced in a current of hydrogen gas, are admirably adapted
for the purpose required. The general method of proceeding has
already been described at p. 187, in the section on Crucibles and
Operations at high temperatures. The coils of copper are best
obtained by passing fine wire through a flatting-mill, and after-
wards curling the ribbon on a glass rod. The copper must be
heated to redness and then reduced, however clean it may appear
to be, as it is otherwise impossible to be certain of the absence of
organic impurities, such as oil, dust, &c. It is also convenient to
press the ringlets into a tube with a rammer, so as to make them
into plugs about an inch long, which may be introduced into the
combustion-tube with ease. The metallic surface produced by
reducing the oxidized surface of the copper is spongy and very
hygrometric; the quantity required for each analysis should
therefore be exposed in the water-bath for the same time as the
corks, and should be introduced as rapidly, and with as little
handling as possible, into the combustion-tube.

584. *Caoutchouc-tubes.*—The chloride-of-calcium-tube is con-

nected with the potash apparatus with a caoutchouc tube tied by
silk. Some works recommend the use of vulcanized india-rubber
tubes for this purpose, but as far as I am able to judge from my
own experiments, they are far more difficult to render tight by
tying with silk than those made in the laboratory in the manner
described further on. This does not arise from any imperfection
in the vulcanized tubes themselves, but from the fact that they
are less adhesive than the others; and even if tied with consider-
able care, the apparatus is frequently found unable to bear a
moderate pressure for a considerable time without indicating a
small amount of leakage. The caoutchouc tube should be double,
and fit the potash apparatus and the chloride-of-calcium-tube
with tolerable accuracy; the exit of the latter should, as has been
said, be of the same size as that of the former instrument.

585. *The combustion-furnace.*—This piece of apparatus is con-
structed of sheet-iron, and has had several improvements made
in it by different chemists, none of which are, however, of suffi-
cient magnitude to affect its principle. It is made of the form
seen in figs. 283, 284, 285, 286, 287, and 288, and should be at least
30 inches in length, in order to enable very long combustion-tubes
to be used when required, as happens with the analysis of very
volatile liquids, and in the estimation of nitrogen in the gaseous
state. It is merely a long narrow sheet-iron trough, fig. 283,
a section of which, across the line *a b*, has the form of fig. 284,

Fig. 283.
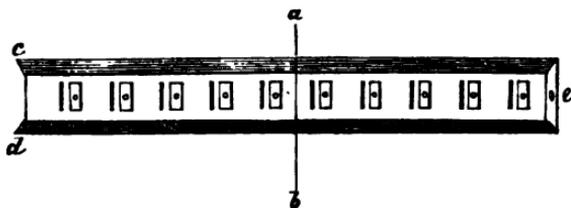
Fig. 284.

from which it will also be seen that the furnace is slightly hol-
lowed up at the bottom, in order that air may reach the fuel
through the slits (fig. 283), even when resting on a flat surface.
The posterior end, *c d*, fig. 283, is not closed in. At intervals

of about 2 inches all down the furnace are small sheet-iron supports, the top of each of which corresponds with the aperture, *e*, in the front end. These supports are intended for the combustion-tube to lie on during the ignition, and to prevent it from being cut by them when at a high temperature; they are slightly curved and bent over on the upper surface, as seen in fig. 285.

Fig. 285.

The other points connected with this apparatus will be alluded to in the description of the method of performing the combustion. The screen, figs. 286 and 287, is used to regulate the onward passage of the fire along the tube, and the other, fig. 288, to protect the cork.

Fig. 286.   Fig. 287.   Fig. 288.

586. *Operations previous to all analyses.*—It is of course imperative that the substance to be analysed should be in a state of purity, and no means of attaining this end should be neglected. If the body contains any inorganic constituents, either belonging to it or merely arising from difficulty in the purification, they should be carefully estimated before the organic analysis takes place. The weight of ash, if any, left on combustion in an open vessel, must be ascertained, and in some cases it is proper to submit it to analysis.

587. The state of the substance with reference to water must be known, and most solid bodies are to be dried at 212° Fahr. until they cease to lose weight. Where they are decomposed at this temperature, they must be dried *in vacuo* over sulphuric acid. Some bodies which retain water with great obstinacy, and bear a tolerably high temperature without decomposition, are to be heated in an oil-bath until they are sufficiently dry, the temperature being carefully regulated by a thermometer.

588. *Analysis of substances free from nitrogen.*—The apparatus

being prepared as directed in the previous instructions, a certain quantity of the substance is to be weighed out either into the bottle or watch-glass, and is to be kept in the water-bath until required. The combustion-tube is cleaned and made very hot, and a glass tube (kept for the purpose) is introduced into it, and air sucked out in such a manner as to remove every trace of moisture. Enough previously fused and pulverized chromate of lead to fill the tube to within an inch of the end, is then measured out and heated in a porcelain capsule over the gas-lamp for about half an hour; every trace of moisture will by that time have been expelled; during this operation the powder becomes darker in colour. When cold, a little is introduced into the combustion-tube, for the purpose of rinsing it out; this is rejected and placed among that which has been used, and is preserved for re-fusion. A little of the powder is then placed aside in the porcelain capsule, for a purpose which will be presently mentioned. This last-named portion should be about sufficient to occupy 1 inch of the combustion-tube. The rest of the chromate is then to be transferred to a small clean and dry mortar, with the exception of about an inch, which is allowed to remain in the tube. The substance the weight of which, and the bottle or watch-glass, has been previously ascertained to the third or, if gramme weights are used, the fourth place of decimals, is shaken into the chromate of lead in the mortar, and the vessel, with any remaining particles, is carefully placed aside until the proper time to reweigh it. The substance is now intimately mixed by gentle trituration with the chromate of lead, and the combustion-tube being taken in the right hand and the mortar in the left, by a species of screwing motion the mixture is transferred to the former, at each addition the tube being slightly raised with its open end upward, and a slight tap against the side of the mortar being given to make the powder descend in the tube; in this manner, by a very small expenditure of dexterity, almost the whole of the mixture will be transferred in a very few minutes to the combustion-tube; if neatly performed, the quantity remaining should not exceed a grain. The portion of chromate

R

which was directed to be placed aside in the porcelain crucible is
then turned into the mortar, and is triturated for a few seconds,
in order to rinse it out; this portion is then introduced into the
combustion-tube in the same manner as the first portion; any of
the chromate which has by this proceeding found its way into
the little tail at the closed end of the tube, is then brought into
its proper place by holding the tube horizontally, and giving its
front end a few gentle taps against the edge of the table; it is
then laid flat upon the latter, and being held by the tips of the
fingers of both hands, one at each end, a few taps are given to
make the powder lie in the tube in such a manner that a small
channel may exist from end to end, to allow of a free passage for
the evolved gases; the tube is then closed with a dry cork and
placed in its position in the furnace. It should at this stage of
the proceedings present the appearance of fig. 289, where a re-

Fig. 289.
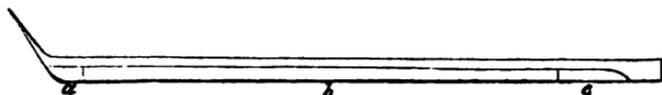
presents the portion of pure chromate first introduced, b the
mixture with the organic substance, and c the rinsings of the
mortar.

589. The previously weighed chloride-of-calcium-tube is then
placed in its proper position and pressed firmly in with its cork,
in such a manner that there is no chance of a leak occurring.
The potash-tube, the weight of which is also accurately known,
is then attached by means of the caoutchouc connector, which is
tied in two places with a strong and not too thin silk cord, having
a knot at either end. The potash-tubes rest on a pad of cotton-
wool enclosed in a flat silk bag or on a piece of folded linen, or
other convenient and soft support, the side, b, fig. 290, being
raised by means of a cork. The whole arrangement, which
should slightly incline from the posterior to the front extremity,
is seen by inspecting fig. 290, where the furnace is seen to rest
upon two bricks placed on their sides. It is an excellent plan,

although not generally adopted, to have the bottom of the fur-
nace slightly hollowed, the convexity being upwards, as seen in

Fig. 290.
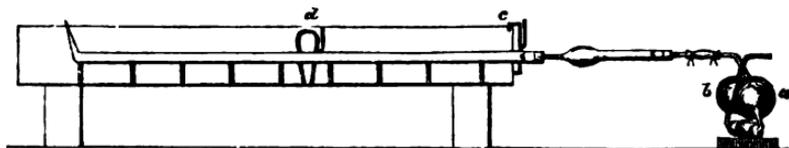
section at fig. 284, p. 359, as by this means it can be supported
upon a flat surface, the draught passing along the hollow formed
by the concavity, to the apertures in the furnace.

590. The potash-bulbs being placed as already mentioned, an
ignited piece of charcoal is held with the tongs near the bulb, *a*,
so as to expand the air in it, which immediately escapes in bubbles
through the solution and makes its escape. When a few bubbles
have passed, the coal is to be removed, and the potash-tube placed
level on its pad, until the liquid which was forced by the ex-
panded air to rise in *b* has returned, and the fluid has risen in
the bulb, *a*; at this point the apparatus is again inclined by
means of the cork as before, and left for at least ten minutes, to
see if the potash solution retains its position; if it does, it shows
that no leak occurs in the apparatus. It is usual to occupy these
few minutes by reweighing the bottle or watch-glass which con-
tained the substance, with a view to ascertain the amount used.
A charcoal fire must also be made, so as to afford an unlimited
supply of ignited coals for the combustion. If, on returning to
the apparatus, the fluid is found to retain its position, the analysis
may be proceeded with, but if it has shown the least symptom
of receding, so as to have a tendency to attain the same level in
both bulbs, the leak must be discovered and made good.

It is scarcely likely to be in the cork which affixes the small
tube to the chloride-of-calcium apparatus, because that has pre-
viously been made tight by sealing-wax; but, on the other hand,
it is not unlikely to be found to exist in the cork which connects

B 2

the last-named apparatus with the combustion-tube; it is proper therefore always to have two or three which fit ready, in order to enable the operator to replace the leaky one if required. The escape may also arise from imperfection in the caoutchouc connector, or the way in which it has been tied; and lastly, it may, although this is very unlikely, arise from imperfect sealing of the point of the posterior end of the combustion-tube.

591. Supposing the apparatus to be quite tight, and a plentiful supply of ignited charcoal at hand, the end, c, is to be covered with a screen, like fig. 288, p. 360, which hangs on by hooks formed by turning over the ends; this screen is intended to assist in protecting the cork from the heat of the furnace. It is proper to allow about 1 inch of the combustion-tube to project from the furnace, exclusive of the portion occupied by the cork, so that 1 clear inch shall be between the ignited portion of the tube and the commencement of the cork. If the latter is scorched, the analysis becomes worthless. On the other hand, the front portion of the tube must be maintained at such a temperature that no water can condense in it. Not the slightest difficulty will be found in satisfying these conditions.

The screen, fig. 287, p. 360, and d, fig. 290, being placed about 2 inches from the front of the combustion-furnace, red-hot charcoal is to be added carefully, so as pretty rapidly to raise that portion of the tube to redness. It is proper to notice, that many operators, even of much experience, are in the habit of using much more charcoal in combustions than is really required, they even filling the furnace nearly to the top. A dexterous analyst, however, may to a certain extent be known by the neat and careful manner in which the ignited charcoal is arranged, so as to thoroughly cover the tube, and heat it to redness, without using more than is necessary. This should be attended to, not so much on the ground of economy, as because much of the accuracy of the result depends upon the manner in which the combustion is conducted. Directly the front portion of the tube is red-hot, the screen is shifted backwards for about half an inch, and this is, in its turn, surrounded by the red-hot coals. As soon as the rinsings

are reached, the evolution of carbonic acid commences; and this may be easily known from the passage of the expanded air, by the different manner in which the bubbles affect the potash solution. Directly the evolution of gas slackens so much that the bubbles only make their escape at comparatively long intervals, the screen is to be again shifted backwards for a space equal to the first. It is a good general rule that the gas should not be driven over too rapidly for the bubbles to be counted.

592. In this manner the posterior end is at last reached, and then the screen is to be placed beyond the tail portion and charcoal added, so as to raise the whole tube to redness; if the mixture of the substance and the chromate has been properly made, the evolution of gas ceases very suddenly, and the fluid in the potash apparatus begins to recede; when this appears, the charcoal is to be removed from the end of the tube, and the point being broken off, a piece of dry glass tubing is to be placed over the point, and the suction-tube, fig. 272, p. 346, being attached to the potash-tube, a current of air is to be drawn for about half a minute through the whole apparatus; by this means all the carbonic acid remaining in the combustion-tube is drawn into the potash solution and absorbed. It is generally directed that the air drawn through should not possess any taste, but it is very seldom that this is absolutely the case, especially in the analysis of nitrogenized bodies; it may, however, be taken as a general rule, that the less sapidity is observed the more complete is the combustion.

593. The apparatus is now to be taken to pieces and placed aside to cool for a quarter of an hour or twenty minutes before being weighed. When the chloride-of-calcium apparatus is removed from the combustion-tube, a little water is sometimes observed to have remained in the narrow pipe, not having been drawn into the cotton-wool during the suction; if this occurs, it is to be drawn in by applying the lips to the caoutchouc connector before removing the latter from the chloride-of-calcium-tube; during this operation the latter is of course to be held vertically, the moist portion being uppermost.

Perhaps the neatest way of stating the result of the weighings in the laboratory-book is in the manner seen below, which gives the particulars of the analysis of the platinum-salt of picoline, an organic base found in bone-oil and some naphthas.   Two vertical lines being drawn, three spaces are obtained, and as the left-hand one is invariably appropriated to the substance, the centre to the potash-apparatus, and the right-hand space to the chloride-of-calcium-tube, it becomes unnecessary to write any description against them.

b.d. 246·860		
246·760	661·655	167·340
240·510	656·165	165·820
6·250	5·490	1·520

The left-hand column has, it will be seen, the number "246·860" with "b.d." against it; this was the weight of the watch-glass and substance before being dried; after drying, it amounted to 246·760; and when the substance had been removed, the glasses and any adherent particles weighed 240·510; the difference is the substance used, viz. 6·250 grains.   The potash-tube before the experiment weighed 656·165, and after, 661·655; the difference, 5·490, is the carbonic acid condensed.   The third column shows the weight of the chloride-of-calcium-tube before and after the experiment, and gives 1·520 as the water condensed in it. The quantity of carbonic acid multiplied by 3, and the product divided by 11, gives the amount of carbon; and the water produced, divided by 9, gives the hydrogen in the substance analysed. On performing this with the numbers given above, and converting the results into per-centages, we have

Carbon . . . . . . 23·96
Hydrogen . . . . 2·70

as the result of the analysis, which agrees very closely with the theoretical quantities, which are

Carbon . . . . . . 24·07
Hydrogen . . . . 2·67.

A neater method of calculating the result of the analysis is to multiply the substance by 11 and the carbonic acid by 3, and then divide the latter product by the former. It is obvious that to multiply the substance by 11, it is merely necessary to repeat the same number, placing it underneath, and advancing the bottom line one figure to the left. In making the calculation thus, it occupies little space, and may therefore always be made in the note-book underneath the results of the combustion, and is thus preserved for the purpose of verification.

It sometimes happens, especially in warm weather, that the film of moisture which existed on the bulbs in the first weighing does not deposit readily after the combustion, in consequence of the apparatus becoming heated. In this case the potash-tube, corked at both ends, must be kept in a clean dry place until it ceases to increase; this sometimes takes nearly an hour.

594. In good analyses the carbon is generally a little below the real quantity, generally from ·1 to ·15 of a per cent., and the hydrogen slightly in excess to about an equal amount. In carefully performed analyses upon perfectly pure substances, exceedingly correct numbers may be obtained, as in the above result, where the loss of carbon is only ·11 of a per cent. and the excess of hydrogen ·03.

595. With reference to the quantity of substance to be used, it is rather difficult to give a rule which shall hold in all cases. It is, however, seldom that a greater quantity of a solid than 9 grains, and less than 5, is used; 6 grains generally form a very convenient quantity. With fluids it is better to burn four or five with low carbon, and about three where a large per-centage of that element is present. Much, however, depends upon the volatility and combustibility of the substance, and the above quantities can merely be regarded as approximative. Perfectly accurate analyses of very volatile fluids may be obtained upon 2·5 grains if the carbon is high.

596. *Analysis of substances containing nitrogen.*—When substances containing nitrogen are burned with chromate of lead, some of the higher oxides of nitrogen are generally formed, which,

being absorbed by the potash solution, give rise to errors in
excess in the carbon determination.   Where the amount of nitro-
gen is very small, as in platinum-salts, for example, a layer of
reduced copper turnings, placed in the anterior portion of the
combustion-tube and kept at a bright red heat during the analysis,
will decompose the whole of the acid gases, the oxygen combining
with the copper, and the nitrogen being evolved in the gaseous
state, which passes unabsorbed through the potash apparatus.
When the per-centage of nitrogen is more considerable, it is dif-
ficult, and sometimes impossible, to decompose the whole of the
acids formed, and then it is necessary to use oxide of copper as
the substance to yield the oxygen necessary to convert the carbon
of the substance into carbonic acid.   In fact, oxide of copper is
in many analyses equally convenient with chromate of lead, its
chief disadvantage being its proneness to absorb moisture during
the mixture with the substance in the mortar.   This tendency
decreases as the oxide becomes denser from being repeatedly used.
It is best prepared by heating the nitrate to dull redness, being
stirred frequently with a copper or iron rod, preferably the former.
It is used both in fragments and powder.   The fragments are
best for the combustion of liquids, as will be described further on.
The used oxide may be made as good or even better than before
(in consequence of its becoming more dense and less hygrometric),
by moistening it with dilute nitric acid and heating to redness.

597. To perform the analysis, a combustion-tube is selected of
the proper length ; it is then filled as far as will be required with
the oxide : this serves as a measure of the quantity to be used.
The oxide is then put into a Hessian crucible, which is covered
by inverting another over it.   After being heated to dull redness,
it is to be allowed to cool until it will not burn the cloth with
which it is to be held in the hand.   The oxide is then transferred
by a clean dry funnel of brass plate, into a large dry tube, capable
of holding more than is required ; it is then corked, and put aside
until cold.   The substance is to be weighed in a long glass tube,
and about an inch of oxide having been rapidly inserted into the
combustion-tube by means of the funnel before alluded to, a por-

tion of the substance is added, and then about 2 inches more oxide. The two are then mixed with a copper wire, bent at one end into two turns of a screw; by alternately pulling the latter up and thrusting it down through the mixture, at the same time turning it, the thorough incorporation of the two is soon effected. About 3 inches more oxide, and another portion of substance is then added, and the operation repeated. One more performance of this procedure finishes the operation. The rest of the oxide is then poured into the tube, and the metallic copper thrust in with the assistance of a perfectly dry glass rod; and after tapping the tube, to clear a channel for the gases, it is ready to be connected with the chloride-of-calcium-tube, &c.

598. By proceeding in the manner above directed, not only is the hydrogen obtained remarkably correct, but the whole proceeding occupies little time, and the arrangement is extremely convenient. The use of the brass funnel will be found greatly to facilitate the proceedings. It should be made with a very large opening in comparison with funnels generally; so large, in fact, that it will only just enter the combustion-tube.

It is better to mix the substance and oxide by degrees as directed, than to add oxide, then substance, then oxide, &c., until the tube is filled, and after all is inserted, to mix with the screw, because it is not so easy in the latter case to make the wire traverse the tube to the further end through the long column of oxide of copper. The combustion should be made very slowly.

599. *Analysis of liquids.*—Before proceeding to analyse liquids, it must be carefully ascertained that they are really in the condition in which they are supposed to exist. Many of them have a great tendency to attract moisture from the air; others become oxidized and otherwise altered by keeping. Where this is the case, it is better to digest them for a sufficient time over some substance having a powerful tendency to absorb water, such as chloride of calcium, solid caustic potash, quicklime, &c. The choice of substances must of course depend upon the habitudes of the body under examination. If the quantity at the operator's disposal is very limited, the retort with a tube, by which to

B 5

insert the fluid without soiling the neck, fig. 205, will be found invaluable. They may be made with great ease from pieces of waste tubing, old retort-necks, &c. When the fluid to be ana-lysed is tolerably volatile, and does not leave a residue of carbon on distillation, it may be inclosed in little glass bulbs. These are made from quill-tubing, by drawing it out as in fig. 291.

Fig. 291.

One of the tails is to be removed at a, and the enlarged portion is to be heated in the blowpipe-flame, and expanded into a bulb in the manner represented in fig. 292. The open end is then to be

Fig. 292.
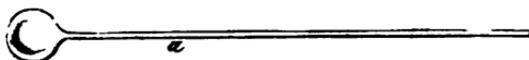
held for a second in the lamp-flame, to round the edges of the aperture, and thus lessen the danger of fracture.

The best method of handling these delicate instruments is by means of a pair of small pincers with long beaks, to which are adapted pieces of cork in order to prevent the glass from being crushed. Being thus supported at about a, fig. 292, the globe is to be heated for a second in the lamp, and the point is imme-diately plunged under the surface of the fluid, a part of which enters on cooling and consequent contraction of the air; the portion which has entered is made to boil, and if the point is now again plunged beneath the surface of the fluid, the vapour con-denses, and the bulb becomes very nearly filled. It is now usual to seal up the apertures and reweigh the bulbs, to ascertain the quantity introduced, the necks being broken off before dropping them into the combustion-tube; but if the operations are per-formed with moderate celerity, this sealing is quite unnecessary, except in the case of exceedingly volatile fluids. The bulbs are dropped into the tube among the oxide. An inch and a half of

the latter is first introduced, then one bulb, then three or four inches more oxide, then the other bulb, and the tube is afterwards filled up with oxide, so that at least 12 or 14 inches shall be in front of the last bulb. Two of the latter are generally used, but in some cases three are more convenient.

600. Where the fluid cannot be distilled without leaving a residue, as is the case with most of those having a very high boiling-point, a loss would take place if the bulbs above alluded to were used, a film of carbon remaining in them after the combustion. Under these circumstances it is necessary to weigh the fluid in a small glass tube, supported upon the balance-pan by a perforated cork, or, preferably, by the little instrument represented in fig. 293, which may easily be made by any person out of a piece of tin plate. It is shown supporting in a vertical position the tube holding the fluid to be analysed. The size may also be the same. A layer of oxide being introduced into the combustion-tube, the small one containing the fluid is dropped in, and the rest of the oxide is inserted. The little vessel must have its opening towards the anterior portion of the combustion-tube, in order that the oxide of copper when introduced may fill it, and displace the fluid.

Fig. 293.

601. Where the liquid to be analysed is decomposed by heat, so that it is impossible to introduce it into the bulbs in the usual manner, two resources present themselves: either the use of a tube as just directed, or drawing it by suction into a weighed bulb, with two narrow pipes, like fig. 291, and again weighing.

The analysis of fluids requires a few precautions, which it is necessary to describe. In the first place, the advance of the ignited charcoal must be very gradual, especially if the liquid is particularly volatile. When the first bulb is nearly reached, and the whole of the front portion of the tube is in a state of ignition, a piece of red-hot charcoal may be held near the former, so as to expel a portion of its contents; this must be done very carefully, the eye being directed constantly to the potash apparatus to see if the bubbles come over too fast. It is essential, as soon as the

distillation of the fluid commences, to keep a red-hot coal dur-
ing all the remainder of the analysis close to the point of the
combustion-tube, to prevent condensation there, as if this occurred,
it could not be expelled afterwards without a sudden burst of
vapour which would endanger the result.

602. I have so far modified the process for burning volatile
fluids, that they require no more time and, what is of great im-
portance, far less attention than is necessary even for an ordinary
solid.   For this purpose I place all the fluid in one bulb and drive
it all out at the very commencement of the analysis into a column
of about 30 centimetres of cold oxide of copper; this latter por-
tion is never directly heated until the end of the analysis, the
fluid being volatilized by the heat conducted by the oxide.   Of
course I pass oxygen at the last over the reduced metal to remove
any carbon combined with it.   The tube is therefore arranged thus:
at a, fig. 294, I place a small plug of recently ignited asbestos
about 5 centimetres long, then a mixture of fused and powdered

Fig. 294.

chlorate of potash and fine oxide of copper at b (about 15 centi-
metres), and then 5 centimetres of asbestos followed by 10 centi-
metres of coarse oxide of copper.   The substance in one bulb is
placed at i, then the tube to h is filled with granular oxide of
copper of about the coarseness of dust shot, and finally, at g, I
place a few centimetres of metallic copper.   I commence by heat-
ing the tube to redness at a and between the screens e and f;
when fully red, I fill with live coals the space between the screens
c and d; the whole of the fluid is thus immediately driven amongst
the oxide of copper occupying the space between the screens
e and d.   In a short time this oxide becomes sufficiently hot to
cause a slow and perfectly steady distillation of the fluid over the
red-hot column of oxide from e to h, where it is burned.   No
further attention is requisite until the carbonic acid ceases to

enter the bulbs, when the screen, *e*, is removed back, but it is always found, if the fluid is pretty volatile, that very little remains.   When the tube is red-hot from *c* to *f*, the oxide of copper and chlorate are slowly heated to redness.   Combustions made in this manner I have seldom found to fail in giving perfect results. One great advantage of this method is, that if the space from *e* to *d* is of the proper length, there is no fear of either a sudden rush of gas or of the combustion being tediously slow.

603. *Analysis of fusible solids.*—Substances which are quite solid at the ordinary temperature, but which melt at a moderately elevated one, may be weighed in little pieces, which are to be dropped into the combustion-tube at intervals, chromate of lead or oxide of copper being allowed to occupy the spaces between the fragments.   On warming the tube, they melt and become diffused throughout the fragments in a state well adapted for their combustion.   If care be taken to heat very gradually, such bodies as paraffine may be burnt without any melting for the purpose of diffusion.

604. Some viscid and therefore troublesome substances may be weighed upon small flat pieces of glass, which are to be dropped in in the same manner as the bulbs, taking care to diffuse the matter to be burnt by warming the tube.

Small trays are more convenient and much neater for containing viscid bodies for analysis; they are easily made by splitting small glass tubes down both sides with a pastille* in the direction of their longer axis, and then drawing them out and upwards at each end in the blowpipe-flame as in fig. 295; the points at *a* are then

| Fig. 295. | Fig. 296. |

to be removed, so that the tray when finished resembles fig. 296. They are to be weighed, both empty and with the substance.

* The method of making them will be found in the section on Glass-working.

About an inch of oxide of copper or chromate of lead is to be introduced into the posterior end of the tube, then the tray and substance, and then the remainder of the chromate, &c. Sometimes, however, it is better to divide the substance between two or even three trays, which are to be separated from each other in the combustion-tube by a few inches of oxide or chromate.

605. *Analysis of substances difficultly combustible.*—There are many ways of effecting the conversion of the carbon of refractory bodies into carbonic acid, where oxide of copper or even chromate of lead are incapable of doing so completely. The last-named substance has its oxidizing power greatly increased if a little pure dry bichromate of potash be mixed with it.

A common method of effecting the combustion of very refractory organic substances, is by passing a current of oxygen gas through the tube, either during the whole time or only at the conclusion of the operation. The manipulation in the former case will be evident from the description of Hofmann's gas-furnace. Sometimes the oxygen is liberated from a few small fragments of fused perchlorate of potash placed among the oxide of copper, which is first introduced into the posterior end of the combustion-tube. When the latter has been heated to redness, except the very last portion, the heat is gradually applied to the perchlorate, in such a manner that a steady uniform series of bubbles may pass through the potash apparatus. It must be remembered that this process is not applicable in the case of nitrogenized compounds, for the same reason that chromate of lead is inadmissible; but, fortunately, it is seldom that bodies containing nitrogen are difficult to burn, the greater number being particularly easy of combustion. It is true that substances are sometimes met with containing considerable quantities of nitrogen, and yet very difficult to completely burn; we are then between two difficulties; for if it be attempted to burn it in oxygen, an excess is obtained, and if we do not use the gas, a deficiency. The difficulty disappears if we resort to combustion in a current of oxygen, taking care, *after* the preliminary heating of the tube for the purpose of removing moisture, to insert a considerable column of

reduced copper in the anterior portion of the combustion-tube. In this way all the nitrogen previously oxidized will be reduced and escape in the free state.

606. The following method of burning organic bodies in a current of oxygen gas is due to Laurent*, and may sometimes prove a convenient arrangement.

Fig. 297.
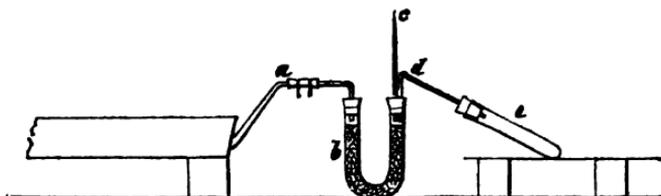
The posterior end of the combustion-tube has its point, a, fig. 297, attached by means of a caoutchouc connector with the U-tube, b, one limb of which is filled with fragments of caustic potash, and the other with chloride of calcium. The limb furthest from the combustion-furnace has two tubes inserted into it; one of these is connected in the usual manner with a hard glass vessel, e, containing the chlorate of potash. The latter rests upon some coarse wire trellis forming a grate, upon which the charcoal used to heat the chlorate is supported. The tube, c, serves as a safety-tube, as, if the current should prove too rapid, it enables us by breaking the point to arrest it at any moment; it also permits a current of air to be drawn through the entire apparatus at the end of the analysis in order to displace the oxygen; the point being broken off, the air is to be sucked out with a tube like that shown in fig. 272.

607. Whenever oxygen is passed through the apparatus, or the substance analysed contains nitrogen, the bubbles of dry gas passing through the potash-bulbs remove a considerable amount of moisture; this error, by diminishing the weight of the last-mentioned instrument, causes an apparent loss of carbon. To

* Ann. de Chim. et de Phys. [3] xix. 360.

obviate this, it is merely necessary to attach to the end a small tube filled with fragments of caustic potash. If made very small and light, it may be weighed with the bulbs, and thus its use will not involve extra trouble. Its shape and size will be seen by reference to fig. 298. Where great accuracy is desired, the use of this tube should never be neglected.

Fig. 298.
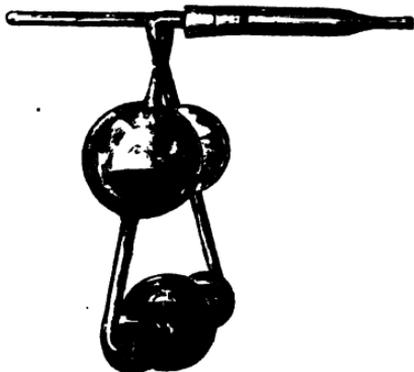
In the analysis of substances very difficult of combustion, it is sometimes a good plan to have 3 or 4 inches of oxidized copper turnings in the front part of the combustion-tube; the large surface of oxide thus exposed to the vapour is very effectual in rendering the combustion perfect. It is especially useful in the combustion of liquids when no granular oxide is at hand.

SPECIAL MODIFICATIONS.

608. *Substances containing sulphur.*—If sulphur is present, it is necessary to interpose a tube containing peroxide of lead between the chloride-of-calcium apparatus and the potash-bulbs. It is better to make the combustion with chromate of lead in this case, when, if the quantity of sulphur is small, the peroxide of lead may be dispensed with.

Substances containing chlorine, iodine, or bromine, should be burnt with chromate of lead, a few inches of metallic copper being placed in the front of the combustion-tube. The latter precaution is particularly essential where iodine is present.

609. Where chlorinated substances are burnt with oxide of copper in a stream of oxygen, it is also necessary to use copper turnings, the current of oxygen being arrested immediately on its being seen that the copper in front of the tube is becoming oxidized.

610. Excessively volatile liquids are very troublesome to burn in the ordinary manner; the tension of their vapour lowers the potash when the tightness of the junctures is being tried, and makes it impossible to ascertain the fact with certainty.

In addition to this, a portion of the vapour escapes combustion when the front of the tube is being heated. It is true that this might be avoided by the method said to be adopted by some chemists, namely, dropping the bulbs containing the liquid into the tube in a sealed state, and applying just sufficient heat to burst them by the expansion of the *liquid*, not by the *vapour*; but this is an operation of such nicety, that few would care to risk the chance of creating vapour which might not only burst the bulb but perhaps eject the fluid from the potash apparatus.

The analysis of such fluids may, however, be effected by introducing a weighed portion into a very small tubulated retort, made in the manner described in the section on Glass-working. It is

Fig. 299.
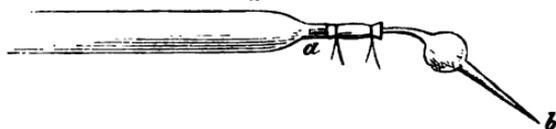
connected by a small caoutchouc tube with the anterior portion of the combustion-tube, which is drawn out for the purpose. It is sealed at both ends when affixed to the combustion-tube, and when the whole of the oxide of copper is heated to redness, the point, *a*, fig. 299, is broken by pressing it against the side of the combustion-tube. The fluid is made to distil with extreme slowness by the approach of a coal held at a considerable distance, or other convenient means; and when all the fluid has volatilized, the point, *b*, of the tubulature is removed, and air is drawn slowly through the whole apparatus, to remove the last traces of vapour remaining in the retort, and the carbonic acid is at the same time drawn into the potash-bulbs.

611. *Ultimate analysis of gases containing carbon.*—Many gases containing carbon may very conveniently be analysed by the method of organic analysis. To effect this, they are made to stream

slowly over ignited oxide of copper, the products being received in the usual manner. It is obvious, that, although the absolute quantity of gas burnt is unknown, the relative proportions of carbon and hydrogen may be found, and the constitution of the gas ascertained.

M. Regnault describes an instrument of very simple construction, which enables given volumes of gaseous hydrocarbons to be burnt, so that if the specific gravity of the gas has been previously ascertained, the weight of the bulk analysed is easily calculated. In fig. 300, *a b* represents the tube to contain the gas to be analysed; it is capable of containing between 400 and 500 cub. cents. At the top, a small tube, *c r*, is attached, bent at right angles, and cemented at *r*, to a small steel stopcock. At its lower end it is again contracted, so as to form a narrow tube, *a f*, which is cemented into a cast-iron apparatus of somewhat peculiar construction, which is also one of the chief features in M. Regnault's gas-analyzing apparatus, the description of which is quoted at p. 324. This cast-iron apparatus forms a three-way cock (R in the engraving), having a second piece, *g*, intended to receive the glass tube, *g h*. This stopcock is seen in section in figs. 301, 302 and 303, which show the three positions it is capable of assuming.

Fig. 300.
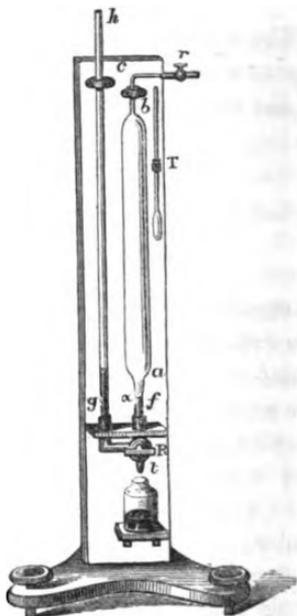
The first of these indicates the method of opening a communication between the pipette, *b a*, and the tube, *g h*. In the second, the tube, *g h*, and the pipette communicate; and, at the same time, *t* being open, the mercury is allowed to escape, for the pur-

pose to be mentioned presently. The third position of the cock is such that the pipette, $b f$, alone has communication with the air, the mercury escaping from it, while that in $g h$ remains.

Fig. 301.   Fig. 302.   Fig. 303.
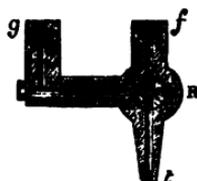
612. To fill the instrument with mercury previous to admission of the gas, the stopcock must be placed in the first position, so that although the pipette and the tube, $g h$, communicate, no mercury can escape by the inferior orifice, t. The metal is then to be poured in at h, until the pipette and $g h$ are full, which is known by the mercury escaping at r. When this is done, the stopcock is brought into the third position, which enables the mercury to escape from t; it is carefully collected in a bottle and weighed, as by this means the bulk of the pipette is ascertained. The metal must not be permitted to fall below a, there being a mark at that point. To fill the instrument with the gas to be ana- lysed, mercury is again introduced as before, and the vessel pro- ducing the gas is attached, by means of a caoutchouc tube, with the stopcock, r. As the gas enters, mercury escapes; but as soon as it has fallen a little below the mark a, r is closed, the three- way cock is brought to the first position, and mercury is poured in at h with extreme care, until it exactly reaches the mark a. The difference in the height of the mercury in the two tubes is then to be ascertained by measurement, and being added to the height of the barometer, the pressure of the gas in the pipette is found, and the temperature is taken by the thermometer, T, fig. 300.

613. The anterior end of the combustion-tube being connected with the stopcock, r, mercury is to be poured in at h to expel the gas, which is thus forced over the oxide of copper, the products

being received in the ordinary way. It should be remembered, that as mercury is used to drive the gas forward, it must be added in very small portions, or the combustion will be imperfect, from the rapidity of the passage. The latter is also to be regulated by the very cautious opening of *r*, which for this purpose should have a small bore.

614. *Estimation of nitrogen.*—A great number of methods have been invented for the determination of the nitrogen in organic substances; of these there are four which are more particularly used, as having been found to possess the important attributes of precision and convenience in execution; they are those of Varrentrap and Will, Liebig, Bunsen, and Dumas; the others will merely be alluded to, as the space allotted to organic manipulation will not permit the details of all the processes to be entered into.

615. *Estimation of nitrogen by the method of Varrentrap and Will.*—In this process the organic body, which must not be a nitrate, is burned with soda-lime, the ammonia which is evolved being condensed in dilute sulphuric or hydrochloric acid in a tube of the form seen attached to the combustion-tube in fig. 304. The details of the process belong to works on analysis, but there are points in the manipulation which it is necessary to mention. If much nitrogen is present, it is better to add a little pure sugar or starch to the substance to dilute the ammoniacal vapours and prevent the absorption taking place with such rapidity as to cause

Fig. 304.
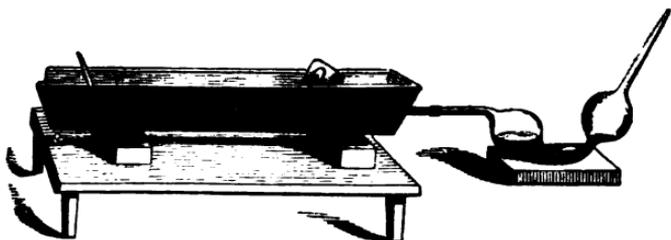
the fluid to enter the combustion-tube. It is advisable always to add a little starch or sugar, because if the organic matter is small in quantity the gases evolved from the starch carry the ammonia

forward into the bulbs. Where hydrochloric acid is used to con-
dense the ammonia, it is usual to convert the latter into the pla-
tinum-salt, from the weight of which the per-centage of nitrogen
or ammonia may be calculated. In Peligot's modification of the
process, the amount of ammonia is calculated by the alteration in
strength of the acid after the process. The neutralizing solution
used to ascertain the strength after the operation, is a solution
of lime in sugar-water, which, if carefully preserved in a well-
stoppered bottle, will last unimpaired for a considerable time.

616. The standard acid is measured out in each experiment
from a pipette made to contain a certain quantity up to a mark
upon the narrow portion. For the ordinary size of Horsford's
nitrogen-tube, as seen in fig. 304, a cubic inch answers very
well.

617. In the 'Chemical Gazette' for April 1847, a form of
nitrogen-tube is described by Mr. Alex. Kemp, which is intended
to render the recession of the acid into the combustion-tube im-
possible; its mode of action is seen by reference to fig. 305. It

Fig. 305.
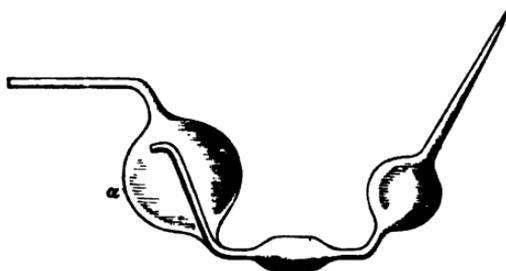
is plain that if regurgitation should take place, the acid merely
enters the bulb, *a*, without finding its way into the combustion-
tube. The acid for condensation is chiefly contained in the smaller
bulb, a little being, however, allowed to enter the other. On the
5th of the same month, Mr. Warren De la Rue described a similar
instrument which he had been in the habit of using for eighteen
months previously; the same idea appears, therefore, to have

suggested itself to both these gentlemen. If the precaution of mixing sugar with the substance be adopted, this modification becomes unnecessary, and it is better to avoid its use, from the fact that it is not only more fragile, but also more expensive than the other; and, what is of more importance, requires more time to thoroughly remove the acid solution of the ammonia. As the commercial soda often contains some nitrate, it must be examined for that salt before use, and, if it is present, the sample must be rejected, or the amount of error may be ascertained by experiment and allowed for.

618. Where nitrogen determinations are of every-day occurrence, as in laboratories where soils and manures are constantly being analysed, the glass tubes are frequently dispensed with, especially where extreme accuracy is unimportant, and gun-barrels are substituted. The breech having been removed, it is closed with a cork as at *a*, fig. 306, a tube passing through it to allow

Fig. 306.

of a current of air being drawn through at the end of the operation to sweep all the ammonia into the acid. This tube is closed by fusion previous to the combustion, and at the termination the point is broken off. The substance and soda-lime are prevented from passing beyond *b* by a plug of recently ignited asbestos; the mixture extends from *b* to *c*; from *c* to *d* is occupied by the rinsings of the mortar, and *e* is another asbestos plug. The tightness of the cork which attaches the bulb-apparatus to the tube, and also that at *a*, must be ascertained before commencing the combustion. To effect this, it is necessary to blow air in at *f* by the mouth, so that when the pressure is removed by taking away the lips, the air forced in, in endeavouring to escape, raises the fluid in the bulb, *g*, in the manner shown in the engraving;

if after ten minutes it has not receded, the joints may be considered tight.

619. *Estimation of nitrogen by the qualitative method of Liebig.*— This mode of analysis, which depends upon examining at several stages during the combustion, the relative proportions of carbonic acid and nitrogen gas evolved, does not require any very special manipulation. The substance is burned with oxide of copper and copper turnings, and the evolved gas is conveyed into several tubes filled with mercury; they are one after the other placed over the evolution-tube, which must be made to turn up at the end, so as to throw off the gas into the tube without fear of its escaping in the manner alluded to at § 523. The graduations on the tubes, so that they are all equal, are not necessarily of any particular value, as the result merely depends upon the relative volumes of the nitrogen and carbonic acid. It is absolutely essential to prevent the formation of binoxide of nitrogen during the combustion; and as it may make its appearance at any time while the analysis is going on, it is necessary to examine the gas at several epochs. This may be done by allowing it to half fill the tube, and then raising the latter out of the mercury and removing the finger partially from the bottom, so as to permit the mercury to escape; by this means, if only a trace of the binoxide is found, red fumes will be perceived on looking down the tube through its whole length, as directed in some cases of fluid testing. When a sufficient number of tubes have been filled with the gas (seven or eight are generally directed, but four or five will answer the purpose in a well-managed analysis), they are to be inserted one at a time into a glass vessel of the form of fig. 307, containing mercury. The level within and without being equalized, the volume is to be estimated. A pipette, fig. 308, is to have a little of the combustion potash solution introduced, and having the end inserted under the surface of mercury, is to have a little drawn in to fill the bend up to the line, *b.* The curved portion being introduced under the edge of the tube in the cylinder, as in fig. 307, a little of the solution is to be injected by slight blowing at *a,* while the point of the pipette is beneath the edge. The alkaline ley

absorbs the carbonic acid very readily, but the action may be hastened by raising and lowering the tube in the cylinder. It has been previously remarked that especial care must be taken in manipulating tubes and other vessels filled with mercury, as the weight of the metal increases their fragility. In the present case this danger may be avoided by pressing the lower edge of the tube against the cylinder while raising it up and down. The proportions of carbon and nitrogen are estimated by the difference in the volume before and after the absorption.

Fig. 307.

Fig. 308.

It must be remembered, that where the number of atoms of carbon in the substance are more than eight times that of the nitrogen, the method ceases to afford reliable results.

620. *Determination of nitrogen by the method of Bunsen.*—This process, which is a modification of the last, is susceptible, like all Bunsen's methods of research, of really extraordinary accuracy, and can, moreover, be worked out on very small quantities of substance. In fact this minuteness is necessary from the very nature of the process. A piece of good combustion-tubing is selected rather thicker in the glass than that ordinarily used for organic analyses : it should be about ⅝ths to ¾ths of an inch in internal diameter. It is drawn out like *a*, fig. 309, and the part *b*, fig. 310, is held in the blowpipe-flame, being constantly turned until the glass has thickened very much. About half a grain of substance is then well mixed with about 100 grains of oxide of copper, some turnings (like those usually used in nitrogen analyses) are then introduced, and the tube is drawn out again at the other end, so as to allow a space of at least 7 inches in the wider portion. The following apparatus is then arranged. The Woulfe's bottle, A, contains zinc and water for the preparation of hydrogen gas, which passes through
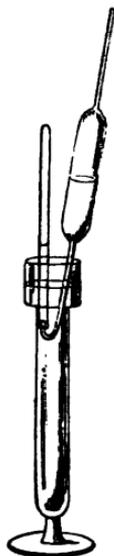
sulphuric acid in the bottle, B, by which means it becomes dried. From thence it passes by the glass tube into the caoutchouc connector, c, which contains a piece of glass rod, the object of which will be rendered apparent directly. The tube prepared as above is connected at one end with the caoutchouc-tube, c, and with an air-pump by another. Sulphuric acid is now introduced by the thistle-funnel, and the tap, p, of the air-pump is left open to permit the escape of the gas. When the hydrogen has displaced all the air, which will be in about five minutes (as the current should not be too strong), the cork of the gas-bottle is removed to prevent the passage of the gas, the tap, p, is closed, and the caoutchouc-tube, c, is tied to the piece of rod contained in it, so as to

Fig. 309.   Fig. 310.
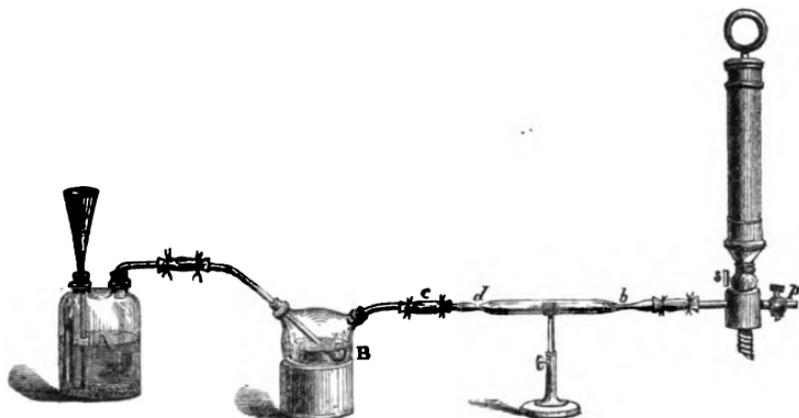
render it tight. A slight vacuum is produced by making a stroke of the piston, and the tap, s, is to be turned off. A strong blowpipe-flame is now made to play upon the parts d and b which are to be closed, the operation being greatly facilitated by the vacuum.

The iron mould in two pieces, seen in fig. 312, is then to be filled with a paste of plaster of Paris, great care being taken to

Fig. 311.

s

disperse the air-bubbles by stirring. The tube containing the substance is now imbedded in the plaster, and the other half placed

Fig. 312.
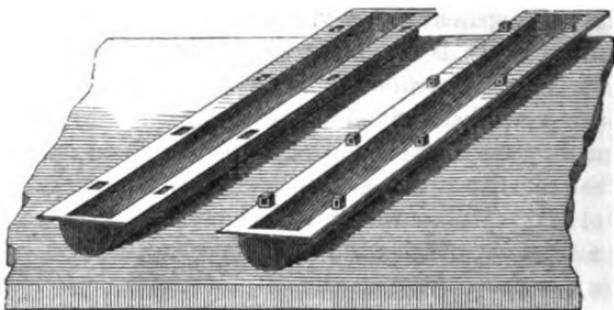
over it as soon as it acquires sufficient consistence to permit of being inverted without the paste falling out. The two are then wedged together, as in fig. 313. The mould is perforated in many places

Fig. 313.
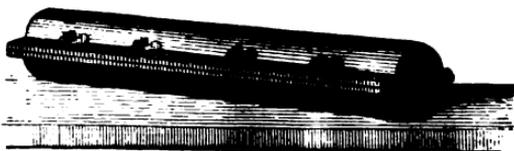
to permit the escape of the aqueous vapour. It is proper now to place the whole arrangement in a very hot place, such as the top of the table-furnace, fig. 1, until the greater part of the water is expelled. The moulds are then placed in a furnace and heated to dull redness for about one hour. When the heating is over, the mould should be removed and placed upon the floor of the ash-pit, some cinders being above and below it, and thus allowed to cool until it may almost be handled; it is then to be uncovered and put in the hottest part of the sand-bath, and gradually removed into the cooler portion until it is quite cold. The tube being now removed, the point is to be broken under a graduated tube filled with mercury. The gas consists of a mixture of car-

bonic acid and nitrogen, the bulk of which is to be estimated, but not until saturated with moisture, which may be done by allowing a drop of water to pass up under the mercury. In measuring the gas, it is better to take the height of the column of mercury inside the tube above that in the trough by means of a pair of compasses, instead of attempting to level the mercury by depression*. To remove the carbonic acid a ball of caustic potash is used, which is cast on a wire by means of a bullet-mould; the potash is moistened by breathing on it before being introduced, which latter operation must be carefully done to prevent air gaining admittance at the same time. Of course the indications of the thermometer and barometer are observed at each epoch of the process. After it has been ascertained that no further diminution of the gas takes place by absorption of the carbonic acid, the first ball of potash is removed and a second is substituted; but the latter one must not be moistened, as its object is to remove the moisture already present. The volume is again ascertained, and the usual corrections being made, the proportion in equivalents is found by calculation.

621. *The absolute method of determining nitrogen.*—This method has been divested of its complexity since the time when it was first introduced, so that it has become an extremely simple process, and one that does not require any great amount of skill in the performance. A combustion-tube is prepared without a point, being rounded at the posterior end. It should be from 2 feet to 2 feet 6 inches long, and be filled as in the engraving.

Fig. 314.
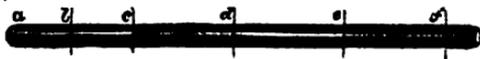
From *a* to *b* is bicarbonate of soda; *b* to *c*, oxide of copper; *c* to *d*, the mixture of the substance with oxide; *d* to *e*, coarse grains of the oxide; and *e* to *f*, metallic copper. The temperature required in the combustion, combined with the pressure of the mercury,

* The measurement will be far more accurate if a cathetometer is employed.

s 2

would almost infallibly blow out the tube if the precaution was not taken of wrapping a piece of sheet brass or copper round it. The end containing the bicarbonate need not be covered, however, as it will not be so intensely heated during the operation.

622. The apparatus is arranged for the combustion as seen in fig. 315, the delivery-tube being connected with the combustion-

tube by a perfectly sound cork.   To ascertain this soundness, a portion of air is to be expelled by a gentle heat, and the height to which the mercury rises as it cools and contracts noted; if it remains constant for a short time, the junctures are perfect.   The delivery-tube, although beneath the mercury, is not placed under the jar at first, but some of the bicarbonate is heated, the gas being received in a test-tube filled with mercury; a little of the solution of potash used in combustions is then introduced by means of a bent pipette, and if the absorption is complete, the combustion may be proceeded with, but if not, more of the bicarbonate is to be decomposed until the desired result is obtained. The bell-jar is filled partly with mercury and partly with the potash solution; equal bulks are generally used.   The combustion is carried on with extreme slowness, to prevent any possibility of the formation of binoxide of nitrogen, or rather to ensure the perfect decomposition by the metallic copper of any that may have been formed.   Great care must be taken that the quantity of substance used is not too large for the jar to contain the gases produced by its decomposition.   The potash solution, if permitted to come in contact with the hands, will make

the cuticle so slippery that it would be impossible to retain the jar in the act of inverting it at the mercurial trough; every care must therefore be taken to prevent contact of it with the fingers. To effect this, the proper quantity of mercury is poured into the jar, then solution of potash to within $\frac{1}{4}$ of an inch of the top, the glass plate being placed on and held down by the two first fingers of the right hand, while the thumb and third finger clasp the cylinder, the left hand assisting at the other end; the cylinder is steadily and rather rapidly inverted, and the two first fingers and plate being immersed in the mercury, the plate is removed, and the jar may then be held vertically by any of the methods mentioned in the section on Supports.

623. Of course all the carbonic acid is absorbed by the alkaline solution, and at the end of the combustion the portion of bicarbonate of soda remaining undecomposed is to be ignited, in order to sweep the remaining nitrogen before it into the gas-measurer. When the operation is completed, the glass plate is slid under the jar, and the latter is transferred to a cistern of water; the plate being removed, the mercury and potash solution sink from their superior density and are replaced by water; the volume is then noted, and the necessary corrections are made.

The bicarbonate of soda may be replaced with advantage by carbonate of manganese*.

624. *Gas-furnaces for organic analyses.*—The extreme ease with which gas-flames may be regulated, and their cleanliness and economy, have led several chemists to endeavour to substitute them for charcoal in combustions. Dr. Lionel Beale was perhaps one of the first to suggest this method. He describes his apparatus as an iron chamber, at the lower part of which is placed a long brass tube, perforated in its whole length with small holes, from any number of which the gas can be permitted to issue by moving a piston, and thus the quantity of gas which escapes into and mixes with the air of the chamber can be regulated. The mixed gases

---

* For a new and apparently excellent method of determining nitrogen, the reader is referred to Dr. Maxwell Simpson's paper in the 'Quart. Journ. Chem. Soc.,' vol. iv. p. 289. The details are too long for insertion here.

pass upwards and are ignited on the surface of iron wire-gauze, which is stretched over the top of the chamber. A *sliding* partition accurately fits this chamber, and reaches up to the wire-gauze, dividing it as well as the chamber into two parts, the length of which may be varied according to the extent of combustion-tube to be heated. The gas is only allowed to escape into one of the two cavities into which the chamber is divided by the partition, by moving the piston in the brass tube accordingly. By this arrangement any length of tube may be heated; and by simply moving the sliding partition and piston in a corresponding degree, the heat can be gradually extended from one end of the combustion-tube to the other. The general appearance of the apparatus will be seen from fig. 316.

Fig. 316.
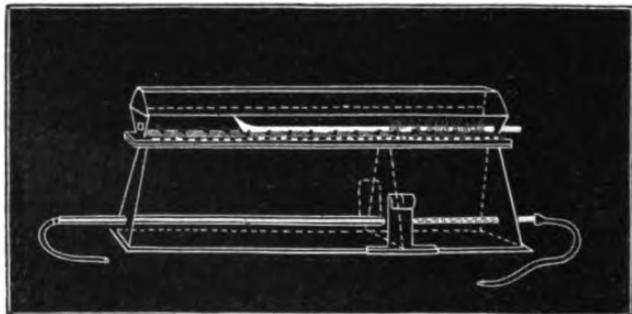
625. Dr. Hofmann has constructed an excellent furnace for the same purpose; it is a combination of an elaborate modification of Dr. Beale's arrangement, with an apparatus for performing the combustion in a current of oxygen gas; by this means the most refractory substances, such as graphite, may be completely burned. The following is his description of its construction. The letters refer to figs. 317, 318, and 319. "A is the combustion-furnace, which is supplied with gas by the tubes *a, b, c, d,* communicating with two pairs of stopcocks, *e* and *f*; a combustion-tube, *g,* open at both extremities, and supported in the usual manner, communicates in front with the chloride-of-calcium-tube, B, a potash bulb apparatus, C, and a potash-tube, D; at the back, the com-

bustion-tube communicates by means of a system of desiccators, consisting of a potash-tube, E, a sulphuric-acid-tube, F, and a

Fig. 317.
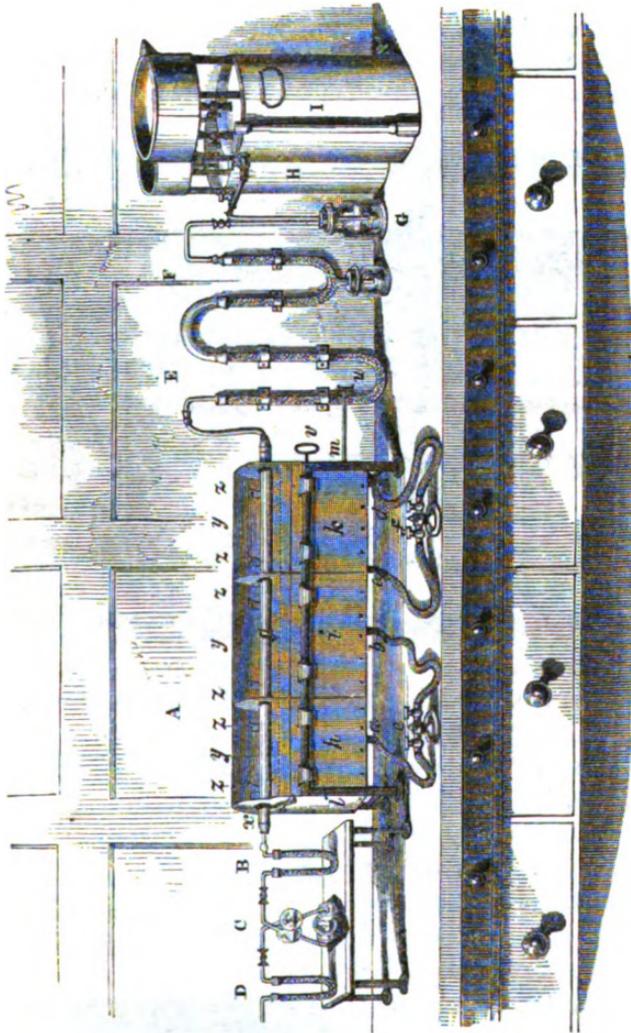
sulphuric-acid-bottle, G, with the gas-holders, H and I, containing respectively oxygen and atmospheric air. The bottle, G, serves,

moreover, as a bubble-gauge for measuring the rapidity of the current.

"The furnace consists of three separate compartments of strong iron plate, *h, i* and *k,* which are supported by a stout iron stand, *l m.* The arrangement of these compartments requires a few explanations; their construction is evident from figs. 318 and 319:

Fig. 318.
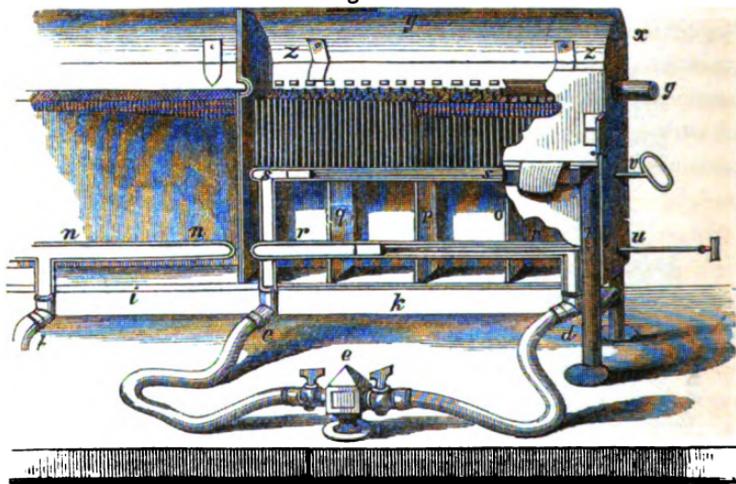
h and *i* are simply rectangular iron boxes, open at the bottom and covered at the top with wire-gauze, which are supplied by a horizontal perforated gas-pipe, *n n,* fig. 318. The last compartment, *k,* fig. 318, has a somewhat more complicated construction. It differs from the two others by being subdivided into four smaller chambers by the three diaphragms, *o, p* and *q,* of iron plate, the gas being supplied by two pipes instead of one.

Fig. 319.

The lower pipe, *r r,* resembles in every respect the gas-pipe, *n n,*
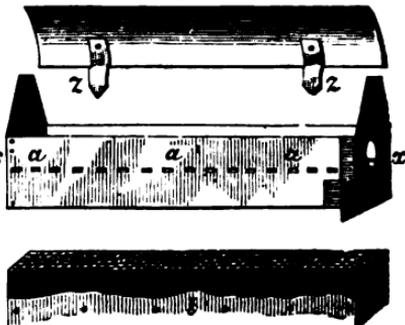
of the other compartments. The upper pipe, *s s*, on the other hand, supplies the gas to two rows of vertical fine tubes, somewhat similar to those used in Leslie's gas-burner, the extremities of which project through the wire-gauze cover of the compartment, fig. 318. Both pipes are provided with air-tight pistons, which enable the operator to manage the heat produced by this part of the apparatus according to the requirements of the analysis. Fig. 319 shows the manner in which the frame, *x x*, which supports the combustion-tube, is fitted over the wire-gauze cover of the case. It is provided with a series of holes, *a, a, a*, allowing a current of air to enter, which bends the flame round the combustion-tube; this figure gives, moreover, a separate view of one of the side pieces, *y*, which by means of the tongues, *z z*, are fastened upon the frame, in order to form a kind of dome, from which the heat is reflected downwards upon the combustion-tube.

"The combustion is conducted in the following manner :—A combustion-tube, open at both ends, and 2 or 3 inches longer than the combustion-furnace, is filled with a layer of oxide of copper, corresponding to the length of the two compartments, *h* and *i*, placed into the furnace and connected at one end with the desiccators, E, F, &c., the other end being open at the time. The tube is then heated by the air-flame of the three compartments, and a slow current of dry air forced through it by means of the gas-holder, I, for about five minutes, which removes every trace of moisture. The current being interrupted, the front end is corked, and the supply of gas so far diminished in compartments *h* and *i*, that a mere sheet of flame remains upon the wire-gauze, while it is entirely turned off from the compartment *k*. As soon as the tube has sufficiently cooled, the front end is connected with the chloride-of-calcium-tube, B, the potash-bulbs, C, and the potash-tube, D, and a little platinum boat containing the substance to be analysed, introduced at the other extremity, and pushed in about two-thirds of the division, *k*. All joints being well secured, the gas is again fully supplied to compartments *h* and *i*, and the layer of oxide of copper corresponding to the length of these divisions heated to a dull redness. The distillation of the 'sub-

s 5

stance' may now be commenced. For this purpose the gas is admitted, by means of the flexible tube, *d*, to the lower gas-pipe, *r r*, and the piston, *u*, pushed so far from the inlet as to supply the gas to the chamber, *o l*, only, whilst it is excluded from the other chambers, fig. 318. In this manner an air-flame is obtained, which keeps the posterior extremity of the combustion-tube at a dull red heat. A small quantity of gas is next admitted to the upper gas-pipe, *s s*, by means of the flexible tube, *c*, the piston, *v*, being drawn so far from the inlet as to confine the gas to a very few of the little tubes, at the extremity of which mere points of flame are thus produced. The distillation now proceeds with perfect regularity, the slow air-current, which must be kept up all the while, as well as the high temperature of the posterior portion of the tube, driving all the products of combustion towards the red-hot oxide of copper, which effects their perfect combustion. The piston, *v*, is gradually drawn out, so as to bring all the jets into play, and the supply of gas to the jets increased as far as possible without producing too smoky a flame. As soon as the temperature of the jets is no longer capable of expelling volatile matter from the substance, the piston, *u*, of the lower tube is gradually pushed in, and the gas supplied to all the chambers of compartment *k* until the whole of the combustion-tube is exposed to a uniform air-flame throughout its whole length. A new quantity of matter is thus expelled, but unless the substance under examination be volatile, a large quantity of carbon is left in the boat.

626. " At this period the air-current is replaced by a slow stream of oxygen from the gas-holder, H, the arrival of which in the combustion-tube is marked by a brilliant phenomenon of incandescence. After a few minutes the boat is left clean, and the combustion is terminated. The current is, however, kept up for a very short time longer, and stopped only when pure oxygen may be traced at the mouth of the potash-tube, by means of an ignited splint of wood.

627. " By this time the products of combustion are perfectly swept from the tube and lodged in their receptacles; moreover, the copper is completely reoxidized; the flame is now gradually lowered, and the gas at last entirely turned off; and if the com-

bustion-tube, after the detachment of the chloride-of-calcium-tube, &c., and the removal of the empty platinum boat, be carefully corked, the whole arrangement is ready for another combustion, in which the operation of drying of course becomes unnecessary.

"Liquids may be likewise burned with the apparatus; in fact, on account of the facility with which the temperature of the compartment, k, can be managed, this mode of proceeding is particularly adapted to liquids. Even very volatile liquids, such as ether, &c., may be safely burned; in this case the combustion can be completed without any oxygen, and no fear of an explosion need be entertained.

"In the case of substances containing nitrogen, the copper turnings, perfectly dried in a current of hydrogen, must be placed in the combustion-tube *after* the preliminary desiccation, and the current of air must be very slow; it is, moreover, advisable to place some copper turnings behind the boat with the substance, over the posterior compartment; the copper is thus heated to redness, and deprives the air-current of the greater part of its oxygen.

628. "The first putting together of this apparatus requires considerable time, and the securing of so many joints is attended with some difficulty; but once fitted up, it enables the operator to analyse with great dispatch, scarcely more than an hour being necessary for making a complete combustion. The arrangement is particularly useful when a considerable number of analyses have to be made. There are, moreover, several additional advantages which deserve to be noticed. The determinations both of carbon and hydrogen are very exact, especially the latter, all sources of accidental moisture being excluded. On this account it is possible to reduce the amount of substance used in the analysis to a minimum, not more than from 150 to 200 milligrs. being required. The possibility of determining the amount of ash or the quantity of silver, platinum, or barium, &c. in a substance, together with the carbon and hydrogen, is likewise frequently a very great convenience. The number of accidents is,

moreover, much smaller. The combustion-tubes very rarely crack if the application of heat be sufficiently gradual. For this purpose it has been found convenient to light the gas in the commencement, below the wire-gauze, until the furnace has become hot, then to turn it off and to light it above the wire-gauze. But if an accident actually takes place with a combustion-tube, it almost invariably occurs in the preliminary heating of the oxide of copper, and in such cases the 'substance' is perfectly safe, and has only to be shifted to another tube. The combustion-tubes usually stand six or eight combustions, but frequently as many as ten or twelve may be made with the same tube, so that there is also a considerable saving in expense.

" The only inconvenience incident to the apparatus is, that it is liable to get out of order. The wire-gauze especially has to be often renewed, and on this account a construction has been selected which renders it possible to replace the wire-gauze in the laboratory without sending the furnace to a gas-fitter.

629. " The furnace given in the above illustrations is composed of three distinct divisions, which may be separately fixed upon the support. By this provision the apparatus becomes adapted to a variety of operations, especially to nitrogen determinations, which require a shorter tube. This separation, however, is not absolutely necessary, and for the special purpose of the carbon and hydrogen determinations, a furnace in one piece answers equally well."

630. The U-tubes which appear in the engraving, fig. 317, are, with their contents, much more bulky and heavy than the straight one, fig. 66, and, moreover, they do not possess any great advantage over the latter. Where, however, from any special circumstance, a U-tube is desired, it may advantageously be arranged somewhat as in fig. 246, p. 314, where the tube, e, which is to be inserted into the cork of the combustion-tube, enters a little tube intended to receive the chief bulk of the water, and thus enable the instrument to be used much longer without changing the chloride of calcium than would otherwise be the case. The inner tube must be much shorter than is there represented.

631. The U-tubes, as sold, are generally too heavy to be conveniently suspended from the balance, and tubes of large calibre are not always easy to be had; it is sometimes convenient therefore to make them of two pieces of light tubing, connected together at bottom by a small tube bent twice at right angles, and fastened by corks and sealing-wax. It is to be strengthened by a support of wood tied with string between the two large tubes. A U-tube of this construction is also useful in many experiments with gases. Plugs of cotton-wool are placed at the extremities to confine the chloride of calcium.

632. It is sometimes preferable in ordinary carbon and hydrogen determinations, to use an aspirator to draw a current of air through the apparatus after the analysis is ended; in this case a preliminary experiment may be made to find the increase in weight which a chloride-of-calcium-tube acquires by the passage of about 200 cub. cent. of air. The number thus found is to be deducted from the weight of the chloride-of-calcium-tube after the analysis. The stopcock, a, of the aspirator, b, fig. 320,

Fig. 320.
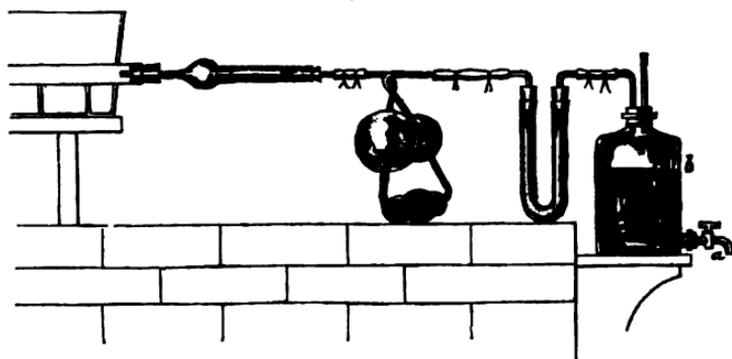
being turned on after the combustion is finished and the point of the tube is broken off, 200 cub. cent. of water are allowed to flow out, when of course exactly that quantity of air is drawn through the apparatus. The cork of the aspirator is provided with two tubes, and one of these is bent at right angles

and attached by a caoutchouc connector to the second potash-tube, while the other is intended to allow of the passage of the air which escapes through the bulbs during the combustion, but it is closed by a small cork or a piece of wax just before the stopcock is opened to allow of the flow of the water.

In the analysis of volatile fluids with high percentages of carbon, the accurate estimation of the hydrogen is often exceedingly important; the arrangement shown in fig. 320 is then of great assistance, because the quantity of fluid burnt is generally very small, sometimes only 2·5 grains, in which case the hydrogen derived from moisture in the air may introduce serious error.

It is often advisable at the termination of the analysis to connect to the tail of the combustion-tube a small tube filled with fragments of caustic potash, to absorb any carbonic acid or aqueous vapour that might otherwise find its way into the apparatus. This, to a certain extent, renders unnecessary the precautions last described.

SECTION XXIV.

GLASS-WORKING.

633. There are few acquirements of more use to the chemist than a moderate proficiency in the construction of glass apparatus: the mere fact of being to a certain extent independent of the instrument-maker is at once a great object gained. It frequently, nay constantly happens that an experiment is dependent for success upon the use of an instrument of a shape different to that kept in the laboratory; the operator who can readily supply any deficiency of this kind is far more likely to make progress in his researches than one who has to wait until it can be obtained from the glass-blower.

634. Small retorts, tube-funnels, siphons, test-tubes, pipettes, &c. are always in requisition; no pains should therefore be spared to acquire facility in the use of the table or other blowpipes for purposes of this kind. But it must not be forgotten that some persons are liable to fall into the other extreme, and spend valuable time in the construction of apparatus which might be better obtained from the instrument-maker; for instance, it would be a waste of time for any one, unless singularly skilful at such practices, to attempt the construction of Liebig's potash-tubes, fig. 67, § 107, while, on the other hand, it would be very useful and highly advantageous to be able to repair one if broken. The advantage of possessing a certain amount of practical skill in mechanical operations should not therefore be overlooked, for it may be said to constitute an important element in the qualifications of a chemist. Even in so simple an affair as the construction of a combustion-tube, p. 357, much is gained by doing it in a neat and proper manner, without regarding the annoyance which most persons cannot help feeling at the sight, much less the use of one that is ill-made and clumsy. ?

635. The most common operation with glass in the laboratory is the bending of tubes, and it is also the simplest. They should

be selected for this purpose of tolerable thickness, and not too large in diameter; very thin ones are troublesome to bend, and are seldom useful when done.   Supposing a tube to be required for the washing-bottle (§ 200), or for delivering gas in small experiments, a piece should be selected about the size and thickness depicted in the margin.   It will not be necessary to use the blowpipe, the flame of a gas- or spirit-lamp being suf-

Fig. 321.

ficient.   About an inch should be heated, until it is per-ceived by a slight motion of the hands that it begins to yield; it is constantly turned round on its axis, in order that all parts may be equally heated, and when found to be sufficiently soft, removed from the flame, and being held by the ends, they are inclined gently towards each other, care being taken that the movement is in the same plane, *i. e.* so that if it were continued long enough, the two portions would at last meet throughout their whole length, without having any tendency to one side.   This is accomplished by holding the tube in such a manner that a line from the eye would pass through both por-tions of the tube, fig. 322, where the eye being at *a*, any ten-dency to one side of either limb would be readily seen and corrected.

Fig. 322.
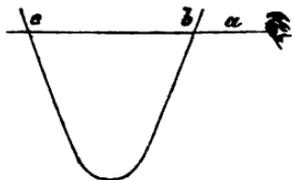
In all operations of glass-working, the state of the glass with regard to its temperature is judged of as much or more by the feel than by the sight, for glass requires a much higher tempe-rature to show a red heat than metal. It is necessary also to learn to distinguish between the appearance caused by the ignition of reduced lead in the glass, or ignited charcoal deposited from the flame, and that shown by red-hot glass.   It is a great object in all operations at the glass-working table to acquire that lightness of hand, combined with steadiness, which enables a tube to be held without distortion although very soft.

636. Very thin tubes are liable to become malformed on bend-ing, especially if large, the outer or convex portion flattening,

and the inner angle having wrinkles; this may be avoided either by closing one end and gently blowing into the tube while bending, or by filling it with sand and making the curve at the lowest possible temperature over a charcoal fire.

This method of bending tubes by means of sand will be found of the greatest utility in the construction of U- and V-tubes for drying gases, condensing volatile fluids, &c. By means of a small quantity of ignited charcoal, supported on a piece of wire-netting elevated on bricks, so as to allow of free combustion, I have always found that tubes from $\frac{1}{4}$ to $\frac{5}{8}$ths of an inch in diameter, and of the hardest glass, may be bent with perfect ease. It is of course imperative that the sand should be dry. It is necessary also to avoid too high a temperature, or the sand would have a tendency to adhere to the glass.

637. The Herapath's jet, fig. 48 (§ 60), is so convenient and manageable, either with or without a blowpipe-bellows attached, that where there is a supply of gas it will render almost any other description of instrument of this class unnecessary. By carefully regulating the supply, any description of flame may be obtained, either oxidating or reducing. It is to be remembered that the gas should never be turned on too fully, as in that case the combustion is less complete, and the oxidating and reducing portions of the flame scarcely to be distinguished from each other, and very often the former not obtained at all. In fact, the temperature may be raised to a greater degree by regulating the amount of gas than by increasing the blast. In working with soft glass containing lead, it is to be carefully kept away from the reducing-flame, films of lead becoming visible which may be difficult to remove by exposure to the oxidating flame. The latter may always be known by its peculiar nebulous appearance, and from being beyond the luminous and reducing portion. Before introducing thick glass into the flame, it is to be carefully heated to prevent cracking from sudden and unequal expansion, and on removing it, every precaution is to be taken to prevent too rapid cooling. It is to be held at the very extremity of the visible flame, being continually rotated and gradually removed

further and further from the jet; after this it should be held in the
current of hot air ascending from the lamp, and finally it is to be
put in a warm place, such as the sand-heat, to cool gradually.
A hot piece of glass, even if so thin as to render very slow cooling
unnecessary, is never to be placed upon the bench or working-
table, as a film of carbon, difficult entirely to remove, adheres to
it.   Sometimes it is better to bend tubes in successive small por-
tions, so as to avoid too sudden a curve.

CUTTING GLASS.

638. (1) *By files.*—Glass tubes are cut into lengths by filing
a notch on them with a sharp three-square file, and breaking the
tube at the point marked, in the manner that a twig is snapped,
the hands being held in precisely the same position.

639. If the tube is thin, great care must be taken to avoid
too much pressure with the file, as the glass would then be
crushed.   If the tube is large in diameter, the file-mark must
be carried half round.   The notch should be deeper on the side
furthest from the operator when being broken.

640. (2) *By the diamond.*—Cutting-diamonds usually have
one part that acts more readily than the others; this position
should be ascertained by trial on a piece of flat glass, and marked
on the handle in such a manner that it may be easily found when
required.   When a piece of glass is to be cut, it should be laid upon
a perfectly flat surface, because, if a hollow exists underneath the
plate, it is liable to cause fracture when pressure is applied to the
upper surface.

641. (3) *By spring-coals or pastilles.*—One of the most con-
venient methods imaginable of separating glass into various
forms, is by the use of spring-coals.   The following formulæ
are given for their preparation, the first by Gahn, the second by
Mohr.   1. Two and a half ounces of gum-arabic, and half an
ounce of gum-tragacanth, are dissolved in five and a half ounces
of water.   Then one quarter of an ounce of storax, and the
same quantity of gum-benzoin, are dissolved in one and a half
ounce of spirit of wine; the two mixtures are to be worked,

with three and a half ounces of powdered charcoal, into a stiff paste. 2. Half an ounce of gum-tragacanth in powder is to be dissolved in water to an elastic mucilage, allowing it to macerate for about one hour. Then add one quarter of an ounce of benzoin, dissolved in sufficient spirit. Rub the two fluids in a mortar, with as much powdered charcoal as will form a tenacious paste. The pastes formed by either of these processes are to be formed into sticks about the size of ordinary quills, and slowly dried in the water-bath.

The benzoin is merely for the purpose of adding a pleasing odour during the burning, and if finely powdered charcoal is worked up with a thick mucilage of gum-tragacanth and a little gum-arabic, it answers equally well. I form the sticks by taking a mass of the mixture and rolling it on a stone slab with a piece of smooth hard wood until the mass is about the length and thickness of a black lead pencil. The sticks thus formed are to be laid out upon a tray dusted with charcoal-powder to prevent them adhering; the tray and contents are then placed on a moderately warm part of the sand-bath for half a day, to dry. I have also found that the addition of a very small quantity of linseed-meal (that which has been prepared from expressed cake) has a remarkable tendency to strengthen the spring-coals, and prevent the red-hot ends from dropping about.

642. To use them, one is to be ignited, and suffered to burn to a point, the combustion being aided during the whole time by gentle blowing. A crack being made in the edge of the tube or other vessel to be cut, the ignited point is to be placed about a tenth of an inch from it, and in the direction in which the crack is wished to extend; the latter will almost immediately run to the ignited point, which is then to be removed about the tenth of an inch further; in this manner the crack may be led in the desired direction, so as to enable a flask or other vessel to be cut to any shape. If a spring-coal is not at hand, a substitute may be found in a small stick of well-dried deal, which is to be burnt until a charcoal point is obtained, but it soon goes out, and has to be repeatedly ignited. A red-hot iron may also be used to

lead a crack. It is strange, that, from some molecular pecu-
liarity, probably caused by the heat, it is impossible, as a general
rule, to make the crack extend entirely round a tube, a small
portion, about an eighth of an inch, remaining intact; this is,
however, too small to be of importance, and after the parts are
separated, forms a point which may be easily removed by the file.
A flask, retort-neck, &c. is sometimes divided by tying a thread
saturated with turpentine round, and setting fire to it, at the
same time rotating the vessel to enable the flame to extend
equally. As soon as the spirit is consumed, the vessel is sud-
denly dipped into cold water, when it generally separates into
two portions; the fissure corresponding to the line marked by
the thread. This method is, however, less to be relied on than
the process by the spring-coal. The latter remark also applies
to the use of red-hot iron rings, which were much used by the
older chemists for dividing glass vessels; they were applied red-
hot to the flask, which was then dipped into water, when it
usually parted at the line marked by the heated ring.

PIERCING HOLES IN GLASS.

643. *By heat.*—A hole may be very conveniently made in tubes
and other thin glass apparatus, by directing a pointed flame from
the blowpipe upon the spot where the aperture is to be, until it
is red-hot; the mouth is then applied to one end of the tube, the
other being closed by the finger or a cork; the glass is by this
means blown into a thin bubble and bursts; if not, it is reheated,
and on blowing a second time, the object is attained. This is,
perhaps, the best method of obtaining an aperture in the side of a
tube where it is intended to insert another. Figs. 323, 324 and 325
illustrate the method of proceeding; the flame being directed for a
few seconds strongly at *a*, fig. 323, the tube which is closed at *b*
by a cork, is blown into strongly; the glass is by this means
forced into a thin bubble, fig. 324, *a*, and on repeating the pro-
cess, bursts. On removing the thin glass, it presents the appear-
ance of *a*, fig. 325. The flame is directed upon the aperture for
a few seconds, and while the edges are red-hot, the tube, *b*, fig.

325, is approached, and having its edges also made red-hot, is applied to the aperture and pressed rather strongly to make it adhere, and is immediately slightly pulled away to render the glass at the juncture thinner; the end, *c*, of the tube, *b*, fig. 325, is then to be closed, and the flame directed all round the juncture of the two; the mouth being then applied to *d*, air is thrown in, which, by expanding the edges of the join, will make it still

Fig. 323.   Fig. 324.   Fig. 325.
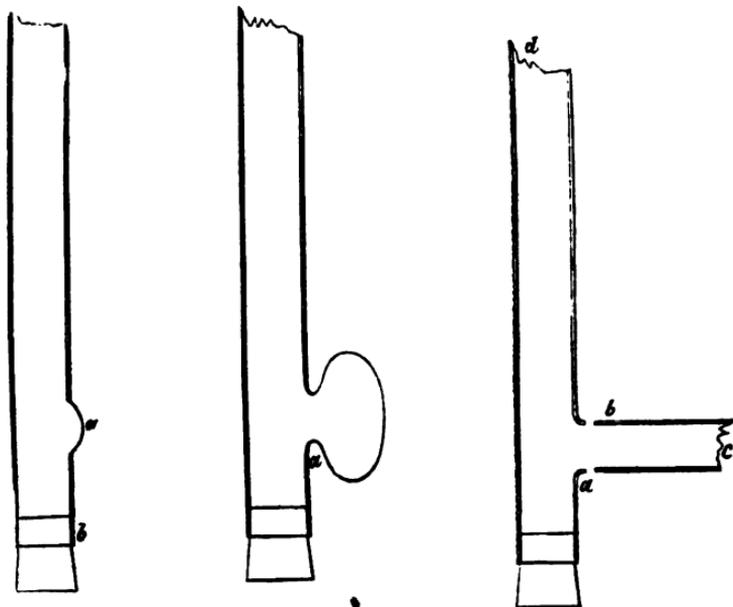
thinner and less liable to crack on cooling. When, by a few repetitions of this, it is seen that the joint is tight and not wrinkled, it is to be very slowly cooled. If it is wished to construct a siphon, the tube, *b*, which is much longer than could be conveniently represented in the figure, and for this purpose of smaller calibre, is to be turned up as at *b*, fig. 326, and bent again at *c*. A long tube, a little smaller in calibre than the one to which *b* is soldered, is then bent into a siphon, and inserted in

the other, the lower end of its longer leg penetrating to *a*; a caoutchouc-tube is previously slipped over the end of the longer tube at *d*, and serves to enable the two to be united by tying with silk.

644. It will be seen that by this means a convenient and easily-constructed siphon is formed, one of its chief advantages
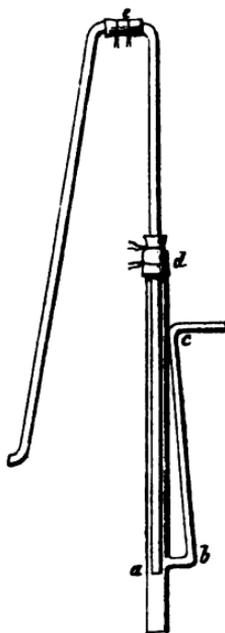
Fig. 326.   Fig. 327.
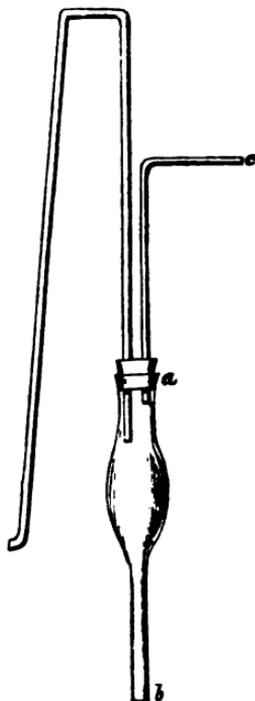
being, that as the caoutchouc junction allows a certain amount of motion, the chances of fracture are much diminished; and, moreover, if the instrument be broken at the bend which unites the longer and shorter leg, another tube has merely to be bent and inserted into the tube, *d a*. In many cases the two limbs

of the siphon may be connected by a caoutchouc-tube (as at
e), and by this means all danger of fracture is removed.

The same object may be attained, perhaps still more easily, by
taking the end of a broken chloride-of-calcium-tube and inserting
a cork at *a*, fig. 327. Holes are made in this cork, through which
two tubes are passed, one forming the siphon, and the other in-
tended to enable the air to be drawn through in the usual manner.
It is to be observed that in all siphons the aperture correspond-
ing to *b*, fig. 327, is to be closed before applying the lips to *c*.

645. A very convenient, and in many instances extremely
useful method of piercing an aperture into tubes, bulbs, &c., and
at the same time of forming a tube, is in the manner seen in
fig. 328. A strong and pointed flame is directed at *a* until the glass

Fig. 328.
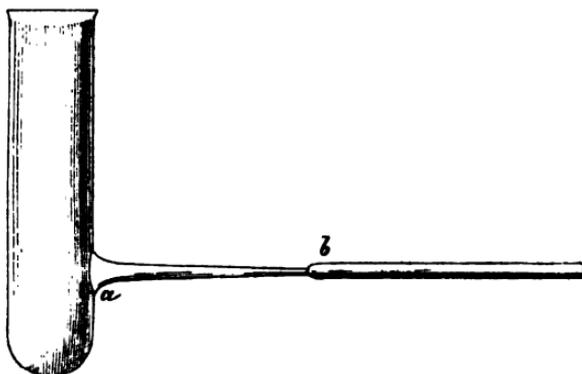
is perfectly melted and very soft; a piece of rather infusible glass
rod, *b*, is introduced into the flame until the end is red hot; it is
then pressed rather forcibly upon the melted spot at *a*, and im-
mediately withdrawn; by this means a small tube of about an
inch or an inch and a half long will be formed. Retorts to
which this has been applied for the purpose of introducing a fluid
without soiling their necks, are seen in §§ 382 and 653.

646. Holes may be drilled with ease through thick plates of
glass, stoppers, &c., by means of a common brad-awl dipped in

turpentine, the instrument being used precisely in the same man-
ner that it would if the hole was being bored in wood. I have
made a neat aperture through a glass stopper half an inch thick
in less than ten minutes, by this means. This is a convenient
method of making the hole in a glass plate, by which to suspend
the watch-glass or capsule over the surface of sulphuric acid con-
tained in a beaker, as in fig. 60, p. 66. When a glass stopper
has become fixed in the neck of a bottle and broken off, this is a
good method of extraction, for the glass may thus be crumbled
away, and finally removed altogether.

647. *Closing of tubes.*—This is an operation of constant occur-
rence in all laboratories, either for the purpose of making test-
tubes, or little bottles to contain specimens.

Fig. 330.   Fig. 331.   Fig. 332.
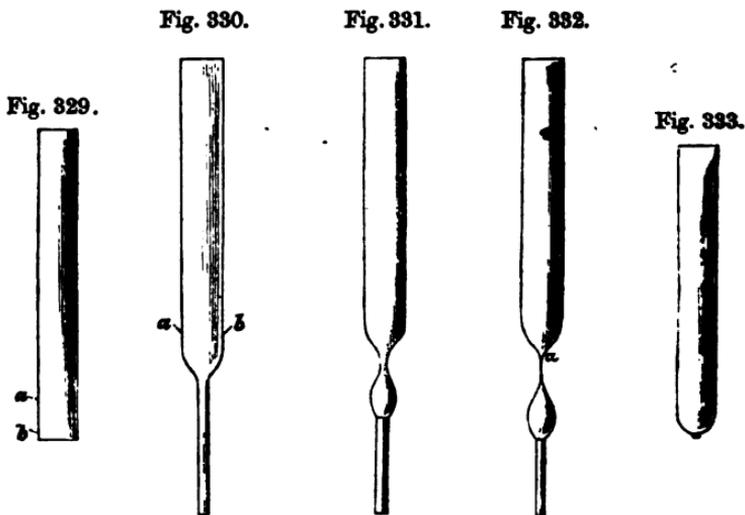
Fig. 329.

Fig. 333.

The tube is to be strongly heated at one end, from *a* to *b*, fig.
329. Another piece being then attached, the heat is to be
directed at *a b*, fig. 330, the tube being continually rotated, in
order to equalize the heat; it is then drawn out, as at fig. 331,
and the flame being strongly directed at *a*, fig. 332, the super-
fluous glass is to be drawn off. The tube, after a little turning
in the flame, then appears like fig. 333. The mouth is then

applied to *a*, fig. 334, and air cautiously thrown in until the end becomes rounded and free from the point seen in fig. 333. It should now resemble fig. 334. The mouth should then be heated until the sharp edge is fused, or if it is desired to expand it as at *a*, fig. 334, the end should be ignited for the tenth of an inch, and a piece of charcoal, previously filed or rasped to a proper shape, inserted and turned round in such a manner as to enlarge

Fig. 334.   Fig. 335.   Fig. 336.   Fig. 337.   Fig. 338.

the aperture; this will cause the cork to fit more completely, and at the same time strengthen the tube.

648. It is very frequently required to draw out tubes to a capillary termination, either for pipettes or otherwise. It is generally better to thicken them before drawing out, by rotating them for some time in the flame, and rather pressing up than otherwise, but not sufficiently to cause a fold or wrinkle; by this means they will take the form seen in fig. 335; and if it is then drawn out, as in fig. 336, and cut off at *a*, a strong but extremely fine aperture may be obtained. The calibre will of course be regulated by the degree to which the tube is pulled.

If it is wished to form a small pipette, it may be done by closing *a*, heating strongly at *b*, and thickening and pressing up the glass so as to obtain sufficient to form a stout bulb. On

T

blowing strongly but steadily, still rotating the tube, a globe will be formed sufficiently large for most purposes. The formation of pipettes leads to a consideration of the methods of blowing bulbs. The simplest method of doing this to a beginner, will be, to take a piece of tube about the size and stoutness of fig. 337, and close it at one end; it is then to be thickened by rotation in the flame, and pressing the glass carefully up with a piece of metal until sufficient has been accumulated at the end; by this means a section of the tube will resemble fig. 338. The thick portion is then to be strongly heated, and air thrown in by blowing steadily as soon as the tube is removed from the flame. A bright cherry-red is the best heat for this purpose. The tube is to be turned not only while in the flame, but also while the bulb is being blown. If too much pressure is exerted, a kidney-shaped bulb of extreme thinness, and perfectly useless, will be obtained. The eye should be steadily kept upon the expanding glass the whole time the air is being thrown in, so that the pressure may be arrested at the proper moment. If the bulb obtained is not sufficiently large, it may be reheated and blown into again. When it is required so large that sufficient glass cannot be accumulated at the end to form it, a large piece of tube may be joined to a smaller. For this purpose the larger piece is drawn out at both ends until of the diameter of the smaller one, fig. 339. The end, *a*, is then thickened and drawn out small, but

Fig. 339.
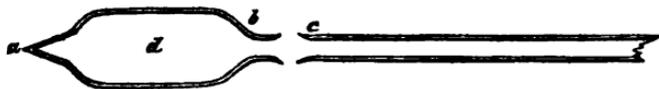
not closed; *b* is then introduced into the flame of the blowpipe, and closed; it is then to be heated, and on blowing strongly at *a*, the end, *b*, forms into a small but excessively thin globe, which is broken off, so as only to present an enlarged edge, as seen in the figure: the same is done at *c*. The aperture, *a*, is then to be closed by fusion. If, now, the edges of *b* and *c* are held in the flame, and both are equally heated, they may be

perfectly united by pressing together; they are then to be
slightly drawn in an opposite direction, to reduce the thickness
of the join, and then reheated and blown into until the thickened
portion disappears and becomes equally distributed; a little more
careful drawing out will then make the tube of the same size at
the join as elsewhere. The portion, *d*, is then to be heated in
the flame, and expanded into a bulb, by careful blowing. If
another piece is connected at the end, *a*, in the same manner, a
large pipette is at once formed.

649. An excellent pipette for delivering small quantities of
fluids in delicate experiments may be made as follows:—A small
but thick tube is to be thickened at one end, and then drawn
out; by this means a tube of very small bore, but of consider-
able strength, is obtained. The extremity of the drawn-out
portion is to be closed, and the glass at that part where the
capillary portion joins to the rest of the tube is to be thickened
considerably, by turning it in a good flame, and pressing up the
glass, using the capillary tube as a handle. The heat is then
to be raised, and a bulb blown, so that the instrument has the
form of fig. 340. I am in the habit of using pipettes made in
this manner from ordinary quill-tubing, in adjusting the quantities
of fluids to be weighed for analysis.

650. The funnels so much used in distillations on the
small scale, and in the preparation of hydrogen, hydrosulphuric
and carbonic acid gases, are readily made in the following man-
ner:—A piece of wide and tolerably stout tube is drawn out and
cut off, of the width of the smaller one to be attached to it, as
in fig. 341. The end, *a*, is then to be corked, and the two may
be joined, as previously directed. Or if what is termed a thistle-
funnel is preferred, a globe of tolerable stoutness is to be formed
at the end of a tube, by soldering a wide to a narrow one, and
expanding the wide portion into a bulb. The end opposite to the
narrow tube is then to be strongly heated and blown into until
a large thin bubble is formed, fig. 342; this is to be broken off,
the aperture made smooth by fusion, and opened with an iron
wire or piece of charcoal.

By bending the tube-funnel, fig. 341, at *b* so as to form a
right angle, and bordering the wide portion, excellent suction-
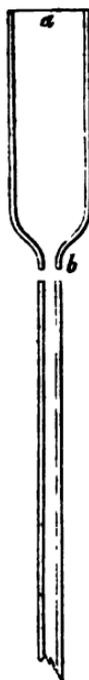
Fig. 340.   Fig. 341.   Fig. 342.
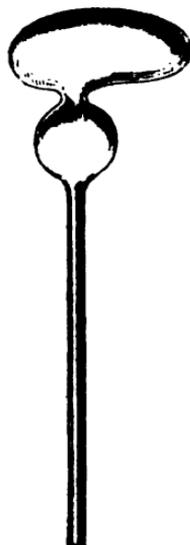
Fig. 343.
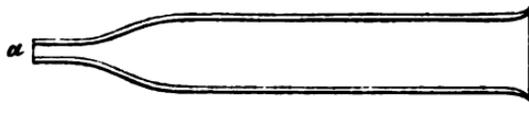
tubes for combustions are made*.   Bent tubes of this latter kind
are also very convenient for connecting many pieces of appara-
tus.   By much thickening a piece of rather wide tube, and then

* See also § 564.

drawing it out until of the relative proportions of fig. 343, I make the small caustic potash-tubes for attaching to the potash-bulbs for organic analysis, as in fig. 298, p. 376. The aperture, *a*, fits the cork of the suction-tube used to draw the carbonic acid through the potash solution after the analysis. The mode of attaching and using these instruments is seen at §§ 562, 564, and 607.

Fig. 344.
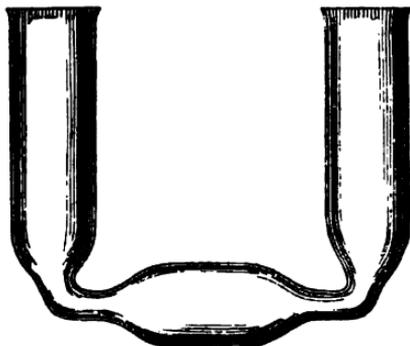
Fig. 345.

651. Where it is wished to construct U-tubes, but, from the largeness of the diameter and thinness of the glass, difficulty is found in bending without distortion, and the process with sand is not convenient, I frequently make them of the form seen in fig. 344. This is very easily done by thickening in two places, and then drawing out, fig. 345. This thickening enables us to bend the tube neatly at *a a*, fig. 345, with great ease, and when done in this manner, the bend is exceedingly strong.

652. Safety-tubes of the form of fig. 346 are easily constructed out of pieces of glass tube. Two sizes are selected, the larger of sufficient diameter to form the funnel, *a*, and the elongated bulb, *b*. At about 2 inches from the end of the tube, the flame of the blow-pipe is made to play strongly until the glass is very soft; it

is kept constantly turned until it has very much thickened.
and become about a third less than its original
diameter; it is then removed from the flame,
and drawn out until of the same size as the
small tube, as at *a*, fig. 347. It is again
drawn out about 2 inches further down, as at
c, and cut off at *a*, *b*, and *c*. The first por-
tion is joined, by the method given at p. 411,
to about 6 inches of the smaller tube; the
other end of the latter is then soldered to
the end, *b*, of the bulb, fig. 347, and about 10
inches more of the small tube is affixed to the
end, *c*; the whole is then bent into the form of
fig. 346. This is the method I always adopt for
the construction of these useful pieces of ap-
paratus; and I find that, if proper care is taken
to reduce the thickness of the welds by the
method described at p. 411, they are no more
liable to fracture at those places than at the por-
tions of the tube where there is no join.

Fig. 346.
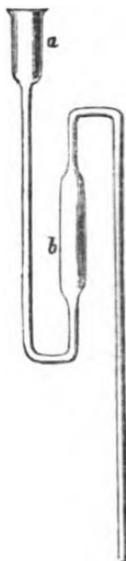
653. I have sometimes had occasion to construct a retort and

Fig. 347.
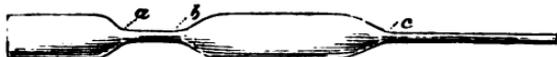
receiver out of one piece of tube, as in the figure.   It has many

Fig. 348.

advantages where the presence of cork or caoutchouc is inad-

missible, and is extremely easy to make. A piece of glass tube, $\frac{1}{2}$ or $\frac{5}{8}$ths of an inch in diameter, is closed at one end like a test-tube, and at about 2 inches further up it is strongly heated and thickened; it is then to be drawn out so as to form the neck of the retort, a. The tubulature, b, is then formed by the method given at pp. 242 and 407, and the end is broken, so as to allow air to enter while the other end, c, is closed; the tubulature, d, is then made, and the neck bent as at a. To introduce the fluid to be distilled, the end, b, is dipped into it, contained in a small capsule, and suction is applied at d by means of a glass tube and cork; when sufficient has entered, the extreme point of the tubulature, b, is held in the flame, suction being continued; by this means the point may be closed without much of the glass being melted, this being essential where the retort is to be used many times. The aperture at d is left open in some cases during the distillation, but where the presence of air is objectionable, the fluid is made to boil until all the latter is expelled, and the end of d is then sealed by momentary exposure to the flame. By this means the distillation may be conducted *in vacuo*, and consequently considerably below the ordinary point of ebullition of the fluid. The receiver portion of the apparatus is, of course, kept cold during the operation.

SECTION XXV.

ELECTRICAL AND GALVANIC MANIPULATION.

654. The manipulation connected with the above subjects having been so elaborately treated of in numerous works specially appropriated to them, it becomes unnecessary to enter upon them here, except so far as they bear directly upon chemical research, and therefore those operations only will be alluded to which are required in laboratory work.

The investigation of Kolbe on the electrolysis of organic bodies, has opened a new field of investigation which is likely to be followed up with activity; the researches of M. Becquerel upon the separation of bodies by electrolysis, and even the application of the electrotype to the coating of chemical vessels (§ 683, p. 430), render it necessary for the student not only to possess the knowledge derivable from works exclusively treating of electricity, but also to be familiar with the means adopted for applying the electrical forces in chemical processes.

655. The operations to be detailed are all of the simplest character, but none the less necessary and useful.

656. The methods of exploding mixtures of gases in the various kinds of eudiometer have already been shown (§§ 551 to 558), and it was mentioned that in some cases a spark from the prime conductor of an electrical machine was insufficient to cause explosion, and the means of overcoming this difficulty were pointed out.

657. It sometimes happens in laboratories that it is desired to make eudiometric experiments, and that an electrical machine is not at hand. In this case the electrophorus will answer equally well, and from the ease with which it is constructed, and, if necessary, repaired, the small space that it occupies, and its freedom from the liability to fracture possessed by cylinder and plate machines, it is even more convenient. To construct it, a plate of tin is made into a circle of about 12 inches diameter, a raised border is then turned up for about $\frac{1}{2}$ an inch, and the ex-

treme edge is turned outwards over a wire, so as to avoid a sharp border. A mixture of equal weights of shell-lac, Venice turpentine and resin is made by gently heating them together until well fused, stirring during the time with a stick, so as to thoroughly incorporate the ingredients. The composition should, when perfectly homogeneous, be poured into the plate with the raised edges until it is quite full, and the composition is to be kept melted (but not too hot) for a short time, or until the bubbles have entirely disappeared. The portion which serves the place of a prime conductor consists of a flat circle of wood, rounded on the edges, and neatly covered with tin-foil; it is rather less in diameter than the lower portion of the instrument. A handle is easily constructed out of a piece of glass rod, and is fastened with electrical cement into the centre of the wooden plate. A brass ball may be attached to the rim; it is, however, scarcely necessary.

658. The tin plate with its resinous surface being warm and free from moisture, is to be excited by beating with a piece of warm flannel. To do this effectually, the latter is to be folded into a slip about 14 inches long, and being grasped by one end, is to be struck upon the resinous surface smartly and in an oblique direction, much in the manner of beating dust off a flat surface. When this has been done for about a minute, the warm dry cover or upper plate of the instrument is to be placed upon the resinous cake and touched with the finger. If the plate is then raised a few inches and the knuckle approached, a powerful spark will pass; and if the plate be again replaced, touched, &c., and so on in the same order, the knob of a Leyden jar being substituted for the finger when touching the upper plate after raising it, a jar may be charged sufficiently to give a powerful shock, and amply sufficient to cause the explosion of a gaseous mixture even under the unfavourable circumstances previously described.

659. The ordinary cylinder and plate electrical machines are so familiar to all persons in any way conversant with philosophical apparatus, that it will be unnecessary to describe them here, and it is almost equally unnecessary to remind the operator that

T 5

before use the instrument should be dry and even slightly warm ; care must, however, be taken that the machine is not placed sufficiently near the fire to injure it, or fuse the cement by which the cylinder is fastened into its bearings, or the pillars into their sockets. The dryness of the glass rod which supports the prime conductor must also be especially attended to.

660. Frictional electricity is but little used in chemical experiments, while, on the other hand, the fluid, in the state in which it is obtained by chemical action, or, in other words, by the use of galvanic batteries, is in frequent requisition in the laboratory. The extreme purity of the gas evolved by the action of the battery on water renders it peculiarly adapted for eudiometrical experiments.

661. Many different forms of battery have been contrived, all being perhaps more or less valuable under certain circumstances ; there are, however, some which are especially so, either for convenience, power, or economy. With regard to the former of these qualifications, Smee's battery is beyond all doubt preeminent. It is, it is true, less powerful than some other arrangements, and in constancy is decidedly inferior to the arrangement of Daniell; but the ease with which it can be constructed and repaired, the fact of its only requiring one exciting liquid and no porous cells, and especially not creating any unpleasant or corrosive vapour, make it so much superior for general laboratory use that its construction will be somewhat minutely described.

662. *Smee's battery.*—Each cell contains three plates, two of active and one of inactive metal. The two active plates are of zinc, and the inactive of platinized silver.

Zinc being almost invariably used for the active element in voltaic arrangements, it will be proper to describe a few precautions affecting its application in all cases. Ordinary zinc is susceptible of both common chemical and also of a local action, which takes place upon merely dipping the metal into the dilute acid used to excite the battery. The local action arises from the presence of impurities, which cannot be removed without causing the metal to lose one of its chief advantages,

namely, its cheapness. But, by amalgamating it, the actions alluded to are prevented, and the crude metal works equally well with the pure. To amalgamate zinc, it is merely necessary to place the plates in a dish containing dilute sulphuric acid, and rub them with a rag, at the same time allowing a few globules of mercury to fall on them. The rubbing will cause the mercury to spread, and it may in this manner be made to entirely cover the whole surface of the plates. The latter should then be rinsed with clear water and put aside in a vertical position to allow the excess of mercury to drain off. By this means the surfaces of the plates acquire, after standing, a beautiful frosted appearance, and local action is prevented. Zinc plates which have been made from rolled metal are far better than when cast, and generally much purer; being smooth, they also work more pleasantly. The plates may be of any convenient thickness, but about $\frac{1}{8}$th of an inch is perhaps the most convenient. They are easily divided, by first greasing them, and then making a deep scratch with any convenient tool in the direction in which the cut is to run. A little dilute sulphuric acid is to be allowed to fill the groove thus made, and then a little mercury is so placed as to amalgamate the exposed metal at the scratch. If the plate is then left, with sufficient mercury in the groove, for a few hours, it penetrates the part where the grease has been removed, and renders it so brittle that a smart tap will enable the plate to be divided in the required direction.

663. The platinized silver for the inactive element may be prepared in two ways. By the first method, the silver in sheets a little thicker than writing-paper is to be roughened by a momentary immersion in ordinary nitric acid. It is then attached to a wire connected with a plate of zinc in a porous cell. In an outer cell is contained dilute sulphuric acid, mixed with a weak solution of chloride of platinum. The action is set up by weak sulphuric acid, in the same manner as in the electrotype process. The object of obtaining the platinized silver with a rough surface, is because the hydrogen gas is by this means liberated more readily. But this object is much more conveniently attained by

the following method of platinizing the silver:—A sheet of the silver is to be placed on a table between two coarse pieces of sand-paper, and the latter being strongly rubbed with a glass stopper, the silver is made to assume a very peculiar appearance, being covered with minute elevations and depressions. The silver plate thus roughened is laid upon a plate of metal as hot as may be, so that it does not scorch paper, and a dilute solution of chloride of platinum is to be applied by means of a rag: the silver will thus become thoroughly platinized and of a deep black. It is necessary that the solution of platinum should not be too strong, as it creates a tendency in the platinum to peel off from the surface of the silver.

The process of roughening by means of sand-paper, as above described, by giving an irregularly corrugated surface to the silver, greatly increases its stiffness, and thereby renders it easier to insert it in the frame than when the nitric acid method is adopted. Moreover, the surface is much better adapted to enable the bubbles of hydrogen to escape.

A strip of copper about ⅜ths of an inch broad is now to be soldered to the top of the silver plate, as at *a b*, fig. 349. A frame is then constructed just large enough to allow the plate to slip between two grooves, and into another at the bottom; these serve to keep it stiff, and lessen the chances of injury. Another piece of wood, grooved in its under side to receive the copper band, *a b*, is then made; it has a hole in it to allow the binding-screw, fig. 350, to pass through so as to enable it to be soldered to the piece of copper.

Fig. 349.
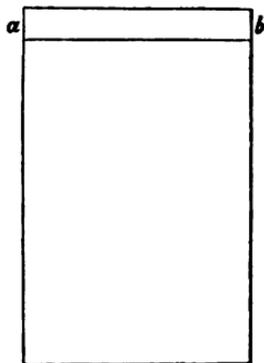
Fig. 350.

The whole arrangement of the negative element is seen in fig. 351. The binding-screw, *h*, is soldered at *c* to the copper strip *a b*. The dotted lines at *i* show the manner in which it passes through

the wooden top of the frame, and those all round indicate the depth to which the platinized silver extends.

Fig. 352 gives a sectional view of the wooden frame in a plane at right angles to $d\,e$, fig. 351, showing the manner in which the zinc plates are attached by means of the second and large binding-screw, $a\,b$. The screw, c, is intended to enable the strips of copper, by which the connexions are made, to be tightly held. At a is the screw which clamps the zinc plates to the frame. The screw, $h\,i\,c$, fig. 351, is not seen in this view. The dotted lines give the direction of the plate of platinized silver. The zinc plates are seen at d and e, fig. 352.
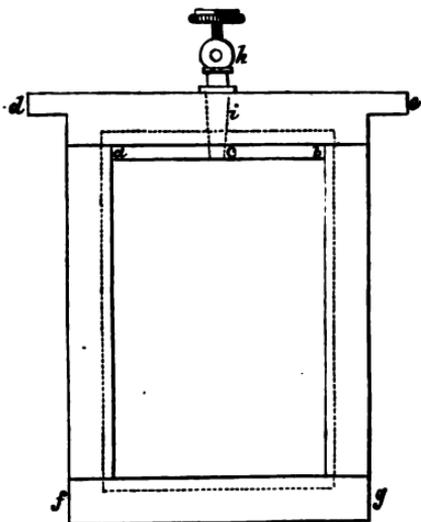
Fig. 351.   Fig. 352.
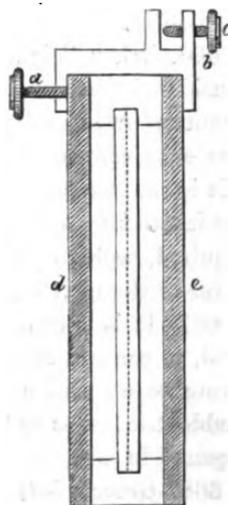
It is proper to varnish the wood-work of the battery and the copper slip, $a\,b$, figs. 349 and 351, with a solution of sealing-wax in methylated spirit, as it greatly preserves them from destruction by the acid. But it is essential that none of the cement finds its way on to the acting surfaces of the zinc or platinized plates, as any portion so covered is rendered useless, and no longer contributes its share to the working of the battery.

The large binding-screw, $a\,b$, fig. 352, is shown separately in fig. 353.

664. To excite the battery, one part by measure of sulphuric acid is cautiously added to twelve parts, likewise by measure, of water, and the mixture allowed to cool and deposit the sulphate of lead which generally precipitates from the acid on dilution.
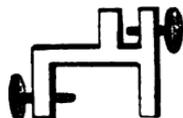
665. The presence of nitric acid in the sulphuric acid used is to be carefully avoided, and also metallic salts must be prevented from finding their way into the exciting liquid.

Dilute sulphuric acid is without action upon amalgamated zinc, but a very small quantity of nitric acid, if present, will cause it to dissolve.

666. When it is desired to form a series of cells, it must be considered whether the experiment to be performed requires a quantity or intensity arrangement; if the former, all the zinc plates are connected together, and also all the platinized silver; this is the case where thermal effects are desired, as, for example, the ignition of a platinum wire; but if a decomposing action is required, each zinc plate is to be connected with the platinized silver of the next cell, and so on to the end of the series.

667. It is extremely convenient, where a series of plates are used, to connect them with a frame, which is slung by means of a string to a small windlass having a ratchet-wheel attached, to enable the plates to be removed out of their cells when no longer required in use.

668. *Grove's battery.*—This, the most powerful of all voltaic arrangements, may be constructed in several ways. The object being as much as possible to avoid screw-connexions in a battery evolving corrosive vapours, the method shown in fig. 354 may be adopted with advantage. Each of the stoneware cells, $b\,b,\ b\,b,\ b\,b$, has within it an amalgamated zinc cylinder, $a\,a$, to which is soldered a copper slip, e, bent twice at right angles. Within the zinc cylinder is placed a porous cell, c, containing a slip of platinum foil, d, to the upper end of which is soldered a ribbon of copper,

f, bent twice at right angles, like those attached to the zincs. The flat surfaces of the turned-up copper ribbons are to be opposed to each other and clamped by the binding-screws, as at *g* and *g*.

Fig. 354.
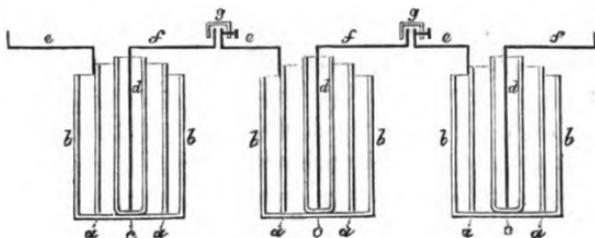
These binding-screws are of the simplest kind, and can, if required, be easily made by the operator himself. As purchased, they are made from castings, but if constructed in the laboratory, it will be more convenient to make them by turning up a piece of stout sheet-copper, as in fig. 355, and after drilling a hole in one side, making a hollow screw in it and fitting a male screw with a milled head. As it would be difficult to make a male screw with a milled head without castings for the purpose, a straight piece of metal may be soldered at right angles to the screw to serve as a purchase in turning. The apparatus for making screws will be described in the section on Miscellaneous Manipulation.

Fig. 355.

669. To excite this battery, strong nitric acid is placed in contact with the platinum inside the porous cell, and sulphuric acid diluted with seven or eight times its bulk of water is placed in the outer vessel. Some recommend only four times its bulk of water, but I prefer the strength given above for ordinary experiments. Where the platinum strips are only $2\frac{1}{2}$ inches long by 1 inch broad, and the zincs 4 inches high by $2\frac{1}{4}$ in diameter, four cells decompose water rapidly, and show the phenomena of ignition of platinum wire, &c. One such cell is strong enough for most electro-magnetic experiments, and I found six sufficient for the electrolysis of butyric acid.

670. The constant battery of Daniell, seen in fig. 356, is valuable

where it is desired to keep up a current of uniform strength for a considerable time. The outer cell, *a a*, consists of a cylinder of sheet-copper, containing within it a porous cell, *b b*, serving to hold the zinc rod, *g*, which is supported within it by means of a wooden bar, *c c*, passing through a hole pierced in the zinc. The copper cylinder and the zinc rod are provided with binding-screws, *e f*. The inner cell containing the rod of zinc is charged with dilute sulphuric acid of the same strength as that used for Smee's battery. The outer cell has a saturated solution of sulphate of copper poured into it, the strength being maintained

Fig. 356.
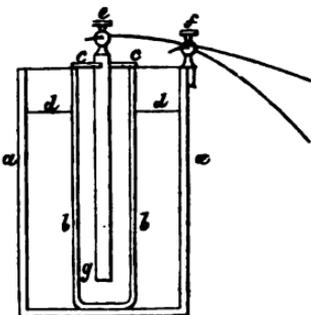
by keeping crystals of the latter salt upon the perforated shelf, *d d*. The zinc rod must be amalgamated. When this battery is first charged, it is more powerful than it is afterwards, but after the first quarter of an hour it will remain quite uniform for several hours.

671. *Bunsen's battery.*—This form of battery, which is very much used on the Continent, has its inactive elements of carbon. They are made by heating, in properly-shaped vessels, a strongly compressed mass formed from a mixture of powdered coke and caking coal, made somewhat plastic by strong syrup. They are much improved, if immersed, after the first heating, in syrup and placed under the air-pump; on working the latter, myriads of air-bubbles rise through the syrup, and on readmitting air, the fluid enters the pores formerly filled with air. On again heating the mass to redness in a vessel well protected from the atmosphere, a fresh quantity of carbon is deposited in its pores, and the carbon becomes denser and better adapted for the required purpose. The mass wet with syrup is to be slowly but thoroughly dried before being reheated.

As it is not so easy to attach binding-screws to the carbon cylinders thus made as it is to the metal ones, a mercury-cup may be used, as will presently be described.

In the section, fig. 357, *a a* represents a porcelain pot, containing a cylinder of zinc, *b b*, to which is attached a binding-screw, *c*. Inside the zinc cylinder is placed the carbon-cell, *e*, which has the mercury-cup formed in it at *d*. The carbon-cell is filled with strong nitric acid, and the zinc is excited either with the dilute sulphuric acid previously mentioned, or a solution of common salt. The binding-screw, *c*, is represented on a larger scale in fig. 358. It is specially adapted for connexions where a ribbon of copper is used instead of a wire.
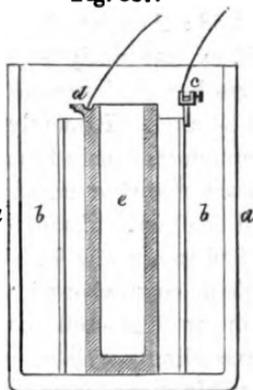
Fig. 357.

Fig. 358.

672. The above form of carbon-battery is not the only one in common use, or perhaps the most convenient. They are often constructed with the carbon element in the form of a solid cylinder intended to be placed in a porous cell of nitric acid, while the zinc element is in the form of a hollow cylinder surrounding the porous cell. Sometimes the carbon is in the form of a hollow cylinder, open at the top and bottom, and enclosing a porous cell to contain the zinc and dilute sulphuric acid; this is, perhaps, the commonest form of the Bunsen's battery imported from the Continent. In batteries of this kind the carbon has a belt of copper round its upper part fastened by a clamp. This belt enables the connexions to be made with far greater convenience than the mercury-cup.

673. The above batteries are those in common use, and are by far the most convenient: for a description of the arrangements of Faraday, Callan, Sturgeon, Wollaston, Hare, Young, Children, &c., the student is referred to works expressly treating on electricity.

MISCELLANEOUS GALVANIC MANIPULATION.

674. *Binding-screws and connexions.*—Several forms of binding-screws have already been described and illustrated by figures 350, 353, 355 and 358; there are, however, two others which demand attention. If, as constantly happens in experiments with batteries, two wires have to be connected, the simple binding-screw, fig. 359, may be used. It merely consists of a brass ball perforated through its centre to permit the wires to pass, and having a screw with a milled head to enable them to be compressed together. If a plate of zinc, or other metal, is to be attached to a screw for the purpose of enabling it to be placed in connexion with other pieces of apparatus, as, for example, in the single-cell electrotype arrangement, the screw, fig. 360, is exceedingly well adapted for the purpose. The slit at the lower end is slipped over the plate, and the two are made fast by means of the horizontal screw, while the vertical one allows a wire to be connected with it to support the object to be copied by the electrotype process, or it serves in other experiments to permit the positive element in one cell to be connected with the negative element in another.

675. It cannot be too strongly impressed upon the student, that all the connexions used in galvanic arrangements should be kept perfectly clean and present a bright metallic surface at the places of contact. The best forms of battery, or other galvanic apparatus, even when, as regards other matters, in the most perfect state, will fail to give good results if the connexions are dirty or have become oxidized. It is generally advisable before forming unions, to amalgamate the wires by rubbing them with protonitrate of mercury, especially where they are intended to dip into mercury-cups, as is necessary in many galvanic arrangements. Faraday recommends rubbing the wire at the place to be amalgamated with tallow and mercury applied with a piece of chamois leather, as by this means there is less tendency to tarnish than when the protonitrate is employed.

676. A very important point where substances are to be exposed to galvanic action is, that the wires which carry the electrodes should be sufficiently large to enable the current to pass with as little obstruction as possible; if, therefore, the rigidity of these thick wires is a source of inconvenience, they should nevertheless be carried as far as possible, and be continued by short ones of sufficient flexibility. The absolute terminations or electrodes are, almost invariably, of platinum, and in general it may be said that the larger they are, within certain bounds, and the nearer together, so that absolute contact is avoided, the more intense will be the action.

677. The form of apparatus in which to expose electrolytes to the action of the battery, depends upon the nature of the products; if, for example, water is to be decomposed, any of the following arrangements may be made use of; and many other fluids may be submitted to the action of the current with equal facility. It must not be forgotten, that water in a pure state offers great resistance to the passage of the electricity, and consequently is decomposed with difficulty; but the addition of a little sulphuric acid, by increasing the conducting power, greatly facilitates the action.

678. In eudiometrical experiments, it sometimes occurs that the proportion of nitrogen in the mixture is so large that it becomes impossible to explode it; when this happens, it is essential to add not only the oxygen required for combustion, but also a certain amount of oxygen and hydrogen in the proportion in which they exist in water. It is perhaps more easy to do this by electrolysing water than by any other means, as then the gases are at once obtained perfectly pure and in the proper relative proportions. In operations like this, where battery-gas is used, it is obvious, that, beyond enabling the otherwise uninflammable gas to be exploded, no other result occurs, as it totally disappears by the combustion and consequent formation of water. In experiments of the latter kind, the gases not being required separate, the apparatus, fig. 361, may be employed. The bottle, *a*, is fitted with a cork, through which two wires pass, each

having a strip of platinum foil, *b b*, attached to it to form the electrodes. These wires are connected by means of binding-screws of the form of fig. 359, with the wires of the battery, which should be stout, in order to afford as little resistance as possible to the current. The cork has a bent tube passing through it, which may be made to conduct the gas to the pneumatic trough. The bottle being filled with recently boiled distilled water, and the connexions being made, the gas evolved will be delivered into the jar previously filled with water, and inverted. When the gas is

Fig. 361.
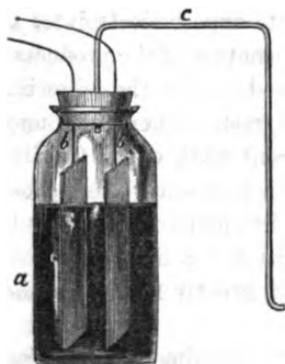
Fig. 362.

not to be used in eudiometrical researches, the boiling of the water may be omitted, and ordinary acidulated water be used instead. Of course the current must be allowed to pass until all the air is expelled, before collecting the gas.

679. If, on the other hand, it is desired to obtain the gases separate, the arrangement, fig. 362, may be adopted. A funnel is selected with a wide aperture at the lower end, and the chief portion of the tube is removed, about an inch being left. A cork made to fit accurately is cemented into its place. Two wires with platinum electrodes soldered to them are then passed through the cork. The funnel being nearly filled with acidulated water, the gas-tubes also filled with the fluid are inverted over the electrodes, and, on contact being made with the battery, the

gas ascends into them.   Instead of a table with a hole in the centre, as represented in fig. 362, the apparatus may be supported on a retort-stand.   This is the simplest, cheapest, and certainly one of the best modes of showing the decomposition of water.

680. If it is desired to obtain only one of the gases, as, for example, the oxygen, a tube of glass having an electrode fastened into it, fig. 363, may be filled with acidulated water, and inverted in the liquid contained in a glass or porcelain vessel, and on connecting the positive wire with *a*, and immersing the negative one

Fig. 365.

Fig. 363.   Fig. 364.
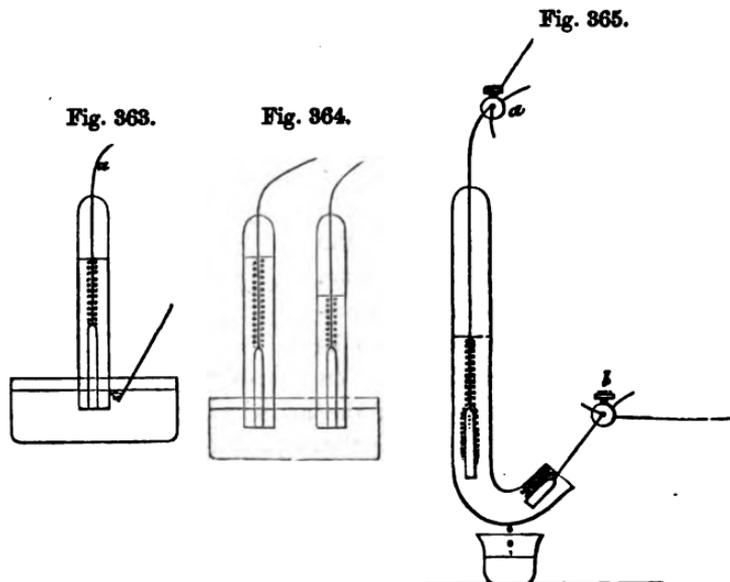
in the fluid, the oxygen will be obtained in the tube. If the hydrogen is required, it will be necessary to reverse this arrangement. Fig. 364 shows another mode of obtaining both gases in separate tubes.

681. A very neat and simple method of obtaining the gas from either electrode for examination by the use of an instrument on the principle of Cooper's mercurial receiver (§ 521), has been described by Faraday.   A wire flattened out at one end is fused into a tube curved at the lower extremity, fig. 365.   This is to

be filled with the fluid to be electrolysed and supported in the position represented in the figure; the other electrode is then inserted in such a manner that the gas from it does not pass into the tube, but away, as seen by the dots; that from the other electrode is thus collected in the tube, the water or other liquid falling in the tube and being collected in the vessel placed beneath. The nature of the electrodes connected at a and b of course determines the kind of gas obtained.

682. Where the object is not to collect a gas, the apparatus in the margin, which may be easily constructed, is useful. A glass tube, a, has a platinum wire, flattened at the extremity, b, fused into it; this wire may be bent up through the little stand and end in a mercury-cup. The other electrode is to be immersed in the fluid as near as may be to the other, but of course without touching.

Fig. 366.

683. *Electrotype.*—There are several modes by which metals may be deposited by means of electricity on properly prepared surfaces. Almost the only application of the art which promises, at present, to facilitate chemical manipulation, is the covering of retorts and flasks with copper, by which means they are rendered less fragile, and if fracture should happen during a distillation, the contents of the retort are preserved. Moreover, the copper by its conducting property causes the flask to become hot in less time than it would without the addition; and in the distillation of fluids of rather high boiling-points, they are particularly convenient, because the coating of copper, by keeping the upper part of the distilling vessel at a high temperature, prevents condensation, and consequently accelerates the progress of the distillation.

To render the glass capable of conducting the electric current, it is first covered with a thin coating of fat varnish, except in one or two places, where spaces are to be left uncovered, in order to facilitate inspection of the contents when being used. Before the
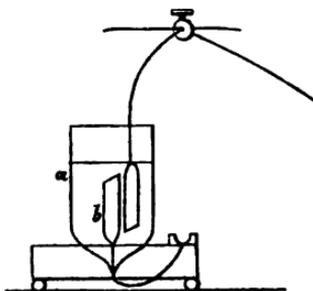
varnish has quite lost its adhesiveness, bronze powder is applied by means of a very soft brush. This covering must be quite

Fig. 367.
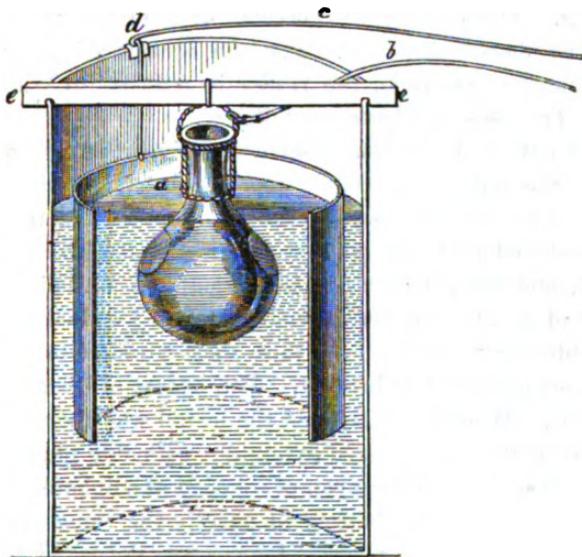
perfect, for wherever the glass is uncovered the copper will not be deposited. Inside a large copper pan, fig. 367, a sheet of copper coiled into a cylinder is attached by twisting, or by means of the binding-screw at d, with a wire connected with the battery. A bar of wood, $e\,e$, spans the vessel, and is notched to keep it in its place. The flask, a, is suspended from this bar by copper wires, and its buoyancy is overcome by filling it with water and adding sufficient shot to sink it. It is essential that the wires, which serve the twofold purpose of supporting the flask and connecting it with the battery, should be in perfect contact with the bronzed surface.

684. The flask is attached to the binding-screw of the zinc rod of a quart Daniell's battery by means of a copper wire, b, the cylinder surrounding it being attached to the copper of the bat-

tery by the wire, *c*. The cupreous solution to be decomposed, consists of two parts of a saturated solution of sulphate of copper and one part of a saturated solution of sulphate of soda, to which as much sulphate of copper has been added as it was capable of dissolving. The coating will become of a proper thickness in about two days.—*Redwood*. For the manipulation connected with ordinary electrotype, the reader is referred to Walker's or Napier's Treatises on Electro-metallurgy.

685. I have had occasion in some experiments to use a copper flask for the purpose of cohobating certain fluids with caustic potash. As it was necessary to have no join, I made them thus. I first modelled a flask in plaster of Paris, of the size and shape required, and from it cast a hollow mould in two pieces. An aperture of about a quarter of an inch allowed melted wax to be poured into the mould; it was then shaken round to distribute the wax equally on the interior. The excess of wax was then poured out. When perfectly cold the mould was opened, and the wax flask removed and coated externally with fine plumbago; it was then suspended inside a pan of solution of sulphate of copper, and connected with the battery in exactly the same manner as the glass flask described above. Copper was deposited for about a week, at the end of which time the metal was found thick enough, and it merely became necessary to melt out the wax and boil the flask with caustic soda. To strengthen the neck, I twisted repeated folds of copper wire round it, and again deposited copper until the wire and flask became one piece. Retorts and flasks of copper are easily made in this manner. On one occasion I constructed an alembic with moveable head by electro-deposition, and I think the method might be advantageously employed in constructing the copper apparatus required in various researches.

SECTION XXVI.

MISCELLANEOUS OPERATIONS.

686. There are a great number of operations, not strictly chemical, with which, from their being constantly performed in the laboratory, it is proper that the student should become familiar; but as they do not come under the headings previously given, it will be convenient to class them together as "Miscellaneous Operations." Under this head will also be included various processes which are more properly the province of the carpenter, instrument maker, &c. than the chemist, but as it so often happens that the latter is unable, from various circumstances, to call in the assistance of the former, and as it is always a greater pleasure to use an instrument constructed by our own hands than when made by another, it is hoped that the following pages, although far from being so complete as could be wished, may nevertheless be acceptable. The reader is, however, requested to observe, that although no directions will be given that have not been frequently used and found to answer perfectly by the author, nevertheless, as his information is confined to the results of his own limited experience, where processes are described involving manipulation belonging to the artisan or mechanic, the same accuracy of description must not be expected as if they were given by the persons alluded to, or even by an amateur. Nevertheless, it will be a sufficient apology for inserting them, that an experiment of great interest frequently depends for success upon the capability of the operator to construct an instrument involving the use of tools with which a moderate acquaintance is preferable to none.

687. Those who have never made the experiment, are probably not aware of the extreme ease with which the various supports mentioned in Section XIII. may be constructed, even by persons unaccustomed to mechanical contrivances. If made exactly as represented, then it would of course be necessary to use a turn-

U

ing-lathe and other appliances with which chemists generally are
not expected to be familiar.   But this is not essential, for almost
all may be constructed of square pieces of wood having square
sockets and bearings, and therefore not involving the use of any
save the simplest tools.   For example, the table-support figured
at page 157, and all its adjuncts, may be constructed with square
instead of round tubes, &c.

688. A laboratory should contain drawers filled with various
tools, neatly packed away in such a manner that when opened
suddenly they may not be thrown against each other, and thus
become blunted and otherwise injured.   A cupboard has advan-
tages over a drawer as a receptacle for tools, as then the chisels,
saws, hammers, files, &c. may rest in leathern loops against the
wall, and thus be visible at a glance.

The tools required depend upon the operator's mode of working,
and the nature of his researches or experiments.

The following list merely includes those I constantly use, and
which it is fair therefore to suppose would be required by most
working chemists.

Chisels from ⅛th of an inch to
  1 inch.
Mortising ditto, various.
Gouges, ditto, do.
Two hammers.
One jack and one hand-plane.
One brace, and one doz. centre-
  bits, various.
One drill stock and drills.
Two instruments for cutting
  wooden screws.
Two screw-plates for metal
  screws.
One pair spring compasses.
One pair callipers.

Bradawls, various.
Gimlets, ditto.
Square.
Cutting-gauge.
Files and rasps, various.
Pincers, various.
One anvil.
Bench-vice.
Fine and coarse saw.
Screwdrivers (two).
Spring tape.
Three-foot rule.
Nails and screws.
Glue-pot and soldering-iron.

With the above tools, there are few repairs that may not be

made, or ordinary supports or other wooden or metal apparatus constructed.

It is to be understood that there is a limit to the legitimate province of a chemist in constructing apparatus. If the operator is conducting researches, or if his time is otherwise valuable, judgment is required to decide between making an instrument and getting it done by a workman. It very often happens that less time is occupied in putting together a piece of apparatus than in finding a workman and showing him what is required.

689. *Cutting wooden screws.*—For this purpose an instrument is sold by all tool makers: it consists of a block of wood, having a round hole through it, one aperture of which is smooth, the other a female screw. Tangentially to the smooth portion of the hole is fixed a knife with a V-shaped termination, which is for the purpose of forming the thread of the screw. Rods of beech or hickory are to be made that will just pass the smooth aperture of the screw-block upon applying moderate force. If, now, one of the rods is fixed vertically in the vice, and the last-named aperture of the instrument is pressed down upon it, so that the rod may enter, and the two handles of the block being grasped one in each hand, the latter is turned slowly round, a downward pressure being kept up, a perfectly sharp and accurate screw will be formed, for which it is easy to construct a head by which to turn it. With the screw-block is sold an iron tool to form the female screw, in which the one last described is to work. This tool is made in two ways by different makers: in one it has a cylindrical termination, which serves to show the size of the hole, which is, in the first place, to be made by a centre-bit in the piece of wood through which it is intended that the hollow screw shall pass; in the other kind, a screw made conical and filed so as to have four sides, each of which is grooved in the direction of its length, is used to cut the female screw. This latter is by far the more convenient for the purpose.

The hole having been made by the centre-bit only large enough to admit the " tap " for a short distance, the latter, carefully preserved in a vertical position, is to be rotated, a downward pressure

being gently applied.   As soon as it has entered about ⅔rds of its length, it is to be rotated in the reverse direction so as to take it out.   The wooden male screw is now tried, and if too large to enter, the tap is again worked for a small distance further, and so on.   If the tap is sent in completely to the head, it will make too large an aperture, and the solid screw will fit loosely, but by inserting the tap a proper distance, any desired degree of tightness may be given to the screw.

690. *Metallic screws.*—Among the laboratory tools must be included a couple of screw-plates, one for small and the other for large screws, with their taps, so as to allow of the construction of metallic screws of different sizes.   Nuts to work on the screws are very easily made from pieces of sheet-copper, a hole being first drilled through rather smaller than the screw, and opened in the process of forming the latter by means of the tap.   If the male screw is to be of copper, the wire should be annealed by heating to redness before passing it through the plate.   The wire should be perfectly straight, and must be a little longer than the screw which is to be made from it.   The end upon which it is intended to commence should be filed sufficiently tapering to allow its entering a short distance without difficulty into a hole in the plate one size larger than the screw intended to be cut.   Two pieces of lead being so adjusted between the jaws of the vice that the latter will be prevented from injuring the threads of the screw, about 1 inch of the wire is allowed to stand perfectly vertical above the surface of the vice, and being greased with a little tallow, the hole in the screw-plate (one size larger than that in which the screw is to be finished) is to be placed over the wire, and the instrument, carefully preserved in a perfectly horizontal position, so that its plane may be exactly at right angles to the axis of the wire, is to be slowly rotated so as to cut a rough screw.   It is to be observed, that it is essential to the production of a perfect screw, that the relative proportions of the aperture in the plate and the wire are so adjusted in this preliminary operation, that there may be scarcely any force required to make the plate revolve and cut its way downwards.

As soon as the plate has reached the vice, if the screw is required longer, a little more of the wire is elevated, and so on until the requisite length is obtained. The length of the wire exposed above the jaws of the vice each time is regulated by its stoutness and strength,—the more fragile, the less must be worked upon at once. The imperfect screw thus formed is to be passed through another aperture one size smaller to finish it. More force will be required this time than before, and great care is requisite to prevent the wire from breaking off and becoming fixed in the plate. The plate is to be very slowly rotated, and after having advanced the distance of two or three threads, must be made to take a retrograde motion for a short distance, and is then to proceed a little further, and so on until the end is reached. The wire should be well greased all the time that the screw is being formed.

691. *Caoutchouc tubes.*—Vulcanized india-rubber tubes, which can now be procured of almost any required size, are in almost every case preferable to those made in the laboratory from sheet-caoutchouc; but those which are used to connect the chloride-of-calcium tube with the potash-bulbs in organic analysis, are much better of the latter kind. The reason of this is, that the vulcanized ones are less adhesive, and, moreover, give way less readily to the pressure of the silken cords; the result being, that there is invariably more difficulty in obtaining a tight joint with them.

692. To construct tubes from sheet-caoutchouc, a piece of the proper size is cut from the sheet and gently warmed until it becomes perfectly flexible. A glass tube, whose exterior diameter is of the size of the interior diameter of the intended tube, is covered with paper, and the piece of caoutchouc is folded round it, the excess being pinched together, so that it is represented by fig. 368. The excess of caoutchouc is then removed at one stroke of the scissors, which must be both clean and sharp to perform the operation neatly. The edges are then pressed together by the thumb-nail, and, if clean, will adhere perfectly. To make the tube sufficiently strong, another should

be made outside the first, and having its seam in the reverse
direction. The glass tube may be easily withdrawn, in conse-
quence of the piece of paper being wrapped round it. The latter

Fig. 368.
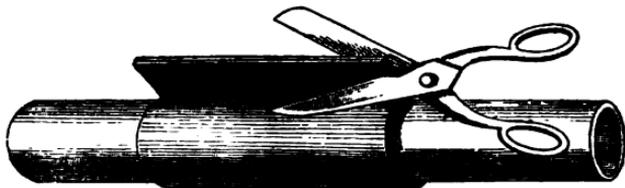
is to be twisted up into a small space, and may then be re-
moved with ease. If the paper is not used, it suffices, after
forming the tube, to slightly wet one end, when it will be found
that the tube and glass will part without difficulty.

693. *Soldering.*—By the use of solution of chloride of zinc, or
soldering fluid, as it is sometimes termed, this operation is so
much facilitated, that all the operations of this class required in
the laboratory may be easily performed. If, for example, it is
desired to construct the little instrument of tin-plate intended
to support, during weighing, the tubes sometimes used to contain
fluids whose composition is to be determined by the process of
organic analysis (fig. 293, § 600), it is merely necessary to turn
a slip of tin-plate round a stout wire of the proper size, and also
to make a disc of the same metal of the size of a fourpenny-
piece. If, now, the disc has a drop of the soldering fluid placed
on it, and also a small scrap of solder, and the whole is held on
a slip of wire-gauze, or other convenient support, over the lamp,
directly the water has been expelled, and the residue has undergone
the dry fusion, the solder will run evenly over the metal. The
cylinder is then to be moistened with the liquid, and after being
placed on the disc, the whole is to be held over the flame. In a few
seconds the solder will run, and spread over the lower part of the
cylinder, and on cooling, the two will be found firmly connected.

694. In ordinary operations of soldering, an instrument called
a "soldering-iron," or "bolt," is made use of. The "iron," how-

ever, consists essentially of a piece of *copper* riveted between two pieces of iron, which end in a rod of the latter metal firmly fixed in a wooden handle. The use of the copper is unavoidable, as the melted solder will not attach itself to iron, so as to allow of its being led along the seam to be joined. It is better to have the end of the tool of considerable solidity, so as to enable it to retain sufficient heat to fuse solder for a considerable time. When the article is finished, the chloride of zinc must be carefully washed off.

695. *Corks and cork-borers.*—The greatest difficulty is sometimes experienced in obtaining really good corks fit for connecting the chloride-of-calcium- and the combustion-tubes in organic analysis. No pains must, however, be spared to obtain them. The cork-drawer should be divided into compartments, to contain the various-sized corks. Whenever a fresh quantity is obtained of the smaller sizes, the best should be selected and put aside in a box by themselves, for the purpose mentioned above. Those which have been once dried, and used in a combustion, and are known therefore to be sound, should be put by in a stoppered bottle for use on future occasions.

Fig. 369.

696. In piercing holes in corks generally, the borers of Dr. Mohr are extremely convenient, and save a great deal of time. They consist of brass tubes of different sizes sharpened at one end, and having a ring soldered at the other to prevent the hand being hurt when using them. A hole is made through the upper end, to allow of a stout wire with a milled head passing through, to enable the hand to possess greater power over the instrument. They are sold in
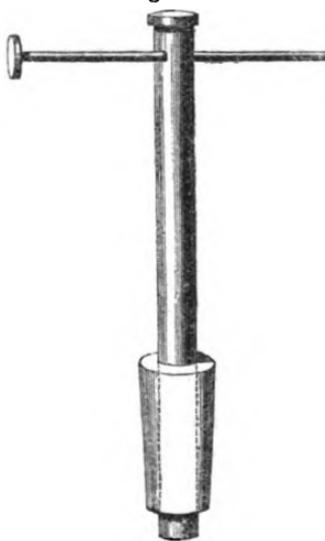
sets of all the required sizes, which fit into each other, and the one smaller than that used, serves to push out the cylinder of cork which is removed by the borer after piercing. The cylinders thus removed are frequently very perfect, and sometimes extremely useful, especially the longer ones. In cutting through large corks or bungs, it is better to slightly grease the borer, to facilitate its passage. The ends may be sharpened, when required, by means of a fine file.

A necessary accompaniment to the case of cork-borers is the rat-tail rasp and file. The former serves rapidly to alter the form or size of the hole in a cork, and the latter to finish off, and render the aperture smooth inside.

697. *Graduation of tubes.*—There are two methods of graduating tubes for the laboratory, either of which may be adopted, according as it is wished to have divisions made at once of a known value, or merely to divide the tube into equal measures of length, and ascertain the value of them afterwards. The latter mode, which is that of Bunsen, is unquestionably the best, and, moreover, the method of performing the operation is both simple and easy.

698. The tubes are, in the first place, coated, by means of a brush, with a thin layer of bees'-wax, which has been previously melted with a little turpentine. The graduating apparatus consists of a board, *a b c d*, fig. 370, having a groove down its centre

Fig. 370.
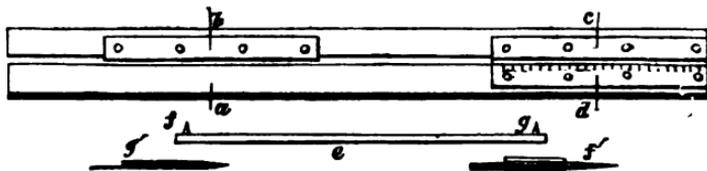
to steady the tubes during the process. In the groove, and kept in its place by the brass plate, *b*, lies a model tube, previously graduated into millimetres. This tube is capable of being moved up or down the board to prevent the necessity of having it of the same length as that to be graduated. It is better to move

the former than the latter, because there is danger of injury to the waxed surface. At *c* and *d* are two strips of metal, which serve the threefold purposes of retaining the tube in its place, enabling every fifth division to be made longer than the others, and keeping the short divisions of equal length. The tube being covered with wax, as previously directed, is to be placed in the groove, and the plates, *c d*, and the model tube, so arranged with respect to each other, that the notches (which in the plate *d* are apart from each other a space equal to five divisions of the model) shall fall in their proper places. To effect this, the wooden bar, *e*, with two steel points, *f* and *g*, is made use of. One of the points is placed on that spot of the tube where the first division is intended to fall, and the model is then adjusted so that the other point drops into the first division. The bar is then advanced five divisions forward on the model towards the end, *c d*, of the arrangement, and the plate *d* is then so adjusted that one of the points being held firmly on the fifth division, on the model, the other being moved so as to describe an arc of a circle, the point passes through one of the notches in *d* and thus makes a longer mark on the prepared tube than when the movement is made between the parts of the plate, *d*, intermediate to the notches. The arc being so small with so comparatively large a radius, it has the effect of a straight line on the tube. The steel points with which the graduations are made, are represented on a larger scale at *f'* and *g'*. The latter has a knife-like edge. The instrument and tubes being thus adjusted, the bar and points are returned to the first position, and one point being held on the first division of the model tube, the other is made to scratch through the wax on the tube to be graduated, and the bar is thus to be advanced a division at a time until the tube is finished. When this is done, it is ready to be exposed to the action of gaseous hydrofluoric acid. This is accomplished by laying it on some horizontal supports in a long leaden trough, the bottom of which is covered with a paste of finely powdered fluor-spar and oil of vitriol. The trough has a tightly-fitting cover of the same material. A moderate warmth is to be applied during the etch-

ing, care being taken that it is not sufficient to cause the composition on the tube to run. Several tubes may be etched at once by a proper arrangement of the trough. Great care must be taken when using the gaseous and even liquid hydrofluoric acid that no glass vessels are at hand except those being etched, as they would become dulled and entirely spoiled. The gaseous acid produces an opaque mark upon the tube, which is at once rendered visible on removing the wax. To effect this, the tube is to be warmed, and the composition is to be wiped off with a rag. To render the divisions distinct, the last traces of wax must be washed off with a little spirit.

699. It is sometimes preferred to etch the lines by means of the liquid acid contained in leaden or gutta-percha vessels of convenient shape. This process etches the lines deeper, but they are transparent, and should therefore be rubbed with white or red lead to render them distinct. The point, g', should not be too sharp, or the lines become so fine as to be indistinct unless looked at very close.

700. Where the value of the divisions to be made upon the tube has been determined beforehand, the method is different, although equally simple. The marks made by the scratching diamond are never so neat and regular as those etched in by hydrofluoric acid, but the former process is perhaps the simpler of the two. If the tube is regular in the bore, it will generally be sufficient to weigh in mercury, to form the longer divisions, and subdivide these afterwards into the desired number of equal parts. It is better, however, to weigh in and mark separately each division. Suppose, for example, that it is desired to divide a narrow tube into hundredths of a cubic inch: a number of small measures are to be made from glass tubes of about ⅛th of an inch internal capacity, and 34·2 grs. of mercury being weighed into one of them, and any bubbles of air removed with a wire, a scratch with a file is made on a level with the upper surface. This quantity of mercury is to be transferred to the other tubes, which are to be likewise marked in the same manner. These are all to be filled to the mark with mercury, and may be sup-

ported in a glass ready for use; as soon as they are emptied they are to be refilled, and it will be found more economical with regard to time to proceed in this manner than to use only one measure, and refill it each time a division is made. A strip of paper, about $\frac{1}{8}$th of an inch broad, is then to be fastened with glue down the whole length of the tube. Against any convenient part of the wall of the laboratory, a strip of wood is to be nailed, of nearly the same thickness as the diameter of the tube to be graduated. Exactly at the height of the eye, a piece of stout sheet-copper or zinc is to be nailed against the wood, so as to form a spring to keep the tube in its place while the paper scale is being marked, as at a, fig. 371. The upper surface of this spring serves as a guide or ruler for the pencil while making the graduations. One of the gauges full of mercury is then to be emptied into the tube, and the latter is to be so adjusted to the spring, a, that the upper surface of the latter exactly coincides with the surface of the mercury. With the assistance afforded by the edge, a straight line is then made on the paper scale; and this is repeated until a sufficient number of graduations have been made. In order to avoid the slight error caused by the meniscus of the mercury in the small gauge-tubes, the glass may be cut off by a file to within a short distance of the mark, and it may then be ground down to the latter on a plate of glass, which will then serve to close the tube. This, however, is seldom necessary, as it has scarcely any influence upon the result. The graduations on the paper may now be made on the glass by the diamond, each fifth division being somewhat longer than the others. It is, however, much neater to accurately copy the paper scale so obtained on another piece of paper, and, after removing the former, to cover the tube with wax, and scratch through with a point so as to expose the glass, and then make the etching with hydrofluoric acid. The way I have found most convenient for transferring the second paper scale, obtained as above, to the wax,

Fig. 371.

is, in the first place, to have the paper upon which the first scale is copied glued on a slip of wood of the same thickness as the tube. The waxed tube and the scale are then to be placed side by side in the same spring as in fig. 372, and by a point the lines are drawn by means of the ruler, *a*, from the scale to the tube, both being brought by means of *a* to a level with the eye before transferring the divisions. As soon as the scratches are made through the wax, the tube is ready for treatment with the gaseous or fluid hydrofluoric acid, as already mentioned. The error of observation in using tubes graduated in this manner (caused by the fact that the convexity of the mercury during the process of graduation lies in a different direction to that which exists when the volume of gas is being read off) must not be neglected, but in all accurate experiments should be corrected according to Kolbe's rule, given at § 560.

Fig. 372.

701. There is another method of graduating tubes to a given calibre which I have often adopted; it gives excellent results, is very easy of execution, and takes but little time. The tube has two long narrow slips of paper, about 5 millimetres apart, pasted or gummed down its whole length. The tube is then fixed in a perfectly vertical position, mercury poured in from the tubes as described above, and as each portion is added, the eye is carefully brought on a level with the upper convex surface of the mercury, by means of a mirror, as described in § 559. A pencil mark is then made exactly on a level with this surface. This is proceeded with until the entire tube is filled with mercury. A diamond pencil and ruler are then used to scratch the divisions. To make each fifth division longer than the others, the paper is to be removed with the penknife at every fifth mark, just sufficiently to permit the lines to be prolonged to the desired extent on each side.

702. *Stopcocks.*—In every possible case the size of the threads of all the stopcocks, connectors, &c. in use should be the same,

in order that no difficulty may be found in attaching together the complicated systems of apparatus which are essential in some researches. It not unfrequently happens that the neck of a glass balloon has to be cemented to a cap, in order to connect it with an air-pump, previous to filling it with a gas to the action of which some substance is to be submitted at a certain temperature. This illustration is selected because it includes nearly all the manipulation requisite in experiments involving the use of stopcocks, connectors, &c. The first step is perhaps to obtain the gas in a bladder or gas-holder, by transferring it from the gas-jar in which it has been collected over water: the method of performing this operation has already been minutely explained in § 514, p. 315, but it did not fall correctly into that portion of the work to describe the method of cementing the necks of gas-jars and balloons into brass caps. The mixture for the purpose may consist of

> Common resin . . . . . . 5 parts.
> Bees'-wax 1   „
> Red ochre 1   „   .—(*Faraday.*)

The two first ingredients having been melted at as low a temperature as possible, the red ochre, previously well dried, is to be stirred in by small portions, and the heat is to be kept up until all frothing has ceased; the vessel may now be removed to a cool place, and the stirring is to be continued until the mixture has become quite thick.

The balloon, the neck of which is to be cemented into the cap, is to be gradually heated until so hot that it would melt the cement. The latter having been brought into a fluid state on the sand-bath or over a very small gas-flame, is to be applied equally to the whole of the neck of the balloon, in such a manner that when the previously warmed cap is placed over it and pressed on, an excess of cement should exude *outside*, so that it may, after cooling, be removed with a knife. The relative sizes of the neck of the balloon and the cap ought to be so adjusted that the latter would just slip on if a ribbon of moderately thick pasteboard were

once rolled tightly round the former. The apparatus, when finished, has the appearance of fig. 233, § 494, p. 302.

703. To connect the balloon with the air-pump, a stopcock with double male screw and a double female connector are required. These pieces of apparatus are represented in figs. 373 and 374. One of the ends of the stopcock is screwed into the cap of the balloon, a leather washer, which has been previously soaked in a mixture consisting of melted wax and a little oil, intervening between the flanges. The double female screw, fig. 374, enables the balloon to be attached to the exhausting syringe, *a*, fig. 376. The bladder containing the gas is closed by a "bladder-piece," fig. 375, and *h*, fig. 376, which is tied on with twine and
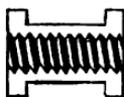
Fig. 373.   Fig. 374.   Fig. 375.
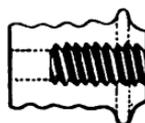
has a double male stopcock screwed into it, the same as that given in fig. 373, and which has been described as connecting the balloon to the syringe.

A double female connector joins this stopcock to that belonging to the exhausting apparatus. The whole arrangement is seen in fig. 376, where *a* is the syringe; *b*, its stopcock; *c*, another stopcock; *d*, the double female connector before described; *e*, the stopcock belonging to the balloon, *f*. The bladder, *g*, is tied by string to the bladder-piece, *h*; its stopcock, which is seen at *i*, is attached by another double female connector, *k*, to the second stopcock, *l*, of the syringe. The bladder being attached, and *i* shut, *l* is opened to allow of the air in the connecting tubes being removed. The cocks, *b*, *c*, and *e*, are then turned on, and the air-pump is worked until the gauge (not seen in the engraving) indicates the requisite degree of exhaustion; *b* is then closed, and *i* is cautiously opened; the gas will then pass from the bladder into the balloon, when *e* being closed after a few minutes have

elapsed, the connector, *d*, is to be unscrewed, and the balloon full of the required gas removed for use.

Fig. 376.
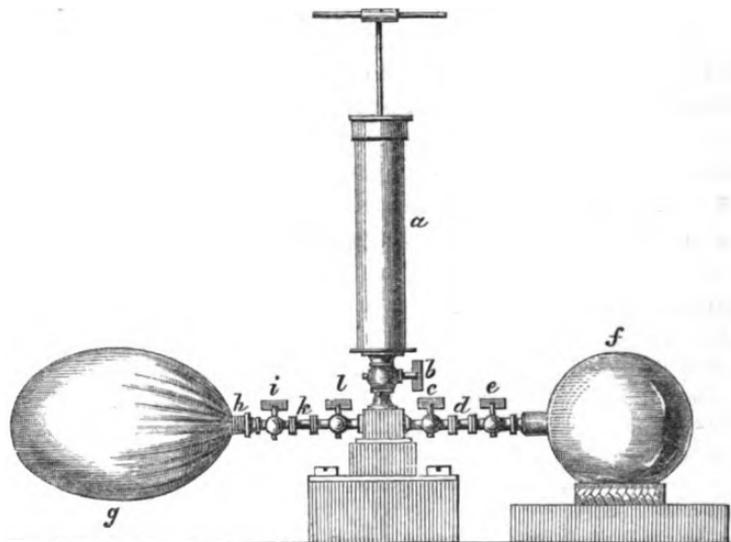
704. It is advisable in choosing stopcocks, to select them with as small an aperture through the plug as is sufficient for the purpose, for by this means the chances of leakage are diminished. When the plug of a stopcock has become fixed, the screw underneath is to be removed, and also the little collar, and a few blows are to be made with a piece of wood, not metal, on the square nut which is at the end of the plug. Care must of course be taken in doing this not to injure the stopcock. If this is ineffectual, the instrument may be oiled and left for some time for the latter to penetrate. In the event of this not succeeding, it may be placed in a small vessel of oil, which is to be put for a day or two in a warm part of the sand-bath. This seldom fails to effect the loosening of the plug.

A very useful contrivance, by which it is often possible to do without a stopcock, is made by inserting a piece of solid glass

rod in the caoutchouc connector between the extremities of the glass tubes used to convey a gas.

An illustration of this has already been given in describing the manipulation requisite in using the method of Bunsen for determining nitrogen.

705. *Knots.*— In arranging chemical apparatus, especially where caoutchouc connectors are much used, it is very frequently required to make joints tight by means of knots.   There are also occasions on which the skilful use of string or wire to keep stoppers tight under considerable pressure, &c. is of great value. In some nautical works there is much valuable information on these points, but the chief portion is of course only interesting to seamen.   All the knots of any value to the chemist have, however, been inserted in the 'Practical Pharmacy' of Mohr and Redwood, from which the following are taken.

706. "The end of the string is doubled and laid on the tube as shown in fig. 377, *d* being the short and *c* the long end of the string. The tube being held in the left-hand, the thumb of that hand is laid over the loop, *a,* so as to retain it in the position represented, while *c* is carried round the tube several times, and finally is passed through the end of the loop, *a,* as shown in fig. 378.
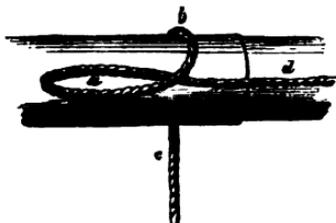
Fig. 377.   Fig. 378.
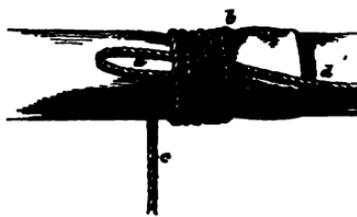
" The end, *c,* being held tightly in this position, the other end, *d,* of the string is pulled so as to reduce the loop, or until it clasps *c* and securely fixes it.   The ends, *c* and *d,* are now cut off, leaving the ligature as represented in fig. 379.

707. " *The pyrotechnical knot.*—This knot is used for the same purpose as that last described. In making it two loops are formed, as shown in fig. 380; these are brought opposite to each other, as in fig. 381, *b* being placed in front of *a* ; they are then slipped over the tube, as in fig. 382,

and the two ends of the string pulled. When the coils are brought close
to each other and made tight by drawing the ends in opposite directions,

Fig. 379.

Fig. 380.

a pretty secure knot is produced. Rockets are tied in this way, and hence
the name. A few coils of the string form a good ligature for an india-
rubber connector; and it has these advantages, that it may be tightened at

Fig. 381.

Fig. 382.
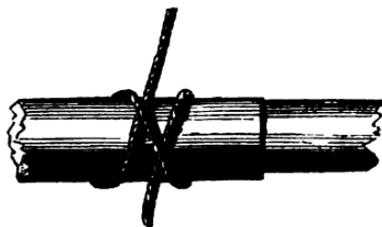
any time by pulling the ends, and also, that it is easily untied without
cutting the cord, by merely pulling each ligature away from that next to it.

708. " *The champagne knot* is used for fastening down the corks of bottles.
A loop, such as fig. 383, is first formed; then the end, *m*, is turned into the
angle, *o*, and carried behind or beneath the loop, as in fig. 384. The part *p* is

Fig. 383.
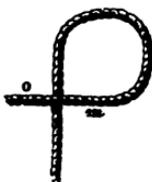
Fig. 384.
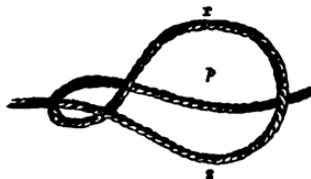
drawn through the loop, as in fig. 385, and in this state it is placed over
the neck of the bottle, immediately under the lip, *p* being on one side and
r s on the other side. The two ends are then pulled, so that the knot being
tight around the neck of the bottle, the free ends shall be opposite each

other, and these are turned up over the cork, twice twisted, and finally tied in a common knot, as shown in fig. 386."

Fig. 385.
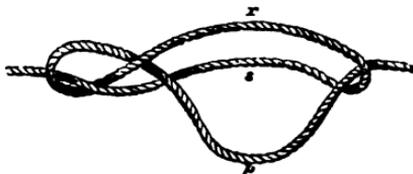
Fig. 386.

709. I have found the last of these knots useful in confining the stoppers of glass bottles in which reactions were to be effected by exposure to 212° in the water-bath, in cases where the use of pressure-tubes was objectionable from the small quantity of material which they were capable of containing without increasing their length to an inconvenient degree.

710. *The Barometer.*—These instruments are constructed in a variety of ways, and those met with in commerce are often exceedingly defective and incorrect. The instrument used for registering the pressure of the atmosphere in quantitative experiments on the gases should be of the best kind, and, if possible, its indications should be compared with those of one known to be accurate. That construction is generally preferred which has the whole scale of brass and moveable, to allow of adjustment as the level in the cistern fluctuates, so that the numbers marked upon the scale shall always express the real distances from the level of the metal in the cistern, no matter what variations may take place in the latter. To effect this the scale terminates in an ivory point, which should, immediately before an observation, be made just to touch the surface of the mercury; that this is the case may be known by the point and its reflection in the mercury exactly meeting.

When the tube of the barometer is small, the diameter must be known, as the capillary attraction between the glass and mercury

exerts an action sufficiently great to render it necessary to make a correction; a table for this purpose will be found at the end of the volume. A correction for temperature is also essential, and Table VII. is inserted for this purpose; but it must be observed that it has been calculated on the supposition that the scale of the barometer is of the form previously alluded to.

711. Messrs. Negretti and Zambra construct barometers with a scale graduated on the tube itself, and in correcting for temperature a different table must be referred to; this will also be found at the end of the volume. This latter table may also be used where the brass scale only reaches a short distance, the rest of the instrument being of wood, and the neutral point being adjusted by raising or depressing the cistern. In that case the correction is not perfectly accurate, because the value of the compound expansion cannot be accurately ascertained; but if the only available instrument be of this kind, an approximative value may be obtained by assuming the compound expansion to be the same as that of glass, and Table VIII. is then to be used.

712. The barometer must be fixed in a perfectly vertical position; if, therefore, any doubt exists as to the perpendicularity of the wall against which it is intended the instrument shall rest, such fact must be ascertained by the plumb-line, and the position of the barometer altered accordingly.

713. A thermometer should also be attached to the barometer; and an arrangement is generally adopted which permits the bulb to be immersed at will in the mercury in the cistern, so as to indicate as accurately as possible the true temperature of the metal. A small screw-stopper is provided to close the aperture in the cover of the cistern by which the thermometer enters, when the latter is not inserted.

714. *The Goniometer.*—This instrument, although not strictly a chemical one, is, like the barometer and many others, indispensable to the chemist in many of his experiments.

715. Several instruments have been devised for measuring the angles at which the planes of crystals incline to each other; there are only two, however, which specially demand our attention, as

being not only the most commonly used but the most convenient; these are the common goniometer of M. Carangeau, brought into general use by Haüy, and known by his name, and Wollaston's reflective goniometer.

The former of these is only adapted for approximative measurements, and even then is of limited application, because the angles of very minute crystals cannot be determined by it; moreover, it is especially ill-adapted for the crystals obtained in organic researches, because the latter are generally easily frangible; and, as will be seen presently, the common goniometer is liable to scratch and otherwise injure the crystals to which it may be applied, unless they are tolerably hard.

716. Haüy's goniometer depends upon the principle that the opposite angles developed by two right lines, in crossing each other, are equal. Fig. 387 shows the instrument by which the above rule may be applied to determine the angle at which the planes of a crystal meet. As usually made, it consists of a brass semicircle, divided into degrees, and having two arms, $a\,b$ and

Fig. 387.

$d\,f$, usually of steel, susceptible of movement backwards and forwards in the slits, $g\,h$, $i\,k$ and $d\,m$; it is possible, therefore, to lengthen or shorten the arms as we please. The arm, $a\,b$, is retained in its horizontal position, but $d\,f$ is intended to indicate the angle of the crystal by the position of its inner face, f, on the graduated arc. If we apply the edges, a and d, to the two faces of a crystal in such a manner that they rest on them accurately in the manner indicated in the engraving, the angle contained between the inner face, f, and the zero is the angle sought.
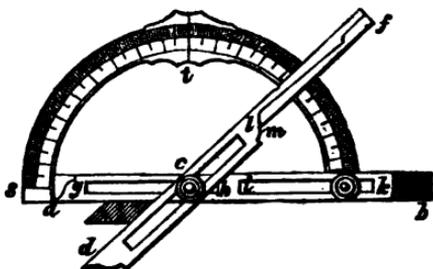
717. Previous to making a measurement, the bar, $d\,f$, is to be made to assume a more acute angle with $a\,b$ than that desired to be determined. The crystal whose dihedral angle is to be mea-

sured, is then pressed without unnecessary violence between the points. The instrument should now be held between the eye and a lamp, or window; when, if no light is to be observed between the faces of the crystal and the surfaces a and d, they may be considered as coinciding sufficiently, and the angle is to be read off.

718. If very small crystals are to be measured, the arms $a\,b$ and $d\,f$ are to be shortened by means of the slits, otherwise it would be impossible to obtain such an accurate coincidence of the edges of the bars and the planes of the crystal as to allow of good measurements being made.

719. The reflective goniometer of Wollaston* is entirely different in principle, and possesses numerous advantages over that used by Haüy. By it crystals scarcely discernible to the naked eye may be accurately measured, if possessing brilliant surfaces; an instance of this occurred soon after its discovery. In the island Jean Mayen, in the Greenland seas, there is found a crystalline jet-black sand; a portion of this having been obtained by Dr. Clarke, he fixed on the moveable plane, h, to be presently described, a minute but brilliant crystal, the planes of which were inclined at an angle of $92\frac{1}{2}°$. Dr. Wollaston, who repeated the measurement, obtained exactly the same result, and recognized the sand as identical with that of Bolsenna.

Fig. 388.

720. The instrument consists of a vertical metallic circle, $a\,b$, fig. 388, graduated on its edge to half degrees, and supported on a very massive and steady frame, c. The circle is capable of rotation by means of the large-milled head, d. A smaller milled head, e, is
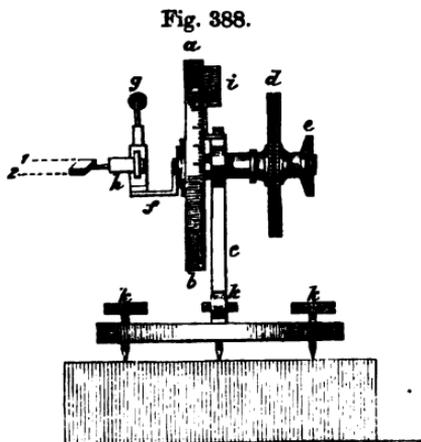
* This instrument was, I believe, first described in the Phil. Trans. for 1809, and in Tilloch's Magazine for Feb. 1810, vol. xxxv.

connected with an axis passing through that which serves to move *a b*, and which is consequently hollow. This latter axis enables us to move the bent arm, *f*, which in its turn carries a rod, *g*; this rod, at its end nearest to *f*, is split, to enable it to carry a small plate of brass, *h*, to which the crystal is eventually to be attached by means of wax, in such a manner that the edge where the planes meet (the angle of which is to be measured) is parallel to the axis of the instrument. It will be seen that the rod, *g*, is at right angles to the axis of the disc, and, in fact, this is the only position in which the goniometer can be used; but it is a singular circumstance, that many chemical works, in illustrating the goniometer, give the rod, *g*, a position coinciding with the axis of the disc: this is calculated to mislead, as in that position it is almost impossible to obtain the necessary adjustments for the two faces of the crystal. The plate is, by means of the mechanism described, susceptible of a considerable number of movements, each of which may be not only made to any desired extent, but are, from the stiff way in which the parts move, not liable to be deranged by accidental vibrations of the apparatus. A vernier, *i*, is firmly attached to a bar, which in its turn is securely screwed to the massive support, *c*.

721. Before using the goniometer, it must be placed upon a block of wood, standing at such a height on a massive table, that, the elbows resting on the latter, the fingers reach easily to the crystal and the milled heads which move the graduated circle and arms. The circle must have its edge towards the window, which latter, to enable the observation to be made conveniently, should have horizontal bars. The most proper distance for the goniometer to be placed from the window is about 7 or 8 feet. We now proceed to ascertain, by means of a spirit-level attached to the stand of the instrument, whether the graduated circle is in a perfectly vertical position, and if not, it is to be carefully adjusted by means of the levelling screws, *k k k*.

722. By this time the crystal may be attached to the wax as described above. It has been said that the window

should have horizontal bars; this is necessary to enable the two faces of the crystal to be alternately placed in exactly the same position; and it is also necessary to have another line at an inferior level; the latter may be made for the purpose, by stretching a black ribbon in a position perfectly parallel to the bars of the window, but at only a slight elevation above the ground; or any distinct line naturally existing may be used, such, for instance, as the line of junction between the floor and the wall beneath the window. If, now, the crystal has brilliant planes, and the eye be brought close to it, it will be found easy to obtain a reflexion of the bar of the window on the plane which is first to be adjusted; if the bar is not immediately seen on placing the eye nearly close to the crystal, it may be readily brought into view by a slight elevation or depression of the bar, g. It will now be found, by continuing to raise or depress g, according to the position of the crystal, that the reflected bar may be made to gradually approach and finally merge into or coincide with the inferior line mentioned above. But it generally happens that, in the first trials, the two lines when approximated to each other are seen not to be parallel; if then the milled head, g, be slightly rotated to the left or right, as may be required, it will be easy to make the two lines perfectly coincide throughout their whole length.

It now only remains to adjust the second face of the crystal, that it may reflect the two guiding lines as accurately as the first one did. If the operator will now refer to fig. 388, he will see the position of the crystal during the adjustment of the first plane. It is necessary now to make the plane, marked 2, fulfil exactly the same conditions as regards the reflected images of the upper and lower bars.

To effect this, the smaller of the two vertical milled heads, e, is to be rotated in a direction away from the operator, the eye being kept in a position as nearly as possible the same as when observing the face marked 1 in the engraving. The bar of the window will now be found to be reflected from the second face in the same manner as from the first, and is equally to be made,

by continuing the motion, to approach gradually to and at last to merge into the lower line. But, as in the first case, it will probably be found that the two lines are not parallel on the first trial; we must not, however, effect the parallelism in the same manner as was done with the first plane, namely by rotating *g*, because such a proceeding would destroy the first adjustment; it suffices, however, for the purpose required to move *g* to the left or right until the lines coincide, this movement being provided for by a pin which joins *h* to *f*.

The two planes are now to be observed again, in order to ascertain whether the adjustments are perfect, and if found to be so, the larger of the two vertical milled heads, *d*, is to be rotated until the zero of the vernier coincides with 180° of the graduations on *a b*. In consequence of the mode of construction of the instrument, it is easy now to rotate the entire system of parts which carry the crystal, without disturbing the position of the graduations with reference to the vernier. In order, therefore, to measure the angle desired, *e* is to be rotated until the reflected bar coincides with the inferior line, the graduated circle being undisturbed; it is now merely necessary to rotate *d* until the reflected bar, as seen from the face marked 2, exactly covers the lower line, when by inspecting the position of the circle and vernier, the angle may at once be read off to minutes of a degree.

723. It often happens that the crystal the value of the angles of which it is desired to know, is too small to be measured with the common goniometer, and yet that the planes are not sufficiently brilliant to permit of the use of the instrument last described; it is sometimes possible to overcome this difficulty by attaching thin laminæ of mica to the faces.

724. Under certain circumstances angles may be measured by the aid of artificial light, the bar of the window being replaced by a small but bright lamp- or candle-flame placed in an elevated position and at a considerable distance, the inferior line being black on a white ground and well illuminated by another lamp, the flame of which is prevented from being reflected by the crystal.

725. *The Air-pump.*—This instrument is in constant use in

the laboratory; it is employed in almost every branch of the science. One of the most common applications of it is for the purpose of drying *in vacuo* preparations which decompose on heating. Numerous instances of this occur both in inorganic and organic research. For this purpose, we place on the plate of the air-pump a shallow cylindrical dish containing concentrated sulphuric acid. A brass disc, pierced with several holes of different sizes, supports the substances to be dried, which may very conveniently be contained in watch-glasses. These latter should be ground on their edges, and have their weight marked on them with a writing-diamond. One of the chief advantages of watch-glasses for this purpose arises from their shallowness permitting the substance under examination to be spread in a very thin layer, which, from the large surface exposed, is well adapted for facilitating the rapid removal of the water (§ 320).

726. Another application of the air-pump is in taking the densities of porous bodies, for the latter, when immersed in water, appear much lighter than they really are, in consequence of the pores being filled with air. If, for example, a piece of coke, the density of which taken in the ordinary manner is 1·223, be placed in a vessel of water and the whole be introduced under the receiver of the air-pump, the first stroke of the piston causes the evolution of innumerable bubbles of air, and, as the exhaustion proceeds, the water appears to boil. Presently the coke rises to the surface, buoyed up by the adhering bubbles of rarefied air, and the pumping is to be continued until the bubbles no longer appear. If, now, the screw-tap of the pump be gently opened, the coke which had risen to the surface sinks like lead to the bottom, and on taking anew its density, it is found to be raised to 1·540. Even greater differences than this are sometimes observed.

727. It is very questionable whether in this instance the true density is obtained by removing the air; in the first place, there may occur cavities in the coke which do not communicate with the surface, and consequently do not allow the air or gas to be removed from them by the pump. In the next place, it remains to be decided as to what is to be regarded as the condition under which

x

the densities of cokes should be taken and compared with each other. Probably the normal state is the proper one. Possibly if the coke was reduced to a fine powder, its density in that state would be the most proper for comparison with other specimens. It must not be forgotten, in circumstances of this kind, that the densities of bodies taken in the pulverulent state often come out higher than when solid, and that even metals in the densest state procurable by hammering, yield lower specific gravities than when in the fine state of division obtainable by precipitation and other methods. This appears somewhat anomalous, but the fact has been placed beyond doubt by the researches of G. Rose, who found some platinum-black to possess the very high density of 22·89, although that of other specimens was as low as 14·89. And he found gold powder, precipitated by green vitriol, to vary from 19·55 to 20·72, whereas hammered gold is seldom denser than 19·4.

728. The air-pump is, as has been said, § 620, used in the determination of nitrogen by the method of Bunsen; the employment of it in Dumas' method has been superseded by the process described in § 621. It is also seldom resorted to now in making the combustions of organic bodies. It is, however, indispensable in numerous operations of a physical nature that constantly become necessary in the course of organic investigations. The mode of employing it has been described in treating of the operations themselves in the previous sections of this work.

729. An exceedingly convenient and economical form of pump consists of a good exhausting syringe, capable of being fastened to a bench in a horizontal position, and having adapted to it several connectors and taps, in order that it may be employed for different kinds of operations. A small stool supporting a ground plate and glass receiver should be provided. The stool is to have beneath it a tap attached to a flexible tube, to enable it to be connected with the syringe for the purpose of exhaustion, and, when desired, removed without destroying the vacuum. This is effected by turning off the tap beneath the stool before separating the apparatus from the syringe. The latter can then be used for other operations,

while substances are still retained *in vacuo*. The flexible tube connecting the receiver with the pump, must have a coil of wire in it, to prevent it from collapsing during exhaustion. I have had an apparatus of this kind in use for a long time, and have found it most convenient in numerous operations connected with organic chemistry, such as in drying the flasks for vapour-densities (§ 129), and at the same time retaining substances *in vacuo* over a surface of sulphuric acid, to remove water, &c. It should have a barometer-gauge capable of being attached by a screw and washer when required.

730. In using air-pumps generally, there are a few precautions which demand attention. Many instruments, especially if their plates are of glass, have a small hollow milled head in the centre of the plate, serving to keep it in its place, and also to prevent fluids spilled on the surface from finding their way into the valves; their use is, however, attended with the great inconvenience of preventing flat dishes from being placed on the ground disc without the intervention of a triangle or other support. If the milled head is absent, care must be taken not to place a flat dish over the aperture leading to the valves, unless there is space enough to allow the air to be pumped out easily; a small piece of paper placed between the dish and the plate at one side is sufficient to prevent any inconvenience arising from this cause.

731. Especial care must be taken to prevent fluids from being spilled on the plate lest they corrode it, or, if of glass, and consequently not liable to corrosion, lest the fluid finds its way into the tubes or valves. A little grease should be applied to the edge of the glass receiver before pumping, in order to increase the tightness of the apparatus. If the plate is of metal, great care must be taken as to the nature of the grease used, some kinds corroding it rapidly, and rendering it useless until re-ground.

732. If it is found that the plate and receiver do not fit with sufficient accuracy to enable a vacuum to be sustained for some time, the spot where the leak occurs may be easily discovered by letting a little water run round the outside of the plate and against

x 2

the outer edge of the receiver; on working the pump and leaving it for some time, the water will find its way inside, and thus show the defective spot. The leak may sometimes be stopped temporarily by applying to the place a little wax softened by melting with a very small quantity of oil.

The air-pump is employed for many operations which do not fall properly within the limited scope of this work, but there are a few other appliances and precautions which it would be improper to omit. If a siphon-gauge is attached to the instrument, care must be taken not to admit air too rapidly into the vacuum, for the gauge might be deranged or even broken by it.

733. Dr. Andrews has described a method of obtaining a perfect vacuum with the pump; the details are too long for insertion, the student is therefore referred to the original paper*.

If solutions containing excess of volatile acids are exposed over sulphuric acid *in vacuo*, the water is soon absorbed, and the acids which were previously held in solution by the water vaporize into the receiver and do much injury. This is particularly the case with solutions of platinum-salts containing excess of hydrochloric acid. The evil may be remedied by the presence of a small capsule of lime. If a considerable number of preparations are required to be exposed to a surface of sulphuric acid *in vacuo*, a piece of apparatus on the principle of what is termed a "dumb waiter," may be employed. It consists of a series of discs, preferably of brass, perforated with small apertures; these are supported on a rod passing through their centre, the rod ending in a brass cover fitting on to the vessel of sulphuric acid, but of course having numerous apertures, so as to allow the acid to exert its absorbent influence without restraint. The brass discs permit a considerable number of watch-glasses or capsules to be placed under the receiver at once. Great care must be taken that the pump is firmly clamped to a solid heavy bench or table, so as to prevent vibration when being worked, as the capsules, &c. might be upset, and cause great delay and loss of valuable material. The arrangement of the exhausting syringe and receiver or stool

* Quarterly Journal of the Chemical Society, vol. v. p. 189.

is convenient in this respect, inasmuch as the stool may be placed
on one table while the syringe is worked at another, and con-
sequently all danger from the vibration is avoided.   Even if the
receiver and syringe stand on the same table, there is less danger
in this respect than with the ordinary air-pump, because the
former having the pumping part and the receiver only connected
by a flexible tube, the vibration is not communicated if the table
be steady, whereas with the latter it is impossible to work the
double-barreled pistons without communicating a little motion
to the entire apparatus, unless extreme care is taken in fastening
the clamps to a very strong table or bench.

734. An air-pump, to be kept in good order, should not be
allowed to enter, or at least remain for any length of time in the
laboratory, as it would inevitably be injured by the acid fumes
floating about.   The plate should be cleaned at frequent intervals
with a little cotton soaked in neat's-foot oil, and the grease
should be removed from the receiver and replaced by fresh when
required.

735. Sometimes it is found that a new pump is incapable of
sustaining a vacuum, although the surface of the plate and the
ground edges of the receiver fit perfectly; if the screws and
washers are not defective, the taps must be examined and re-
ground.   Even after all the joints have been prepared with the
greatest care, still the pump is at times imperfect.   Generally it
is the workman's place to set this right, but there are circum-
stances which render it desirable for the operator to know how
to ascertain the nature of the defect.   The only resource now
remaining is, to connect the various parts of the pump, one by
one, with a powerful condensing syringe, such as those used for
air-guns, and, after plunging the suspected piece of metal under
water, vigorously working the instrument.   It is, of course,
essential that all the apertures, except that in communication
with the syringe, be closed.   If then the metal is porous (as
often occurs, owing to defective casting or the use of bad metal),
air-bubbles escape through the water and indicate the leak.
Sometimes the error may be remedied by dipping the piece into

chloride of zinc, and after making it very hot, running solder over the part; the latter then runs into the fine apertures, and the excess may be removed by the file or lathe.

736. Every pump should be carefully ascertained to be perfect before use. To effect this, a vacuum is to be made as far as possible; the barometer or siphon-gauge is then to be examined; no alteration in the height of the mercury should be observed even after several hours. A first-class pump will retain the mercury in the barometer-gauge, within a small fraction of an inch of the height of the barometer at the time, for days or even weeks, but with ordinary instruments this must not be expected; and if it is desired to retain a pretty good vacuum for a considerable period, the instrument should have a few strokes given to the pistons every few hours.

737. When silver-salts are to be dried *in vacuo*, a dark cloth should be thrown over the receiver to prevent access of light, as its presence often causes decomposition, and consequently erroneous results on analysis.

SECTION XXVII.

REMARKS ON A FEW OF THE PROCESSES AND RE-ACTIONS EMPLOYED IN SOME RESEARCHES.

738. The matter contained in this section is intended to call the attention of the student to some of the broad principles upon which the examination of bodies is founded.   In alluding to inorganic substances, I have seldom entered much into detail, because the chief part of the processes and reactions employed in this branch of the science are dwelt upon with more or less minuteness in most elementary works; but such matters have been mentioned as were considered likely to be instructive, and with which it is absolutely necessary every one should be familiar, if intending to make original experiments.

739. It will, of course, be presupposed that the student would not commence pursuing original experiments until acquainted with the methods of performing qualitative and quantitative analyses; and also that he has perused attentively some of the elementary treatises which exist in our language either as originals or translations.

740. It will also be unnecessary to point out the nature of the very simple calculations required, except in special instances, as they are to bo found in all works on quantitative analysis.

741. Before entering further into the subject, it will be proper that we should endeavour to define the term "Chemical research." It must not be supposed that making analyses constitutes research; analysis is only one of the implements, if we may use the expression, employed in making researches.   Strictly speaking, the term ought to be restricted to experiments having a distinct object in view; such, for example, as the production of a hitherto unknown body, the possible formation of which has been determined by mere reasoning.   But the term has been so long used in a more extended sense, that it may also be made to include experiments undertaken to ascertain the nature and pro-

perties of unknown substances and compounds existing as natural
or artificial products. But, even then, we must not forget that
mere analysis does not constitute research; it is not sufficient
alone to determine the *composition*: it is essential also to fix the
constitution of new bodies, and their position among chemical
substances generally, to entitle the experiments to this appella-
tion.

742. It is more difficult to draw the distinctive line between
the directions belonging to this work, and those appertaining to
works on general analysis in inorganic than in organic chemistry,
because with the former the true constitution of a substance is
more quickly ascertained than with the latter; for, as soon as an
inorganic substance has been accurately analysed, it is generally
easy to determine its real nature; but with organic substances it
is seldom that the determination of the constituent elements
serves at once to establish beyond doubt its chemical relations.
The numerous instances of isomerism which are to be met
with among organic substances, at once show the insecurity of
founding any ideas of constitution upon the mere results of
analysis.

743. It becomes necessary, in consequence of what has been
said, to determine the nature of the products of decomposition
of organic substances, and also, if possible, the result of their
combinations with many other bodies, before pronouncing deci-
sively upon their true character.

744. We shall therefore divide the subject into two branches,
admitting each in its turn of subdivision, namely, *inorganic* and
organic. Inorganic research, as distinguished from mere ana-
lysis, is perhaps somewhat more limited than the organic depart-
ment of the science, in the variety of compounds of a novel kind
which are capable of being educed or formed.

745. The mere analysis of an inorganic substance gives at
once a clue to its position among chemical substances; and we
are consequently enabled to pronounce with some confidence as
to the particular class of compounds which it will form with
other bodies, and even in many instances their properties and

appearance. This is much less the case with organic substances, not merely for the reasons previously given, but also because their comparative instability causes a much greater tendency to decomposition and transformation.

746. Inorganic bodies may be divided into two classes, *non-metallic* and *metallic*. It is true that the line of demarcation is difficult to draw in its strictly scientific sense, but for the purposes of this work we shall understand by a metal, a body possessing the metallic lustre, and agreeing in general characters with the known metals.

747. *Non-metallic bodies.*—If the existence of a new non-metallic substance was announced, there are a few questions which would immediately be asked concerning it, namely, is it solid, liquid, or gaseous, at ordinary temperatures? and what class of bodies does it most resemble? Now whatever its physical condition may be, we can soon acquire a tolerable idea of its chemical relations.

748. One of the first and most important facts to ascertain with regard to all bodies, is its atomic weight. In order to accomplish this, we must carefully analyse some compound or compounds which it forms with substances the atomic weight of which is well known.

749. It has been said that the careful analysis of the substance or compound from which the new body was educed, will enable the student to form a tolerably good idea of the class of bodies with which the non-metallic element is to be associated; but it is not always easy to determine this point with accuracy, or, at all events, until the nature of a considerable number of its compounds has been established.

What, then, are the principal compounds which non-metallic substances yield, and how are they procured? Our space will not permit us to follow out all the compounds formed by non-metallic bodies; but, with a view to show the methods of pursuing this kind of subject, we shall glance at a few of the most prominent and instructive.

750. *All non-metallic bodies combine with oxygen.*—The follow-

x 5

ing are the principal methods by which these compounds are procured :—

I. By direct combustion in air or oxygen.

II. By passage of electric sparks in presence of oxygen.

III. By oxidation with nitric acid.

IV. By distillation with a peroxide.

V. By contact of elements and oxides, under certain circumstances.

751. Each of these methods of producing oxides requires certain precautions, and demands therefore a few remarks.

752. I. *By direct combustion.*—In this manner some of the non-metallic elements pass at once to their highest state of oxidation, others to one of the lower states; and, with some, the nature of the oxide depends upon the temperature at which the combustion occurs.

753. Sulphur and selenium burn in oxygen, and produce sulphurous and selenious acids; they therefore behave alike by this method of oxidation; we shall see presently that this similarity of deportment is not invariable. Sulphur and selenium do not by this method pass at once to their highest state of oxidation.

754. Hydrogen, as every one is aware, does not pass to its highest state of oxidation, but forms water only.

Nitrogen does not unite with oxygen by combustion in the ordinary manner.

Carbon passes at once to the highest known state of oxidation.

Phosphorus, at the temperature of actual ignition, passes into its highest state of oxidation, namely, phosphoric acid; but by slow combustion at ordinary temperatures, it forms phosphorous acid.

755. II. *By passage of electric sparks in presence of oxygen.*— Nitrogen by this process is converted into nitric acid; the reaction is facilitated by the presence of bases.

Hydrogen, carbon, and other bodies inflame and behave as at I.

756. III. *By oxidation with nitric acid.*—It is singular that, while selenium and sulphur by combustion in oxygen yield the

same acid, with nitric acid the reaction is different; and while selenium passes into the same acid as by the first mode of oxidation, sulphur, on the other hand, combines at once with the maximum amount of oxygen, forming sulphuric acid. This fact is instructive, and shows that, however closely two elements may resemble one another and run parallel for a considerable distance, they are liable suddenly to diverge from each other at a point least anticipated.

757. Phosphorus forms phosphoric, and iodine iodic acid when treated with nitric acid. Carbon, on the other hand, forms a most curious substance, or series of substances, of unknown composition, and called by their discoverer* artificial tannin.

758. If the student attentively considers the facts above detailed, he will find that the products of oxidation of non-metallic bodies with nitric acid vary with the nature of the element, and in no case is an oxide formed containing one atom of each constituent.

759. IV. *By distillation with a peroxide.*—This method, available under certain circumstances, results, with sulphur and peroxide of manganese, in the formation of sulphurous acid; it is not a method by which the atomic weight of an unknown non-metallic body could with ease and certainty be ascertained.

760. V. *By contact of elements and oxides, under certain circumstances.*—This is a method by which some of the oxides of such bodies as chlorine and iodine are to be obtained.

761. Non-metallic elements combine among each other to form a great variety of compounds, but few of them are of a class to enable the atomic weight of the resulting body to be determined with ease and certainty. To ascertain the combining proportions of a substance of this class, we should be guided by the nature of the element itself. If a gas, its density, —or if vaporizable at temperatures not too elevated, the density of its vapour,—should be carefully determined. It must not be forgotten, that with bodies not easily vaporized, the density of

* HATCHETT.—It is greatly to be desired that this subject should be re-investigated by modern methods.

the vapour should be taken at temperatures considerably above their boiling-point, if results are to be obtained from which the atomic weight is to be easily and precisely settled.

762. The vapour-density not only enables us, with non-metallic elements, to pronounce upon the atomic weight, but also, taken in conjunction with the analysis of a compound with silver, upon the class of bodies among which it is to be grouped.

763. For the purpose of determining the atomic weight of a substance, it is very desirable to obtain at least one compound that consists of one atom of each of its constituents. Now it is possible to obtain silver-salts of most of the non-metallic elements in which we are sure of the constitution being of the kind required. If, therefore, we analyse a salt of this description, we at once possess the data for determining its atomic weight. Let us suppose that a silver salt has yielded

$$54\cdot04 \text{ non-metallic element}$$
$$45\cdot96 \text{ silver}$$
$$\overline{}$$
$$100\cdot00$$

we say

				At. wt. Ag.	At. wt. non-metallic element.
$45\cdot96$	:	$54\cdot04$	::	108	: $126\cdot98$

764. Now, on determining the density of its vapour, the non-metallic element gave $8\cdot716$: how are we to know to what class of bodies it belongs? A very little reflection will show, that as hydrogen is received as unity for atomic weights, if we received it also as unity for gaseous and vapour densities, the atomic weights of bodies of the same vapour-volume would be expressed by their vapour-density. It is obvious, then, that if a substance possesses the same vapour-volume as hydrogen, its atomic weight will be obtained by dividing its vapour-density by the density of hydrogen. If, therefore, the number obtained by dividing the vapour-density of a non-metallic element by the density of hydrogen is identical with the number obtained by analysis of the silver-salt, it will be certain that the substance under examina-

tion possesses the same vapour-volume as hydrogen, nitrogen, chlorine, &c. Let us try this in the present instance. The vapour-density was, as we have said, 8·716, and if we divide this by 0·0692, we obtain 125·95 as the result, which, although differing somewhat from 126·98 obtained as the atomic weight by analysing the silver-salt, is still quite a sufficient approximation to indicate that the body we have examined has a vapour-volume the same as hydrogen. The body we have selected as an illustration is, as the student has probably perceived, iodine. If, on the other hand, it was necessary to divide the vapour-density by twice the density of hydrogen to obtain the atomic weight, we may infer with safety that the vapour-volume is that possessed by oxygen and elements of the same class.

The mode of obtaining the vapour-density of an organic body, by multiplying its atomic weight by half the density of hydrogen, has been pointed out in a former section (§ 127).

765. There are numerous points connected with the non-metallic elements which demand investigation.

Sulphur replaces the oxygen in carbonic acid, bisulphide of carbon resulting; but no sulphide analogous to oxalic acid has yet been formed.

766. It is said that sulphide of carbon heated under pressure in presence of water is decomposed, a gas being formed; if, now, the decomposition proceeds thus, $CS^2 + HO = CSO + HS$, we have an interesting substance, being carbonic acid, in which one of the equivalents of oxygen is replaced by sulphur. The experiment should be tried. Sulphur, selenium, and tellurium have many points in common; only the first, however, has had its compound with carbon investigated.

767. The action of ozone on various inorganic and organic bodies requires to be tried, and now that it can be prepared from the peroxide of barium, the chief barrier to its use is removed.

768. *On processes and reactions connected with metals.*—The examination of metals, or of minerals, or other substances containing them, is a matter of such every-day occurrence in almost all laboratories, that it is essential for the student to thoroughly

familiarise himself with their properties and peculiarities. The
study of metallic substances has greatly advanced within the last
few years; so much so, that metals which, until recently, have
been considered rare, and obtained with difficulty, and were chiefly
to be found on the shelves of museums, and, even then, in speci-
mens of a few grains in weight, are now articles of commerce,
and likely ere long to become valuable in the arts.

769. Moreover, our ideas of the rarer metals, as they were
once called, are rapidly passing through a transition state, pre-
vious to undergoing a complete modification. The rarity of a
metal depends upon two circumstances, either of which may
cease to exist, and thus cause a metal rare to-day to be almost
common to-morrow. These two circumstances are, difficulty of
procuring the ore, or the expense of extraction. Now the ore of
aluminium, or clay, is one of the most abundant of substances;
and yet, until lately, aluminium was one of the rarest of che-
mical products. Again, vanadium has always been regarded
as a metal of such extreme scarcity as to make it difficult
to conceive its use in the economy of nature; but, quite
recently, it has been found easy to obtain it in tolerably
large quantities by an inexpensive process, from a waste product
obtained in the preparation of uranium-yellow from the Joachims-
thal ores*.

Now vanadium is a metal the reactions of which are so marked,
that undoubtedly if obtainable in quantity at a reasonable price,
it might be made available in the arts†.

770. No substance is to be regarded as useless because we are
not aware of its value; the reproach applies not to the substance,
but to our imperfect knowledge. There are instances on record
of bodies which for years were not known to be of the slightest
value or interest save to the scientific or theoretical chemist, and
yet the same substances have at last been proved to possess

---

* PATERA, Oesterreich.—Zeitschrift für Berg- und Hüttenwesen, 1856,
No. 31; and Chemical Gazette, March 1857.

† The tannate of vanadium is said to be the most indestructible, and
therefore the most valuable of inks.

powers that can only be properly appreciated by those whose sufferings have been relieved by their medicinal virtues.

771. The chemical history of the metals is full of interest. The very difficulty with which some of them are procurable in a state of purity, gives zest to the study of their properties. The extraordinary resemblance which some of them present to each other, and the fact that these assimilating metals are almost always found associated in nature, by countenancing the ideas which have of late been promulgated relative to their being compound, makes us feel that we are on the eve of discoveries which will possibly entirely modify our ideas of elementary bodies, and open new and most interesting tracks for the chemist to pursue.

772. In studying the chemical history of metals, nothing is to be regarded as unimportant which can throw any light upon their nature. It has often happened that the careful following out of a peculiarity in the reactions of a metal has led to brilliant discoveries. If, in examining a well-known metallic substance, any of its usual reactions should appear to be modified, it is most desirable to clearly ascertain the cause, as, by so doing, not only is some useful information certain to be gained, but it is possible that the result may be of greater value than could at first be anticipated. In 1817, while Stromeyer was examining the drugs of an apothecary at Hildesheim, he found that instead of the oxide of zinc ordered by the Pharmacopœia, the carbonate had been substituted. On inquiry, it transpired that the manufacturer had replaced the oxide by the carbonate, in consequence of his being unable to prepare the former in the usual white state, owing to some unknown impurity. A careful examination of this oxide resulted in the discovery of a new and most interesting metal, cadmium. On a subsequent occasion, the same chemist found that several apothecaries at Magdeburg had in their possession a preparation of zinc which had been confiscated on the supposition of its containing arsenic, because, when dissolved in an acid, the solution gave a yellow precipitate with sulphuretted hydrogen; his previous experiments on cadmium had shown him that that metal gave a yellow precipitate with

the same reagent; he was in consequence induced to examine the suspected article, and found, as he had anticipated, that the new metal had again led to difficulties between the apothecaries and their inspectors.

773. It is also necessary that extreme care should be taken to investigate with scrupulous minuteness the properties of any substance that may appear to differ from known metals. The history of Chemistry shows numerous instances of substances being taken for new metallic oxides which were in fact well-known bodies, the reactions of which were disguised by the presence of some impurity, or from the fact of their being in a state of combination, with the properties of which the operator was unfamiliar. Among the most prominent instances of this kind, may be mentioned the substance in the form of a white powder, which Bergman obtained by treating cold short-iron with dilute sulphuric acid, in his endeavour to determine the cause of the brittleness of that variety of the metal. By fusing this powder with a flux and charcoal, he obtained what at the time he believed to be a new metal, but Klaproth showed that it was only a phosphuret of iron formed by reduction of the phosphate of iron which constituted the white powder. More recently, even Berzelius was led to confer the name of Thorina upon the subphosphate of yttria, under the impression that it was a new metallic oxide (§ 174): fortunately for him the error was rectified by himself, and, not long after, he discovered what really turned out to be a new metallic oxide, and as its reactions had some analogies with the substance formerly called thorina, he transferred the latter name to it. Thorina has also, within the last few years, been described as a new metal, under the name of donarium. Another recent instance of a well-known substance being mistaken for a new metallic oxide, is in the case of the supposed new earth Thalia, which was shown* to be nothing but magnesia mixed with a little lime. The error arose from the fact, that strong solutions of magnesia are, contrary to what is generally supposed,

* J. LAWRENCE SMITH.—'Chem. Gazette,' September 15, 1853, and 'Silliman's Journal,' July 1853.

precipitated under certain circumstances by oxalate of ammonia. In short, it would be easy to mention many other mistakes of the same kind which chemists have committed through too hastily pronouncing upon the nature of substances the reactions of which were either not very decided, or closely resembled those of others.

774. *Physical properties of metals.*—In studying metals and their combinations, we must consider not only their chemical, but also some of their physical properties. It is essential to determine their density, and that under various circumstances; first, after fusion, then the button may be well hammered out or rolled by a flatting-mill, and the density again determined. We have already alluded to the fact, that metals in the state of fine powder have sometimes a higher density than when hammered. The hardness and malleability should be determined, and also the ductility. The immense difference in the properties of metals is strikingly illustrated in their degrees of hardness; for example, sodium can be easily cut with the nail, while chromium in its hardness actually rivals the diamond, and if it were less brittle, might even be used for dividing glass, as it not merely scratches but actually cuts it asunder. To determine the colour of a metal is generally easy by inspection, but it must not be forgotten, that as the apparent colour of a metal depends upon the nature of those simple rays which are most reflected by it, so the tint will not be exactly the same when the reflected rays are observed at varying angles of incidence; because, as the angle differs, so the proportion of the different rays reflected will vary.

775. The greater or less power of the metal for conducting electricity, as compared with other metals, should be ascertained, as also its conductibility for heat. Its fusibility and tendency to crystallize in passing slowly from the fluid to the solid state should be observed.

776. In determining the crystalline form of a metal, much will depend upon the nature of the metal itself. Sometimes it is easy to obtain crystals by fusing a considerable quantity in a

crucible and allowing the whole to cool very slowly, by sur-
rounding the crucible with red-hot sand. As soon as the upper
portion has solidified, an iron rod is to be forced through the
crust, and the crucible being held by a pair of ring-tongs, the
fluid is to be poured out. When cold, the solidified crust is
generally found to indicate, more or less, traces of crystallization.
When bismuth is treated in this manner, if the quantity be suf-
ficiently large, very beautiful crystals are obtained, belonging to
the cubic system. In consequence of excessively thin layers of
oxide being formed, most brilliant shades of colour are generally
observed on them. It is possible also to obtain crystals of lead,
tin, and antimony by the same process, but they are very inferior
in appearance. Crystals may also be obtained by electro-depo-
sition, under certain circumstances.

777. At times it is possible to develope figures corresponding
to the planes of cleavage of metals, by treating metallic surfaces
by acids. Thus, if a plate of tinned iron be gently warmed, and
a rag dipped in hydrochloric acid be passed over it, a beautiful
crystalline appearance becomes manifest, commonly known as
moire métallique. The Widmanstadt figures formed on meteoric
iron by the action of acids, many beautiful specimens of which
are to be seen in the British Museum, are instances of the same
kind.

778. Daniell showed, in his 'Introduction to Chemical Philo-
sophy,' that the crystalline texture of a metal might sometimes
be developed by dissection with mercury, as in the case of tin.

An idea of the tendency to crystallize possessed by a metal
may often be obtained, especially if it be a brittle one, by breaking
a mass of it across. The larger the piece of metal the better is
the nature of the crystallization observed, but even with a wire
the lens often reveals a highly crystalline structure.

779. The tenacity of metals is also an important feature in
their history. It would appear that this property is subject to
great variation, according to the temperature at which it has been
fused, or else that extremely small admixtures of foreign bodies
affect the power of sustaining weights to a remarkable degree.

Thus the tenacity of the malleable metals, as measured by the weight that wires of the same diameter (2 millimetres) were capable of bearing without rupture, is given in the following Table* :—

Iron	250	kilogrammes.	Zinc . .	50	kilogrammes.
Copper . .	137	,,	Nickel .	48	,,
Platinum .	125	,,	Tin . . .	16	,,
Silver . . .	85	,,	Lead . .	12	,,
Gold . . .	68	,,			

780. But, quite recently, M. Wertheim, in the laboratory of M. H. Sainte-Claire Deville†, has determined the tenacity of nickel and cobalt prepared from the oxalate, and fused in the latter chemist's blast-furnace, to be described further on, and has found that wires of equal size of iron, nickel, and cobalt supported the following weights :—

Cobalt	115	kilogrammes.
Nickel	90	,,
Iron	60	,,

The diameter of the wires is not stated. The necessity of determining the tenacity and other physical properties of metals under varying circumstances as regards mode of preparation, &c., could not be more strikingly illustrated than by the above example, where, instead of nickel having only one-fifth the tenacity of iron, as indicated in the first Table, it appears to be able to support a strain one-half greater.

781. *Chemical properties of metals.*—In studying the processes and reactions used in researches connected with metals, we are immediately led to consider the tendency possessed by them to combine with oxygen. Their attraction for oxygen varies greatly with the different metals. While some cannot endure exposure to the air for an instant without becoming covered with a

* REGNAULT.—'Cours Élementaire de Chimie,' tome deuxième, p. 413.
† DEVILLE.—'Ann. de Chimie et de Phys.' [3] xlvi. 201.

film of oxide, others can only be made to yield oxides by circuitous methods.

782. It is not easy to determine the exact conditions under which some metals combine with oxygen, as it has been found that those which have only been prepared of late years in quantities sufficient for accurate experiment, combine with that element with greater or less avidity according to the method by which they have been prepared; that is to say, small variations in their physical states, and the presence of minute traces of certain impurities, greatly influence their tendency to oxidize. This fact introduces some difficulty into the method of classifying metals according to their oxidizability. As an instance of this it may be mentioned, that manganese, magnesium, and aluminium have until lately been considered to almost resemble the metals of the alkaline earths in their power of decomposing water, and even of absorbing oxygen from the air; but the researches of Deville and others have shown that magnesium is not much more liable to oxidize than zinc, and aluminium ranks in that respect next to silver, gold, and platinum. It is, in the present state of chemistry, exceedingly difficult to classify metals into natural families in a satisfactory manner, those which closely coincide in properties through a long series of reactions suddenly diverging off, and becoming in other respects so unlike as to render their being grouped under the same head impossible. This has been well shown with regard to aluminium*, and it would not be a difficult task to find other illustrations drawn from the history of many other metals.

783. It is most important for the student to study carefully the various compounds of metals with oxygen; they are so numerous that it is often many years before all the oxides of a metal become known. Some metals in combining with oxygen form powerful bases in the lower, and equally or still more powerful acids in the higher state of oxidation. It is an extremely fortunate circumstance for chemists that they are generally able,

---

* TISSIER.—'Comptes Rendus,' Feb. 16, 1857, p. 350; and 'Chem. Gazette,' March 16, 1857.

without much difficulty, to effect at will the conversion of a metal into its oxides, and of the oxides back into the metallic state; for if it were not so, it would constantly happen that different oxides of the same metal would be taken for derivatives of several metals. This arises from the fact that various oxides of the same metal differ more in many instances than the same oxides of different metals. Thus the sesquioxide and teroxide of chromium are far more unlike each other in general properties than the sesqui-oxides of chromium and iron. The sesquioxide of chromium resembles the sesquioxide of iron in many respects, such as being soluble in acids, precipitable by ammonia, capability of replacing alumina in alums without altering the crystalline form of the salts, &c. But sesquioxide of chromium has no resemblance whatever to the teroxide; the former being a green powder insoluble in water, with the properties just mentioned, while the teroxide is a powerful acid of a ruby colour, capable of inflaming some organic bodies by mere contact, excessively soluble in water, forming splendid crystalline salts with the alkalies, &c., and precipitating metallic solutions with formation of varied and brilliant colours.

784. In some instances it has happened, with metals procurable only in small quantities and with great labour, that mixtures of two or more oxides of the same metal have been mistaken for the oxide of a new metal; thus a compound of sesquioxide and binoxide of niobium was thought to be derived from a new metal, to which was given the name of ilmenium, and the mixture was called ilmenic acid. A mixture of tantalic acid with niobate of niobous acid was also regarded as the acid oxide of a new metal, which was called pelopium.

785. The student will see how much care is requisite in examining metallic oxides with which he is unfamiliar. The description of the modes of separation of them from each other is the province of works on analysis, and will not therefore be dwelt on here.

786. Another point in the chemical history of metals which demands special attention, is their solubility in acids. It is gene-

rally found, in studying the properties of a metal, that there is one acid which dissolves it with peculiar facility compared with the others, and this acid is always one with which it forms a very soluble salt. It is also true, however, that a metal may be violently attacked by an acid and yet not be dissolved by it, but then the resulting product will generally be found to have an acid character, as with the peroxide of tin.

787. The solubility of metals in acids is so intimately connected with the nature of the oxides which they tend to form, that the two subjects cannot be studied separately. It sometimes happens that the same metal with the same acid yields two distinct salts, according to the temperature and state of concentration of the acid. Thus, as has already been mentioned (§ 145), iron in excess forms with cold dilute nitric acid a protonitrate, and with the ordinary acid and heat the pernitrate. The methods by which metals are obtained in solution in any required state of oxidation depend upon the peculiar characters of the substance itself. If, for instance, it is desired to obtain a protosalt of a metal which has great tendency to form persalts, we may proceed in two or three ways. In the first place, an acid is to be selected which has not a strong tendency to impart oxygen. The sulphuric and hydrochloric acids generally fulfil these conditions if the solutions are not made too concentrated, and the temperature is kept sufficiently low. The presence of an excess of metal is also advantageous. If it is feared that the atmospheric oxygen might take part in the reaction and cause the formation of a portion of persalt, a current of nitrogen, or, more conveniently, carbonic acid, may be made to pass through the fluid during the solution of the metal. The fluid for this purpose must be contained in a flask, the cork of which has two apertures, one to admit the tube conveying the carbonic acid, and the other to allow of its exit. The latter may be bent twice at right angles, and be made to dip a short distance into water or mercury.

788. If, on the other hand, it is desired to convert a per- into a protosalt, we may sometimes do so by a process more convenient than the last. For this purpose the metal is to be dissolved in

the acid most available under the circumstances (avoiding the nitric), and the peroxide formed is to be reduced to the state of protosalt by means of some reagent having a strong affinity for oxygen. Two of the most convenient of these are sulphuretted hydrogen and sulphurous acid. The first acts by means of the tendency of the hydrogen of the gas to form water, and the second in consequence of the readiness with which sulphurous acid takes up an equivalent of oxygen to become converted into sulphuric acid; thus, if we take in the most simple manner the way in which sulphuretted hydrogen and sulphurous acid reduce peroxide of iron to the state of protoxide, we find that—

$$Fe^2 O^3, 3SO^3 + HS = 2(FeO, SO^3) + SO^3 HO + S$$
$$Fe^2 O^3, 3SO^3 + SO^2 = 2(FeO, SO^3) + 2SO^3.$$
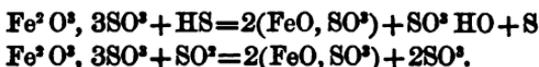
The first equation shows the reason why, when we pass sulphuretted hydrogen through a persalt of iron, a white or pale yellow precipitate is always obtained. If the iron exists as perchloride instead of peroxide, the equation becomes

$$Fe^2 Cl^3 + HS = 2FeCl + HCl + S.$$
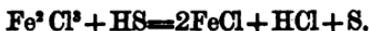
789. Reduction of oxides may also be effected in many other ways, all of which are advantageous under certain circumstances. Chromic acid, for instance, may be converted into sesquioxide of chromium by numerous processes; thus, if we heat bichromate of potash with chloride of ammonium and carbonate of potash, we find that

$$KO, 2CrO^3 + KO, CO^2 + 2(NH^4 Cl) = 2KCl + Cr^2 O^3 + 4HO + N$$
$$+ NH^4 O, CO^2.$$
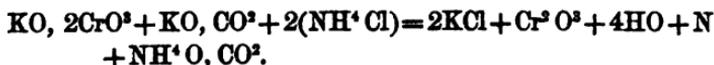
Again, by fusion of bichromate of potash with sulphur, we have—

$$KO, 2CrO^3 + S = Cr^2 O^3 + KO, SO^3.$$

By sulphurous acid we may reduce chromic acid to sesquioxide of chromium thus:—

$$KO, 2CrO^3 + 3SO^2 = Cr^2 O^3 + KO 2SO^3 + SO^3.$$

Charcoal will also reduce the acid, for

$$2(KO, 2CrO^3) + 3C = 2(KO, CO^2) + CO^2 + 2Cr^2O^3.$$

790. We have said that sulphur is capable of reducing chromic acid: it is also capable of reducing binoxide of manganese and other oxides to a lower state of oxidation. In the case of the peroxide of manganese, we have

$$MnO^2 + 2S = MnS + SO^2.$$

791. In selecting reducing agents, we are guided by the peculiar properties of the substance which is to be converted into a lower state of oxidation. If it be desired to remove oxygen from a compound gas, it is easy to pass it over a metal having a powerful tendency to absorb oxygen at high temperatures. Let us suppose it is desired to convert carbonic acid into carbonic oxide: it might be passed over potassium at a red heat, but we should defeat our intention through selecting too energetic a reducing agent; in effect, we should have all the oxygen removed and obtain only charcoal and potash. But if we select a metal like zinc, with a moderate power of absorption of oxygen, our purpose will be effected without difficulty. The ordinary process for preparing carbonic oxide sufficiently illustrates this. Chalk is heated to redness with zinc- or iron-filings; the gas, at the moment of its liberation, is decomposed thus:—

$$CaO, CO^2 + Zn = CaO + CO + ZnO.$$

792. The reduction of a metallic oxide from a higher to a lower state of oxidation is seen therefore to be a process of constant occurrence in the laboratory. Another instance is afforded in the mode of estimating sugar, by ascertaining the quantity of oxide of copper which it is capable of reducing to the state of suboxide, after having been converted into grape-sugar by the action of an acid.

793. The reduction of oxides to the metallic state is also an operation necessary in numerous researches. The methods available are very many, the one to be selected depending not only on

the habitudes of the metal, but also on the fact of the operation being qualitative or quantitative. For the quantitative reduction of metals, no method is more convenient or exact than that by hydrogen gas; the details have already been described (§§ 297 and 477).

794. If the oxide is only reduced with great difficulty, it is generally necessary to convert it into some compound more easy of reduction, such as the chloride or fluoride. The former salt is frequently preferable. For the purpose of reduction, recourse is had to some substance the affinity of which for chlorine at high temperatures is very great. Potassium and sodium fulfil these conditions, but the latter is much cheaper and more convenient to use. The details of the operation depend upon the properties of the metal it is wished to isolate. If it is only moderately fusible and not very volatile, we may use M. Deville's method of preparing aluminium from the chloride, a description of which will be found in the scientific journals, and most of the recently published elementary works.

795. We may also produce the readily oxidizable metals by electrolysis of their chlorides in a state of fusion, as in the processes described by MM. Bunsen and Matthiessen [*].

796. We have said that the solubility of metals in acids is an important feature in their general history, and it not unfrequently happens with metals which until recently have been prepared only in small quantities, that very erroneous views are prevalent on what appears so simple a matter, and it is quite evident that no conclusion can safely be drawn as to their habitudes with solvents, unless the experiments are made upon pure substances. Moreover, the state of concentration of the acid modifies the nature of the result in a remarkable manner.

It is extremely difficult to decide beforehand upon the manner in which a metal will behave towards a solvent. It would be supposed that silver would not dissolve in hydriodic acid, because we should imagine that, as iodide of silver is an insoluble salt like the chloride, the hydrochloric and the hydriodic acids would

---

[*] MATTHIESSEN.—Liebig's ' Annalen,' xciii. p. 277.

Y

behave in the same manner. But, in fact, an aqueous solution of hydriodic acid acts violently on silver with formation of a peculiar compound, which appears to be a hydriodate of iodide of silver. It is merely necessary, to effect the solution, that the acid should be of the proper degree of concentration.

797. From what have always, until recently, been our ideas of the nature of aluminium, we should suppose that it would be readily oxidized by an acid so prone to yield oxygen as the nitric, but, in reality, that acid scarcely acts upon aluminium even at a boiling-heat.

798. It is necessary therefore, in determining the solubility of a metal in acids, to study with care the variations produced by dilution, and also the effect which different temperatures may have on the result. Some metals are dissolved by alkaline solutions with evolution of hydrogen, but this generally happens when the oxide which the metal most strongly tends to form, either has acid properties, or at least is easily soluble in alkalies.

799. The same metal may behave in a totally different manner towards the same acid, according to the conditions under which they are presented to each other; thus iron may be kept for almost any length of time in concentrated nitric acid without any action ensuing, while a dilute acid will act upon it with violence.

800. The various oxides of the same metal behave quite differently in the presence of acids, and the manner in which the two react often affords a clue to the nature of the oxide. The protoxide of lead is readily soluble in acids, while the binoxide is not only quite insoluble in them, but appears to possess the characters of a feeble acid. The intermediate oxide, minium, or red lead, is acted on by acids, but the result indicates that it is a compound of the two other oxides, as protoxide of lead dissolves, while binoxide remains behind. Many metals yield oxides the properties of which differ still more than those of lead; for instance, manganese yields a basic protoxide, while its higher oxides are powerful acids. In fact, the latter metal has a certain amount of analogy with chlorine, inasmuch as permanganate of potash,

$KO, Mn^2 O^7$, is isomorphous with the perchlorate of the same base, KO, ClO^7, a fact which has not escaped the notice of Laurent[*].

801. Some oxides are rather anomalous in their reactions, inasmuch as with acids they combine to form salts, while with bases they behave as if possessing acid characters; alumina is an example of this kind. We have said that minium is acted on by acids with formation of a salt of the protoxide, while the binoxide is left behind as an insoluble residue. Minium is therefore a compound of two oxides of lead, and is an instance of a peculiar class of bodies formed from the union of a basic with a more or less acid oxide of the same metal; in the same manner, the protoxide of iron takes the part of a base towards the sesquioxide, which reacts like an acid in combining with the former to produce an intermediate oxide having the constitution of a salt. Many other instances of the same kind are afforded by other metals, particularly antimony, chromium and manganese. This kind of combination is still more common among the sulphides, which are particularly prone to unite with each other, the resulting compounds being called sulphur-salts.

The tendency of metals to unite with oxygen is sometimes singularly variable according to the temperature; thus mercury, which preserves its metallic state perfectly at ordinary temperatures, combines slowly with oxygen at 700° or 800°, and the oxide is again decomposed into metal and the gas at a rather more elevated temperature, such as that of dull redness. A somewhat similar peculiarity is observed in some oxides which combine with oxygen at one temperature, and again yield it at a higher. Baryta exposed in a current of air or oxygen to a temperature about the same as that at which mercury combines with oxygen, has, like the latter metal, a tendency to absorb the gas, but the reaction occurs far more readily, and as the peroxide formed again yields its oxygen at bright redness, may even be used to extract that element from the air by a continuous process. It is interesting to observe that other oxides than that of barium absorb oxygen at about 750°, and again yield it up when heated to a still higher temperature.

[*] LAURENT.—'Chemical Method,' &c., p. 10.

Y 2

The protoxide of lead in this manner becomes converted into red lead, which in its turn is converted into the protoxide at a greater heat. It has recently been found[*] that the presence of a base, such as lime, has the effect of inducing the conversion of oxide of lead into red lead at the ordinary temperature in moist air. This curious fact might in all probability be made the point of departure of some interesting experiments.

802. *Action of the non-metallic elements on metallic oxides.*— Having thus briefly glanced at some of the more prominent features connected with the combinations of the metals with oxygen, we turn our attention to some of the phenomena which present themselves by acting on the oxides with non-metallic elements and their compounds.

803. In the first place, we will consider the action which sulphur has on metallic oxides. With the oxides of the metals of the alkalies and alkaline earths, sulphur acts in a manner which is partly due to the presence of oxygen; we have therefore both sulphides and sulphates formed. It is easy to prevent the formation of sulphates by the addition of a substance having a tendency to combine with oxygen at high temperatures; if, therefore, we react upon the oxides mentioned with a mixture of sulphur and charcoal, the sulphide formed is not accompanied by sulphate.

804. Some other metallic oxides yield sulphides by the action of sulphur at high temperatures, but it is generally preferable to mix charcoal with the oxide and pass the gaseous sulphur over the oxide contained in a tube which should be heated intensely; few metallic oxides resist this method of treatment.

805. The action of hydrogen and of carbon on metallic oxides at high temperatures, is dependent on their powerful tendency to combine with oxygen. Most oxides are therefore reduced to the metallic state by them if the temperature is sufficiently high, and the circumstances under which they react are properly managed. Thus carbon at a full white heat decomposes even the fixed alkalies, potash and soda. Hydrogen is also used in numerous cases for the purpose of procuring many of the metals in a

* LEVOL.—'Ann. de Chim. et de Phys.' [3] xlii. p. 196.

state of purity from their oxides.   There are, nevertheless, many instances in which hydrogen fails to decompose oxides at all; in others it merely reduces them from a higher to a lower state of oxidation.

806. Chlorine acts on metallic oxides in various ways, dependent on the precise circumstances under which they are presented to each other.   The action is not only modified by temperature, but also by the fact of more than one substance being present. There are numerous examples which might be cited; it will be sufficient to allude to one or two.   If chlorine be passed into a solution of the oxides of cobalt and nickel in hydrochloric acid, the cobalt is converted into peroxide, but not the nickel; and the former may be precipitated by carbonate of baryta, the nickel remaining in solution.   An instance of the effect of the presence of a second substance in modifying the action of chlorine on a metallic oxide, is afforded by alumina.   If chlorine be passed over alumina at a white heat, no action is perceptible; but if charcoal be present to combine with the oxygen of the alumina, the chlorine unites with the aluminium to form the volatile sesquichloride.   The method found to answer best of obtaining the alumina mixed with carbon in a state fit for conversion into sesquichloride, is by calcining alumina with coal-tar.

807. The action of chlorine upon solutions of the oxides of the metals of the alkalies varies with the temperature, the strength of the solution, and the presence of other substances.   If it be desired to obtain oxidation as much as possible, that is to say, to procure the maximum amount of chlorate of potash, the precautions first suggested by Mr. Crace Calvert should be adhered to[*].

808. If, on the other hand, it is desired to avoid the formation of chlorate, and it is wished to procure hypochlorite of potash, the solution is to be made weak, and also to be kept cold.   The formation of the hypochlorite is accompanied by that of chloride of potassium, thus :—

$$2Cl + 2KO = \underbrace{KO, ClO,} + KCl.$$

Hypochlorite of potash.

[*] CALVERT.—'Quart. Journ. of the Chem. Soc. of London,' vol. iii. p. 106.

809. A very interesting class of reactions taking place between metallic oxides and chlorides and non-metallic substances, are those which result in the formation of alkaloids by the substitution of metals for the hydrogen in ammonia or ammonium. The subject is one of considerable intricacy, arising from the great variety of compounds and the numerous methods by which they are obtained. With platinum alone, an immense number of bases are formed, which have been examined by Gros, Reiset, Peyrone, Gerhardt, Magnus and others. It is singular that the metals found associated with platinum have a special tendency to form bodies of this class. Thus palladium, rhodium and iridium are known to form alkaloids. An interesting class of bases also exists containing cobalt. It would be exceedingly desirable to know what metals do, and what do not, possess the power of performing this function, as such a knowledge would perhaps lead to a rational classification.

810. We have thus gone through a very few of the more prominent features which present themselves to our notice on reacting with non-metallic upon metallic bodies. They have been selected with the view of calling the student's attention to some important reactions, which, when studied more in detail, will lead to the accumulation of a mass of information having important bearings upon almost every train of experiments occurring in the laboratory.

811. *On the determination of the atomic weights of metals.*—In determining the equivalent or atomic weight of a substance, it is necessary to form a compound of it with some other body, the general character of which compound has been well established, that is to say, we must be aware of the number of atoms existing in it. It is also desirable that the compound should be of a character which will permit the estimation of its constituents with as few operations as possible. It is not merely necessary that the general formula of the compound be known, but it is also imperative that the atomic weight of the combining body be perfectly well established. There are a few processes especially well adapted for ascertaining the atomic weights of metals; for example,—

I. The conversion of a metal into an oxide the formula of which
   is known.
II. The formation of a chloride.
III. The analysis of a carbonate decomposable by heat.
IV. The reduction of an oxide to the metallic state by hydrogen.

We will illustrate each of these by an example.

812. I. There is every reason to believe that the compound
formed by treating tin with nitric acid is a binoxide; if, therefore,
the amount yielded by a given weight of tin were accurately known,
it would be easy to ascertain the atomic weight of that metal.
Now it has been found that 100 parts of tin yield 127·2 of peroxide,
and as we take the atomic weight of oxygen as the point of de-
parture of our calculation, we say that if 27·2 parts of oxygen
unite to 100 parts of tin, what will two equivalents of oxygen
unite with; we have, therefore,—

$$27\cdot2 \quad : \quad 100 \quad :: \quad \underbrace{16}_{\text{2 eq.}} \quad : \quad \underbrace{58\cdot82}_{\text{At. wt. of tin.}}$$

813. II. The second case is equally simple. Chemists are
agreed that chloride of silver is a compound of one equivalent of
silver and one of chlorine; they are also agreed that the atomic
weight of chlorine is 35·5. Now as 100 parts of silver yield
132·856 of chloride, we obtain the atomic weight of silver, as
follows:—

$$32\cdot856 \quad : \quad 100 \quad :: \quad \underset{\text{1 eq. chlorine.}}{35\cdot5} \quad : \quad \underset{\text{At. wt. of silver.}}{108\cdot04}$$

814. It will be evident that we may assume 108 as the atomic
weight of silver, and it appears to be one of those metals the
equivalents of which are multiples by a whole number of that
of hydrogen.

815. III. It is well established that the atomic weight of car-
bon is 6 and of oxygen 8; if, therefore, the carbonate of a metallic
oxide be ignited so as to obtain the pure oxide, we possess all
the necessary data for determining the equivalent of that oxide,
and to obtain that of the metal, it is merely necessary to deduct
the atomic weight of oxygen. It has been found that 100 parts

of pure crystallized carbonate of lime yield, on powerful ignition, 56 parts of lime; the composition of carbonate of lime is,—

Lime	56·00
Carbonic acid	44·00
	100·00

Therefore

$$44 \quad : \quad 56 \quad : : \quad 22 \quad : \quad 28,$$

<div align="center">At. wt. of   At. wt. of
carb. acid.   lime.</div>

and $28-8=20$, the atomic weight of calcium.

816. IV. It is universally admitted that the peroxide of iron belongs to the class of sesquioxides, its formula being $Fe^2 O^3$. To obtain the atomic weight of iron, it is merely necessary to submit this oxide to accurate analysis. By passing hydrogen gas at a red heat over pure sesquioxide of iron, it has been found that 35·783 yield 25·059 of metal. It is plain from this, that 35·783 of the oxide consists of—

Iron	25·059
Oxygen	10·724
	35·783

Admitting the formula of the oxide to be as above stated, we obtain the atomic weight of iron, thus:

$$10·724 \quad : \quad 25·059 \quad : : \quad 24 \quad : \quad 56·08,$$

<div align="center">3 eq. of O.   2 eq. Fe.</div>

and $\dfrac{56·08}{2}=28·04$. The latter number represents the atomic weight of iron, for which we may substitute 28·00, as the difference doubtless is due to error of experiment. Allowing the latter to correctly represent the atomic weight of iron, it follows that, like so many others, it is a multiple by a whole number of that of hydrogen.

817. The equivalents of many metals are determined by much more complex processes than those given as examples; but whenever such is the case less confidence is felt in the result;

the nearer, therefore, a process for determining an atomic weight approaches simplicity, the nearer it approaches perfection.

818. *General considerations on the elements.*—It is extremely interesting to study the properties of elementary bodies considered as series. It often happens that chemical elements fall naturally into groups of threes, the properties considered most characteristic of them advancing in a distinct and evident manner. M. Dumas has shown that if, in these triads, we take half the sums of the equivalents of the extremes of the series, we shall obtain as a mean, a number closely approximating the equivalent of the middle body, thus:—

	Atomic weight.
Chlorine	35·5
Bromine	80·0
Iodine	127·0

Let us add together the atomic weight of iodine and chlorine, and we obtain 162·5 and $\frac{162·5}{2} = 81·2$. Again, sulphur, selenium and tellurium fall into a natural triad, the properties of which advance in an evident manner, as do also their atomic weights.

	Atomic weight.
Sulphur	16
Selenium	39·5
Tellurium	64·5

On repeating the process before given, we find that

$$64·5 + 16 = 80·5 \text{ and } \frac{80·5}{2} = 40·2,$$

being a number closely approximating to the equivalent of the middle body, selenium; and if the atomic weights of the last two members of this group were better known, perhaps the coincidence might be still closer.

As it would be improper to make assertions of this kind unless corroborated by a greater amount of evidence than that afforded by two examples, let us take others, for instance,—

Y 5

	Atomic weight.
Lithium	6·43
Sodium	23·00
Potassium	39·00

And $6·43 + 39·00 = 45·43$ and $\dfrac{45·43}{2} = 22·71$, a number closely approaching that of sodium. We will take one more example from the metals of the alkaline earths:—

	Atomic weight.
Calcium	20·00
Strontium	44·00
Barium	68·64

819. Applying the rule before given, we have

$$20·00 + 68·64 = 88·64 \text{ and } \frac{88·64}{2} = 44·32,$$

or almost exactly the equivalent of strontium. It is also to be observed, that with the three triads given, the chemical and physical properties frequently advance in a manner quite in accordance with the arithmetical ratio of the equivalents; thus, with the first group given, the chemical energy of the elements is inversely as the atomic weight; moreover, while chlorine is a permanent gas, bromine is a volatile fluid and iodine a volatile solid.

820. Again, this gradation of properties is well defined in the second, and also in the third triad, where we have compared the properties of the three metals. But in the fourth it is still better marked. The sulphate of lime is more soluble than the sulphate of strontia, and the latter than the sulphate of baryta, and other properties present the same progressive tendency. We will not discuss at any length the conclusion which M. Dumas drew from these facts, which was, that the elements were compounds, and that bromine resulted from the union of half an atom of chlorine with half an atom of iodine, and so on of the rest, because such an argument can only be decided by experiments, and these must be of a nature quite different from those at present known to chemists, and involving methods of research to which

at present we have no clue; but the consideration of the arithmetical relations of the equivalents of bodies may lead us to equally interesting, and perhaps more profitable trains of research. We do not find any triad into which fluorine will enter with the same chemical and arithmetical relations as are observed with chlorine, bromine, and iodine; and on looking through the lists of atomic weights, we do not observe the metals generally falling into natural triads. However, from the very complete manner in which the examples given fulfil the desired conditions, it may be safely inferred that numerous other instances of the same kind would be found if we were better acquainted with the substances existing in nature. Great steps are every day being made in this direction, and the results lead us to group together, by very strong analogies, bodies which until lately were not considered to possess any resemblance. Thus it is now ascertained that boron, when properly crystallized, is exceedingly like the diamond, to which also it is only second in hardness. The refractive power is also equal to the last-named substance, so that if procurable in crystals of sufficient size and purity, it would be equally beautiful. Moreover, it appears to be more unalterable than the diamond, for it is not affected by nitre at a red heat.

821. Another singular circumstance is, that bodies having great similarity in a chemical point of view are generally found associated in nature. Thus chlorine, bromine and iodine are all found in sea-water. The arithmetical relations of these three haloids have already been noticed. Silver and lead are so often found together that it is difficult to procure lead free from silver, unless it has been carefully purified. Common sheet-lead submitted to cupellation will almost invariably yield a minute button of silver. Now silver and lead have both high atomic weights, and they do not very greatly differ. Thus lead is 103·7 and silver 108·0. Again, iron, manganese, cobalt and nickel are almost always found associated in minerals. In many respects, also, they have chemical resemblances, such as their power of forming sesquioxides, &c. Their atomic weights are also very close, iron being 28, manganese 27·6, cobalt 29·5, and nickel 29·6. Chromium,

which also forms a sesquioxide, has an atomic weight of 26·7. Again, aluminium is always found in nature associated with iron; they both form sesquioxides, which, like that of chromium, are capable of forming alums; but the equivalent of aluminium is low, and appears to remove it from the group with which we have associated it. If, however, we multiply the equivalent of aluminium by 2, we have 27·34, a number intermediate between chromium and iron. Again, we find certain minerals occurring in nature containing metals of such great similiarity, that sometimes the mineral is known for many years before it is suspected to contain more than one oxide. Thus cerite contains cerium, lanthanium, didymium, and perhaps others. There is no doubt that chemists have more than once allowed the discovery of a new metal to escape them from its reactions not having been examined with sufficient minuteness.

822. The ores of platinum also contain several metals, the properties of which show many points of resemblance; and moreover the atomic weights of nearly all the metals associated with platinum have equivalents the same, nearly approximating, or else more or less approaching a multiple of the equivalent of rhodium, thus:—

	Atomic weight.
Rhodium	52·1
Ruthenium	52·1
Palladium	53·3
Platinum	99
Iridium	99
Osmium	99
Lead	104
Silver	108
Gold	197

823. It is difficult to see so marked a tendency in substances to associate together, their atomic weights having an equal tendency to oscillate between certain numbers or multiples of numbers, without thinking that there must be something more than chance in it; in fact, chance it cannot be, and it remains for us to learn the cause.

824. A somewhat similar peculiarity is observable in the metals tungsten and molybdenum.   These metals have numerous points of resemblance, and their atomic weights bear a very simple relation to each other, thus:—

	Atomic weight.	Specific gravity.
Molybdenum . . .	46	8·6
Tungsten	92	17·6

It is singular, that while the atomic weight of tungsten is exactly double that of molybdenum, its specific gravity is also about double.

PROCESSES AND REACTIONS USED IN ORGANIC RESEARCHES.

825. The separation of organic bodies from complex mixtures with the view of examination or analysis, is in many laboratories a problem of everyday occurrence, but it would be difficult to direct the student to a source of information as to the method to be pursued.   It is true, that, by the study of such works as the 'Traité de Chimie Organique' of M. Gerhardt, any student may ascertain the modes which chemists have adopted in individual cases, but few works treat especially of the steps by which the chemist is to proceed to separate and examine organic substances generally. The design of this book is too limited to permit of entering into the subject at any length, but it is intended to give a sketch of the processes for isolating and determining the nature of a few of the most important.

826. In order to simplify the study of this subject, we shall divide organic bodies into three classes, which in their turn admit of several subdivisions; these are—

Acids.

Bases.

Neutral bodies.

827. In going through organic bodies arranged in series, we are startled to find, in spite of the immense amount of labour that has been expended on them of late years, that at almost every step there is ample material for investigation; where such cases occur directly in our path, they will be noticed.

828. The mode of treating the subjects will be as follows:—

Sources from whence obtained.

Method of separating from other bodies.

Mode of determining nature and composition.

General remarks.

829. The number of substances of organic origin already known to chemists is so immense, that it is quite impossible in a book of limited extent like the present, to attempt to describe more than a few of the methods of obtaining and estimating the substances discussed, and even then only those of most general application. When we remind the student that in the single department of organic acids 800 are already known, it will be evident that a very restricted plan must be adopted.

We shall consider them under the following heads: acids derived from—

I. The vegetable kingdom.

II. Animal products.

III. Treatment of organic bodies by oxidizing agents.

IV. Fermentation.

V. Treatment of organic bodies by acids to form conjugated acids.

VI. Action of heat on acid salts of ammonia yielding acid amides.

VII. Destructive distillation of organic matters, &c.

Great numbers of derived acids are also known in which the hydrogen of an acid is replaced by one or more atoms of chlorine, bromine, iodine, hyponitric acid, &c.

830. We shall study the modes of obtaining and determining the constitution and properties of a few acids from one or two of these sources.

I. *Acids derived from the Vegetable Kingdom.*—It will be proper to consider these acids under two heads, namely, volatile and fixed.

831. *Volatile acids.*—It is to be observed that these acids are equally produced from animal and vegetable sources; but as the most important of them, namely, the acetic, has been longest

known as a vegetable acid, we shall study them under this head.

832. The manipulation connected with the investigation of the volatile acids of the series $C^n H^n O^4$, is generally of a very simple character. It has been found that they seldom occur singly. If, therefore, any process or experiment has indicated the presence of a volatile acid, great care must be taken to ascertain whether more than one be present. This may be done in several ways. We will suppose that on adding a mineral acid, preferably the sulphuric, to some organic product, the peculiar odour of a volatile acid is perceived, the whole is to be acidified with dilute sulphuric acid, and the fluid submitted to distillation. As the distillate is often exceedingly weak, it is to be neutralized with carbonate of soda and evaporated over the naked fire until the solution has been concentrated to a considerable extent, when it may be finished over a sand-bath. It is to be observed that the soda-salts of the principal volatile acids are perfectly stable, and no fear of decomposition need be entertained even if the mass should become dry; and, in fact, it is often advantageous to fuse it, of course at as low a temperature as possible, in order to drive off empyreumatic impurities. The resulting salt, or a portion of it, is to be dissolved in distilled water, and, if necessary, filtered. To the clear solution nitrate of silver is to be added in small quantities, and the precipitate filtered off. Although in experiments of this kind the greatest care must be taken to avoid impurities in the reagents, yet as traces of chlorine might exist in the carbonate of soda, it is proper to reject the first precipitate, which should not, therefore, be large in amount. A small quantity of nitrate of silver is then to be added to the filtrate from the first precipitate, the resulting salt filtered off, and the operation again repeated on the filtrate from the last. In this manner three or four precipitates are to be obtained one after the other, and by determining the silver in each, it will be ascertained whether more than one volatile acid exists in the fluid under examination. The precipitates are to be well washed before being dried. To dry the silver-salts in the water-bath would scarcely be advisable,

until it had been ascertained whether they would endure a temperature of 212° without decomposition.

It must not be forgotten that silver-salts must, if dried *in vacuo* over sulphuric acid, be kept in the dark, or they are liable to blacken and decompose. If a variation in the amount of silver is found in the precipitates, the course next to be adopted will depend upon the amount of material in the operator's possession. It is probable that the silver in one or more of the precipitates will coincide with the theoretical quantity for some of the volatile acids, in which case a combustion may be made, and the result, if successful, combined with the silver determination, will be sufficient proof of the existence of the acid.

833. If the volatile acid has been obtained by acting with nitric acid on organic matters, some difficulty may at first be found in determining the silver, owing to the explosive nature of the salts formed by the nitro-acids; in such a difficulty the salt may be mixed with a little carbonate of soda and ignited, and the soda be afterwards washed out, or it may be moistened with hydrochloric acid, and the silver be estimated as chloride. If a sufficient quantity of acid is to be procured, it is very desirable that its boiling-point should be ascertained, to corroborate the result of the analysis of the silver-salt. If of the $C^n H^n O^4$ series, and it be required to determine the vapour density, it must not be forgotten that the determination must be made far above the boiling-point, in order to obtain a correct result*.

834. If a sufficient quantity is to be procured, and it is desired to obtain them separate, Liebig's method by partial saturation (§ 357) may be adopted.

835. *Fixed vegetable acids.*—The methods of separating and determining the fixed vegetable acids depend to a great extent upon the nature of those present. Tables of the modes of testing for the most common ones are to be found in the manuals of qualitative analysis. If in the course of experiments on vegetables, acids are encountered, the nature of which it is desired to ascertain, the first step is for the student to refer to some

* See also § 136 on this subject.

extensive work on organic chemistry, in order to ascertain whether the vegetable or plant has been previously examined.

836. Some acids, such as the citric and tartaric, are obtained by taking advantage of the insolubility of their lime-salts, which are obtained by neutralizing the vegetable juice with chalk, filtering off the precipitate, and decomposing it with dilute sulphuric acid; the solution contains the acid, while the comparatively insoluble sulphate of lime is removed by the filter. The liquid, on careful evaporation, yields crystals of the acid.

837. In separating organic acids for the purpose of determining their nature and constitution, no opportunity must be neglected of ascertaining any peculiarities in their properties or specialties in their salts, for it often happens that by this means we are enabled to remove other bodies with which they may be associated in plants, and which may so much resemble them in their habitudes as to mask their reactions and lead to confusion. If, for instance, it was intended to separate malic acid from the juice of any of the numerous plants which contain it, by adding acetate of lead, we should incur the danger of precipitating tartrate of lead along with the malate; but, by availing ourselves of the peculiar properties of the malate of lime, we are enabled to obtain a pure salt, from which we may procure the acid with ease in a state fit for examination. If we nearly saturate with chalk, or hydrate of lime in fine powder, the juice containing the malic acid, and, after filtration, boil the liquid, malate of lime is precipitated in a state of considerable purity. By decomposing the last-named salt with acetate of lead, we obtain a pulverulent or curdy precipitate, which has the peculiar property of spontaneously changing, if left in the liquid, into fine silky crystals.

838. Lead salts of organic acids, such for instance as that last described, are often decomposed by sulphuric acid or sulphuretted hydrogen, for the purpose of obtaining the acid in a free state. The gas has the advantage of yielding sulphide of lead, which acts as a powerful decolorizer, and frequently prevents the necessity of using animal charcoal.

839. In separating acids from the juices of plants by salts of

lead, we must be on our guard against the possibility of precipitating sulphates and phosphates at the same time.

840. In some instances it is convenient to remove inorganic acids like those named, by first saturating the juice by carbonate of soda, and then cautiously adding acetate of baryta until they are removed. If, then, the acid to be isolated is precipitable by acetate of lead, that reagent may be added, and the rest of the process performed as described above.

841. In examining the nature of organic acids, great care must be taken to ascertain their degree of basicity. If they have any tendency to form acid salts, the question is at once determined as to their not being monobasic, for acids of this class never form acid salts.

II. *Acids derived from the Animal Kingdom.*—Acids derived from the animal kingdom are, as a rule, less easily obtained in a finely crystallized condition than those from plants. While numerous acids of great beauty and theoretical interest have for many years been known to chemists as products of the vegetable world, it is of comparatively recent date that distinct and certain knowledge has been obtained of the constitution of those derived from animals. In fact, the very high atomic weights of many of the animal acids render it exceedingly difficult in many cases to construct formulæ that leave no doubt upon the mind as to their correctness, because, in most instances, the analytical results will bear more than one interpretation, and it is this fact which, perhaps more than any other, renders it desirable that, where it is possible, the products of their decomposition should be examined with the view of corroborating the formula derived from the analysis.

842. Animal acids are obtainable by a variety of processes from the crude substances which contain them; we shall therefore glance briefly at one or two of the most important, with the view of obtaining an idea of the mode of proceeding.

843. *Solid fatty acids.*—These acids exist both in animal and vegetable products, and sometimes the same acid is derivable from both sources. The difficulties experienced in determining the true constitution of some of the solid fatty acids of high atomic weights

are so great, that even with stearic acid, one of the most fully investigated of them, it can scarcely be said that the formula is established in a perfectly satisfactory manner.

844. Acids of this class are generally obtained by saponifying the fatty matters containing them, by boiling with potash and decomposing the soaps by means of hydrochloric acid. The acids thus set free are crystallized repeatedly until their melting-point is no longer raised by the process.

845. Sometimes the alcoholic solutions of the fatty acids or their soaps are precipitated with the acetates of lead, baryta or magnesia, and the resulting precipitates are decomposed by boiling with dilute hydrochloric acid. The methods of forming the salts of organic acids will be given in the general remarks on organic acids.

846. Some organic acids may be isolated from fluids in which they are contained, by adding, after evaporation, a metallic salt, the base of which forms an insoluble or comparatively insoluble salt with the acid present: hippuric acid, for example, may be separated from the urine of the horse by this means; the metallic salt is afterwards to be decomposed by a mineral acid, in order to set the acid free.

847. Acids of sparing solubility are sometimes separated from complex organic mixtures by treating the latter with cautic potash, filtering the alkaline and somewhat dilute solution to remove the insoluble impurities, and precipitating the substance sought by the addition of a mineral acid. If it be desired to separate uric acid from guano*, the alkaline solution is to have carbonic acid gas passed into it, in order to separate the sparingly soluble acid urate of potash. The latter may be washed with water until quite white, and after being dissolved in boiling-water, precipitated by hydrochloric acid.

848. Lactic acid will be treated of in describing the preparation of acids by means of the fermentation of neutral organic bodies.

---

* The preparation of uric acid from guano promises to become of great importance in the arts, in consequence of the valuable dyeing properties which have been recently discovered in murexide.

849. A very useful process for extracting not only acids but many other bodies from complex organic substances, is by exhausting the mass with alcohol and adding ether; this frequently causes the separation of the substances which it is desired to isolate, owing to their being less soluble in a mixture of alcohol and ether than in alcohol alone. This method may be adopted in separating cholic acid from dry bile.

850. III. *Acids produced by treating organic bodies with oxidizing agents.*—The number of acids produced by this method is very great, so that only a few can be noticed, and those of most general interest. It is to be observed that organic bodies are oxidized in the laboratory by a variety of methods, among which may be mentioned the following :—

> Fusion with alkalies.
> Treatment with nitric acid.
> Treatment with peroxides.

851. *Formation of acids by fusion of organic substances with alkalies.*—By this process a feebly oxidizing action is obtained; the products are of course liable to variation, according to the temperature employed and the nature of the materials. Sometimes an acid appears to be formed at one step of the process, but is decomposed on continuing the heat with evolution of other substances, products of its metamorphosis. Thus in distilling indigo with potash for the purpose of obtaining aniline, anthranilic acid appears to be formed at one stage of the process and subsequently destroyed, as in the following equation :—

$$C^{14} H^7 NO^4 = 2CO^2 + C^{12} H^7 N$$

$$\underbrace{\hspace{2cm}}_{\text{Anthranilic acid.}} \qquad \underbrace{\hspace{2cm}}_{\text{Aniline.}}$$
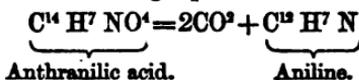
The oxidizing action of hydrate of potash at elevated temperature is manifested in the conversion of camphor into campholate of potash, thus :—

$$C^{20} H^{16} O^2 + KO, HO = C^{20} H^{17} KO^4$$

$$\underbrace{\hspace{2cm}}_{\text{Camphor.}} \qquad \underbrace{\hspace{3cm}}_{\text{Campholate of potash.}}$$
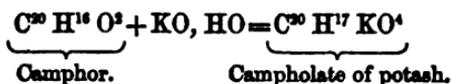
Other acids are often formed in this method of operation, as oxalates and acetates, but they generally undergo a secondary

decomposition, resulting in the formation of other products, such as carbonic acid, hydrogen, hydruret of methyl, &c.

852. *Formation of acids by treatment of organic substances with nitric acid.*—The action which nitric acid exerts on organic substances varies greatly, according to the nature of the body, and the greater or less state of concentration of the acid itself. Thus, blue indigo, which contains $C^{16} H^5 NO^2$, when submitted to the action of weak nitric acid for a moderate time, yields isatine, $C^{16} H^5 NO^4$, the effect of the acid being only to fix the element of oxygen on to the indigo; but if the action be maintained longer, a further change is developed, the carbon is attacked, and a more considerable oxidation is effected, resulting in the production of indigotic acid, $C^{14} H^5 NO^{10}$. And if this indigotic, nitrosalicylic, or anilic acid as it is also called, is treated with strong nitric acid, we obtain picric acid, $C^{12} H^3 N^3 O^{14}$, still more of the carbon and some of the hydrogen being removed, while the proportion of oxygen and nitrogen is increased. The last-named acid is a very common product of the metamorphosis of organic substances under the influence of nitric acid.

853. In treating organic matters with this acid, care must be taken to avoid too violent a reaction, which would result in the expulsion of the substance from the vessel, and perhaps still more unpleasant consequences. Sometimes it is proper to cool the organic substance and the acid separately, and drop the former, if a fluid, into the latter, still retained in a freezing mixture. The fluid is then to be diluted with water and neutralized by an alkaline carbonate, with the intention of procuring a salt. This process is required in obtaining trinitrocresylic acid from the hydrate of cresyl existing in coal-tar *.

* I have ascertained that alcohols of acid properties higher up than the cresylic exist in coal-tar; in fact, by selecting coal-oils of very high boiling-point, volatile acids, apparently homologues of phenol, may be obtained up to and beyond the range of the mercurial thermometer, and yet readily soluble in potash. When the less volatile tarry acids remaining in the retort are dissolved in solution of potash, a fluid is obtained of singular properties. If a piece of calico be plunged into it, and removed in the hand so as not to meet the air, it is almost colourless; but on opening the hand, and allowing

854. It has been said that nitric acid sometimes acts merely by the fixation of oxygen without removing the carbon, as with isatine from indigo; that this is not an isolated case, is evident from the fact that by oxidation camphor becomes converted into camphoric acid without alteration of its carbon.

$$C^{20} H^{16} O^2 + O^6 = C^{20} H^{16} O^8$$

$$\underbrace{\hspace{3cm}}_{\text{Camphor.}} \qquad \underbrace{\hspace{3cm}}_{\text{Camphoric acid.}}$$
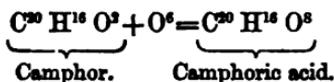
Sometimes, on the other hand, not only both carbon and hydrogen are greatly diminished and the oxygen is increased, but there is also a considerable formation of oxalic acid at the same time, as in the formation of Warren De la Rue's nitrococcussic acid from carminic acid. In acting on organic matters, animal or vegetable, with nitric acid, we must always be prepared to find oxalic acid as one of the products. The salt of nitro-acids are generally explosive, and with some, as for instance the last alluded to, the detonation is so violent as to be dangerous. In acids of this class we recognize a fixation of hyponitric acid which replaces hydrogen; thus picric acid is hydrate of phenyl, carbolic acid, phenic acid, or whatever we choose to designate phenol, in which three atoms of hydrogen are removed and replaced by hyponitric acid.

855. It is curious that in these reactions the resulting acid has sometimes no perceptible relation to the original matter, and even at times appears to be derived from an unisolated body; thus nitrococcussic acid is isomeric, but not identical, with trinitro-anisic acid; it is therefore derived from an acid isomeric with anisic acid.

When such problems as these arise, they are very difficult to solve, and, at the time, perhaps impossible, but doubtless in the above case the isomer of anisic acid, of the formula $C^{16} H^8 O^6$, will one day be discovered, and then the true relation of nitrococcussic acid will be better understood. It is the more to be desired in

the cloth to become exposed, it rapidly becomes blood-red. Probably it is here we should search for Runge's rosolic and brunolic acids.

the above case, because the products of the decomposition of anisic acid in presence of the alkaline earths are of great interest, and it would be exceedingly interesting to compare the products of the destructive distillation of the unknown acid with them.

856. *Treatment with peroxides.*—When we boil those organic bodies which contain much oxygen with peroxide of lead, formic and carbonic acid are produced. In general, when peroxides are used, there is a very complete decomposition, but the resulting products are those which have no decided relation to the original matters, because the action goes too far. This is particularly the case if acids are used simultaneously with the peroxide.

857. Some substances treated with peroxide of lead yield products of great interest, but not being acids they will not be described here.

858. IV. *Production of acids by fermentation.*—Fermentation which acts by reduction, nevertheless often results in the formation of acids, by removal of oxygen from other acids. Even an amide, or a substance resembling an amide, may, by fermentation, be made to produce acids, as will be seen below. Sugar fermented with decomposing cheese, yields lactic acid, which, if allowed to ferment still further, generally produces butyric acid, but sometimes propionic acid instead.

859. The transformation of lactic acid into butyric acid may be represented thus :—

$$C^{12} H^{12} O^{12} = C^8 H^8 O^4 + 4CO^2 + 4H.$$

Lactic acid. Butyric acid.

860. Succinic acid may be produced by fermentation from asparagine, and also from malic acid, thus :—

$$C^8 H^8 N^2 O^6 + 2HO + 2H = C^8 H^6 O^8 + 2NH^3$$

Asparagine or Malamide*.   Succinic acid.

$$3C^8 H^6 O^{10} = 2C^8 H^6 O^8 + C^4 H^4 O^4 + 4CO^2 + 2HO ;$$

Malic acid. Succinic acid. Acetic acid.
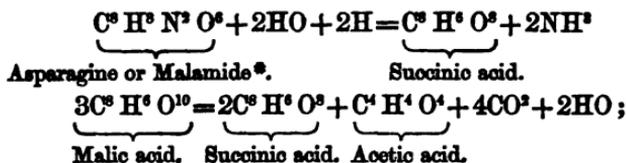
* According to the recent researches of Demondésir, malamide is only isomeric with dry asparagine, from which he states it to differ in form,

or more simply, and disregarding secondary products,

$$C^8 H^6 O^{10} - 2O = C^8 H^6 O^6.$$

Malic acid.   Succinic acid.
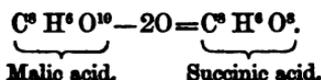
861. We have said that lactic acid by fermentation yields butyric acid, and that malic acid yields succinic acid by the same process; now malic acid also yields butyric acid under certain circumstances; the decomposition may be rendered thus:—

$$2C^8 H^6 O^{10} = C^8 H^8 O^4 + 8CO^2 + H^4.$$

Malic acid.   Butyric acid.

862. V. *Treatment of organic bodies with acids to form conjugated acids.*—In conformity with the rule generally adopted among chemists, we have considered some acids derived by substitution of hyponitric acid for hydrogen apart and among acids formed by oxidizing agents; but this is, perhaps, not the most proper way of looking upon these bodies in a chemical point of view.

863. Picric acid should undoubtedly be regarded as a conjugated acid, as much as sulphobenzoic acid. Even their mode of formation is similar, namely, by bringing the two substances together in the free state; for instance, sulphacetic acid, $C^4 H^4 O^4$, 2 SO^3, is prepared by cautiously mixing monohydrated acetic acid with anhydrous sulphuric acid, carefully cooling after each addition. After keeping the mixture at a temperature not exceeding 140° F. for some hours, the whole is to be poured into a large quantity of cold water, and is then to be saturated by carbonate of lead or baryta; the excess of carbonate being removed by filtration, the sulphacetate is left to crystallize out. Sulphuretted hydrogen may be used to remove the lead from the sulphacetate of that base, and the acid is obtained in deliquescent needles by evaporation *in vacuo* over sulphuric acid.

864. Most of the sulpho-acids are made by more or less analogous processes, such as sulphovinic acid, &c. They are decom-

and chemical properties. Moreover, its rotating power is said to be different.

posed when heated, with production of sulphurous acid. The salts formed by neutralizing conjugated sulphuric acids, such as the sulphovinic acid, with lime, potash, &c. are valuable as the raw material for the production of many substances.

865. Sulphuric acid forms conjugated acids with a great number of substances; for example,—

With alcohols   as Sulphovinic acid.
With acids   as Sulphobenzoic acid.
With hydrocarbons   as Sulphonaphthalic acid, &c.

VI. *On acid amides.*—While *neutral* salts of ammonia by loss of water form amides, so *acid* salts of ammonia form acids by the same process, thus:—

$$C^8 H^5 (NH^4) O^{10} - 2HO = C^8 H^7 NO^8$$
Bimalate of ammonia.   Malamidic or aspartic acid.

$$C^{20} H^{15} (NH^4) O^8 - 2HO \quad C^{20} H^{17} NO^6$$
Bicamphorate of ammonia.   Camphamic acid.

$$C^4 H^5 NO^8 - 2HO = C^4 H^3 NO^6.$$
Binoxalate of ammonia.   Oxamic acid.
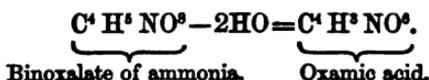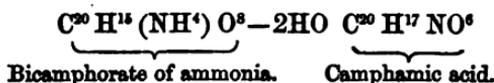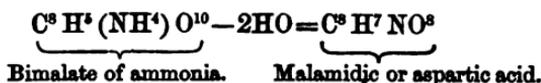
Although, as represented in the last equation, the formation of an amidic acid appears exceedingly simple, yet, in fact, if it be attempted to prepare oxamic acid by heating binoxalate of ammonia, it is found that many other products are formed, including ammonia, oxamide, hydrocyanic acid, carbonic acid, and carbonate of ammonia. The amidic acids are, in fact, sometimes prepared by somewhat circuitous methods.

866. VII. *Production of acids by destructive distillation.*—The study of organic acids produced by destructive distillation naturally divides itself into two branches: in one we are able to trace the relation of the products formed, to the original substance; in the other we are not. Many organic acids, when exposed to heat with proper care, yield a new acid differing from the original by

z

two equivalents of carbonic acid, as, for example, gallic acid, which under the influence of heat is converted into pyrogallic acid, thus:—

$$C^{14} H^6 O^{10} - 2CO^2 = C^{12} H^6 O^6.$$

Gallic acid.   Pyrogallic acid.
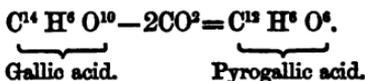
867. Sometimes, by carefully regulating the temperature, two acids are formed, one after the other, two equivalents of carbonic acid being removed to form one acid, and two more subsequently to convert the first pyro-acid into the second. This is well illustrated in the case of meconic acid, which, by heating, yields comenic acid in the first place, and by continuing the heat, pyromeconic acid, according to the following equations:—

$$C^{14} H^4 O^{14} - 2CO^2 = C^{12} H^4 O^{10}.$$

Meconic acid.   Comenic acid.

$$C^{12} H^4 O^{10} - 2CO^2 = C^{10} H^4 O^6.$$

Comenic acid.   Pyromeconic acid.
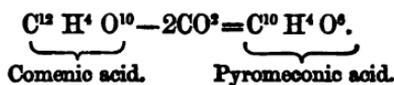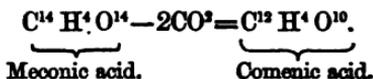
868. Some acids of considerable interest are formed under circumstances which do not permit of our tracing the relation between the parent matter and the resulting substances, and yet these same products may be obtained by definite processes also. As an instance of this, the substance known under the synonyms of carbolic acid, phenic acid, phenol, hydrate of phenyl, and phenic alcohol, is produced abundantly during the distillation of coal, it being obtained in considerable quantity from gas-tar, in which it occurs associated with numerous other acid, alkaline and neutral substances. It is also to be obtained in a perfectly intelligible manner by heating salicylic acid with lime or baryta, thus:

$$C^{14} H^6 O^6 - 2CO^2 = C^{12} H^6 O^2.$$

Salicylic acid.   Carbolic acid.
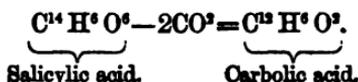
869. Acids of this kind being volatile and not readily obtained in the form of well-defined salts, are best studied by the careful analysis of the acids themselves, and the determination of their

vapour density.   The products of their decomposition should also be carefully ascertained, as the derived acids are often more easily investigated than the original one.

870. Many acids, on distillation with an alkaline earth, yield hydrocarbons the composition of which stands in such simple relation to the original acid, that their study is capable of yielding important corroborative evidence of the constitution of the acid as deduced from its analysis and that of its salts.   These hydrocarbons will be described presently.

871. *General remarks on organic acids.*—It is to be observed with acids, as also with other organic bodies, that the number of equivalents of carbon, hydrogen and oxygen must be divisible by two.   In salts, however, the metal replaces hydrogen, and therefore the number of equivalents of hydrogen and metal added together must make an even number.   If nitrogen be present, the hydrogen and nitrogen added together must make an even number; and in the salts, the hydrogen, nitrogen and metal must be divisible by two.

872. If the acid be one in which hydrogen is replaced by hyponitric acid, chlorine, iodine or bromine, &c., the number of atoms of the replacing element must be equal to the number of atoms of hydrogen removed; and in the salts, the atoms of hydrogen, replacing element, and metal must together be divisible by two.

As instances of what has been said, let us trace the formulæ of acetic acid under the circumstances detailed:—

$$C^4 H^4 O^4 \quad \left.\begin{matrix} C^4 \ H^3 \\ Ag \end{matrix}\right\} O^4 \quad \left.\begin{matrix} C^4 \ H^3 \\ Cl \end{matrix}\right\} O^4.$$

Acetic acid.   Acetate of   Chloracetic
                 silver.   acid.

$$\left.\begin{matrix} C^4 H^2 \\ Cl \\ Ag \end{matrix}\right\} O^4 \quad \left.\begin{matrix} C^4 H \\ Cl^2 \end{matrix}\right\} O^4 \quad \left.\begin{matrix} C^4 Ag \\ Cl^3 \end{matrix}\right\} O.$$

Chloracetate   Trichloracetic   Trichloracetate
of silver.   acid.   of silver.

z 2
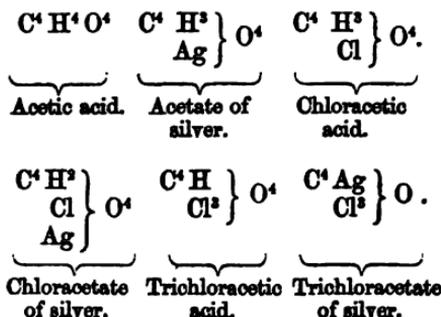
Take also the formula of an acid containing nitrogen, and see how the law holds:—

$$C^{52} H^{43} NO^{12} \qquad \left. \begin{array}{c} C^{52} H^{42} \\ Na \end{array} \right\} NO^{12}.$$

Cholic acid.   Cholate of soda.
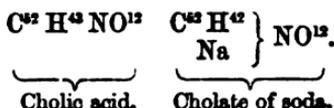
Even in more complex instances we still find the same regularity of arrangement, thus:—

$$C^{12} H^6 O^2 \qquad \left. \begin{array}{c} C^{12} H^5 \\ (NO^4) \end{array} \right\} O^2 \qquad \left. \begin{array}{c} C^{12} H^3 \\ (NO^4)^3 \end{array} \right\} O^2.$$

Phenic acid.   Nitrophenic   Trinitrophenic
            acid.   or picric acid.

$$\left. \begin{array}{c} C^{12} H^3 \\ Ag \\ (NO^4)^3 \end{array} \right\} O^2 \qquad \left. \begin{array}{c} C^{12} H^3 \\ (NH^4) \\ (NO^4)^3 \end{array} \right\} O^2.$$

Trinitrophenate of silver.   Trinitrophenate of ammonia.
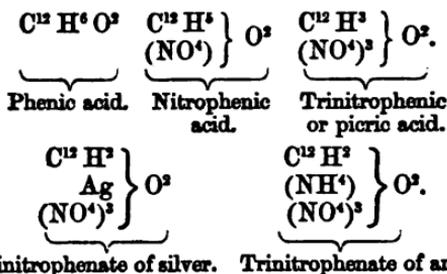
873. In the last illustration the metal ammonium is seen to stand exactly in the same position, and therefore fulfil the same function as the silver in the trinitrophenate of silver. This law of even atoms is of the highest value in research as a means of controlling formulæ. We shall, under other heads, notice the nature of the formulæ of other bodies of different constitution.

874. A new and most interesting series of bodies have recently been described by the late deeply lamented and illustrious chemist M. Gerhardt; they are regarded as being what were, until lately, conceived to be merely hypothetical bodies, namely, anhydrous monobasic acids. It is singular that, in one respect, they resemble the curious hydrocarbons discovered by MM. Frankland and Kolbe, and by them regarded as the alcohol radicals*, viz. that their formula for four volumes of vapour is double that

* In submitting the substances produced by destructive distillation of the Torbane-hill mineral to careful examination, I have succeeded in isolating four distinct hydrocarbons, remarkable for having absolutely the same composition, boiling-point and density, both in the state of fluid and also of vapour, as the organic radicals.

which they possess in their compounds; in this respect, the ethers, the radicals and the anhydrous acids resemble each other. The method of preparation of these anhydrous acids is sufficiently simple; it is thus:—

$$\left.C^4 H^3 O^2, Cl + \underbrace{C^4 H^3}_{K}\right\} O^4 = K Cl + \left.\begin{matrix}C^4 H^3 O^3 \\ C^4 H^3 O^3\end{matrix}\right\}$$

$\underbrace{}$ Chloride of acetyl. $\underbrace{}$ Acetate of potash. $\underbrace{}$ Anhydrous acetic acid.
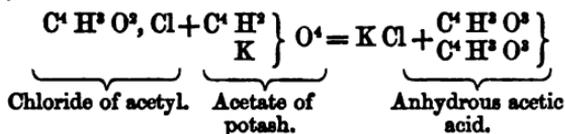
875. These anhydrides easily pass into the ordinary acid in presence of water.

When anhydrous acetic acid is treated with metals, acetates are formed, and, at the same time, a volatile, somewhat oily fluid is produced of agreeable odour, but of which the nature is at present unknown *.

876. We have already alluded to the necessity for ascertaining the degree of basicity of acids (§ 841). It is also to be noticed, that if the acid is bibasic, two amides may be formed from it, one having the properties of an acid, and the other being a true amide; the former being derived from the acid, and the latter from the neutral ammonia salt. Instances of these are to be found in malamidic acid and malamide, or, as it is generally called, asparagine. The former is obtained from acid malate of ammonia by the loss of two equivalents of water, and the latter from *neutral* malate of ammonia by the same process.

877. The most useful salts for determining the atomic weight of acids are those of silver, lime and baryta. But acids, as they differ in properties, differ also in the way in which they form salts. Sometimes one metallic oxide may be used with greater advantage than any other with one, and yet be entirely useless with another acid.

878. The remarkable researches of Pasteur have opened a wide field of investigation as to the action of heat on the salts of organic acids; it is necessary, therefore, to be familiar with the crystallographic and optical characters of organic salts, and particularly their relations towards polarized light.

* I have undertaken the examination of this subject.

879. The salts of organic acids, on distillation, frequently yield what are termed ketones, or bodies analogous to acetone. Unless, however, the atomic weight of the acid is very low, the ketone is almost always accompanied by other bodies.

880. *On organic alkaloids.*—These substances are now becoming more numerous every day; and, in fact, before long, it is not impossible they may even rival in number organic acids. They are found to exist in the animal and vegetable kingdoms, and are also produced by a great variety of reactions; we shall glance at some of the principal ones under the following heads: alkaloids derived from:—

I. The vegetable kingdom.
II. The animal kingdom.
III. The action of potash on the cyanic and cyanuric ethers.
IV. The action of ammonia on the hydriodic ethers, &c.
V. The action of reducing agents on the nitro-compounds of certain hydrocarbons.
VI. The action of reducing agents on nitro-compounds of oxidized bodies.
VII. Destructive distillation.

881. *Alkaloids obtained from the vegetable kingdom.*—Plants remarkable for their powerful action on the system, are generally found to contain organic alkaloids, most of them being highly valuable as medicaments. Few alkaloids can be taken internally, except in very small quantities, without occasioning violent symptoms, many being deadly poisons. It would be occupying far too much space were we to do more than select a few of the most instructive cases for study; we shall endeavour therefore to select one or two of the most well-marked bases, to examine their properties, and the modes by which they are obtained.

882. In the very first rank stand those obtained from the cinchona barks, and from opium. Solid bases capable of forming crystalline salts like those from the former source, are extracted by rather dilute acids. The solution is precipitated by milk of lime, and the deposit, after powerful pressure, is treated

with alcohol, to dissolve the alkaloids which are separated by fractional crystallization, taking advantage of their different degrees of solubility. Sometimes the colouring matter of the bark is removed by caustic alkalies before extracting the bases with acid, thus rendering the subsequent bleaching of the alkaloids by animal charcoal unnecessary. The extraction of the alkaloids of the cinchona barks has become so important a process in consequence of their extreme value as remedial agents, that great skill has been expended by various manufacturers in perfecting the various operations, so as to avoid the production of uncrystallizable and dark-coloured bases.

883. With the opium alkaloids, a different mode of proceeding is adopted, in consequence of the substances sought existing in a state which permits their extraction by means of water instead of acids. Morphia, the most valuable constituent of opium, appears to exist partially as sulphate and partially as meconate; if, therefore, to the aqueous solution of opium a solution of chloride of calcium be added, a precipitate of sulphate and meconate of lime is obtained; and, on carefully evaporating the mother-liquid, the morphia crystallizes out, and is powerfully expressed to remove the adherent fluid. The base is then recrystallized from water, and bleached by animal charcoal until sufficiently white. The first black mother-liquid contains a great variety of alkaloids, many of them of great interest; they are capable of being separated by tolerably easy but somewhat circuitous processes, and yield numerous products of decomposition; the details, however, cannot be entered into here.

884. In examining alkaloids extracted by processes of the kind alluded to above, it is absolutely necessary to make combustions of them after different numbers of crystallizations, in order to ascertain if repetitions of the process alter the composition of the alkaloid by removing other substances. It often happens that two or more bases may be extracted by acids from various parts or products of plants, and on being crystallized they are obtained together, and unless the operation is repeated a great many times, an impure product would be analysed. It is therefore of great

importance to try the action of various solvents upon them, in order to ascertain whether the substance supposed to be homogeneous, may not in reality be a mixture capable of separation into two or more distinct alkaloids. This is one of the circumstances which make it fortunate that organic bases form so many compounds, because each new combination becomes a process of purification.

885. The well-marked salts which such bases form are very numerous, and comprise sulphates, hydrochlorates, nitrates*, chlorates, perchlorates, hydriodates, periodates, hyposulphates, hyposulphites, arsenites, formiates, oxalates, ferrocyanates, sulphocyanides, acetates, tartrates, citrates, valerianates, picrates, and many others. They also form double salts with many metals; this is especially the case with their hydrochlorates, which combine with many metallic chlorides, including, probably, all those which form double salts with the hydrochlorates of the volatile organic bases, to be described presently.

886. These solid crystalline oxidized vegetable alkaloids almost invariably yield volatile bases by distillation with potash; quinine, cinchonine and strychnine, for instance, yield chinoline†.

887. It is extremely curious that the greater part of these bases act with the alcohol radicals as if they were nitriles, that is to say, as if one molecule of them contained three compound radicals. And it is no less strange, that all the volatile bases produced by their metamorphosis under the action of heat are nitriles also.

888. Piperine, the formula and constitution of which are by no means well established, yields by its destructive distillation two volatile bases, only one of which, namely piperidine, has as yet been examined. This, the more volatile, the formula of which

* Where the base is one that would be decomposed by the contact of free nitric acid, it is generally easy to procure a nitrate by double decomposition of the sulphate with nitrate of baryta.

† I have found that cinchonine, instead of only affording chinoline, as had been supposed, yields pyrrol, pyridine, picoline, lutidine, collidine, chinoline, and lepidine; and it is most probable that quinine and strychnine undergo an equally complex decomposition.

was first determined by Dr. Anderson, has been fully studied by M. Cahours*; it is an exception to the usual rule of bases produced in this manner, inasmuch as it is capable of taking up two equivalents of a radical to form an ammonium base; piperidine has therefore the constitution of an imide, or perhaps it contains a bibasic radical. It would be of interest to ascertain whether piperine itself is similarly constituted to piperidine, as regards the number of radicals it is capable of assimilating.

889. The vegetable kingdom also yields volatile bases, which sometimes exist ready formed in the plant, and at others appear to be produced by the action of alkalies on either acid or basic substances. An instance of the production of an alkali from an acid by the action of heat and alkalies has already been given in § 851, in describing the production of aniline from anthranilic acid. Apophyllic acid also, by destructive distillation, yields an alkaloid of which the nature is at present unknown, and in consequence of the great difficulty of preparing the material by the action of nitric acid on cotarnine, is likely to remain so, or at least until a new mode of obtaining apophyllic acid is discovered, which is greatly to be desired, as it possesses high theoretical interest. Its preparation by the decomposition of platino-chloride of cotarnine is not likely to be a very economical mode of procuring it.

890. *Bases from the animal kingdom.*—It is not always easy to assign alkaloids a place among either animal or vegetable products, as they may sometimes be derived from both sources. When such bases as methylamine, or, in fact, any volatile ones, are obtained from animal matters, it is generally, if not always, to be inferred that they are produced by the metamorphosis of bodies of more complex constitution, either under the influence of putrefaction, heat, or some other disruptive agency.

891. The juice of flesh yields creatine†, which, as it has never been found in vegetables or plants, may with propriety be called an animal alkaloid. But creatine on distillation with soda-lime yields methylamine, an alkaloid also obtainable from vegetable

* CAHOURS.—'Ann. de Ch. et de Phys.' [3] xxxviii. p. 76.
† LIEBIG.—'Ann. de Chim. et de Phys.' [3] xxiii. 129.

z 5

sources. Sarcosine, a derivative of creatine, also yields methyl-
amine on distillation. The volatile bases of the alcoholic series
are equally produced by the decomposition of either animal or
vegetable matters.

892. The only base derived exclusively from the animal king-
dom, which we shall study as to the mode of isolation, is crea-
tine; and this has been selected because its preparation is
exceedingly instructive as a guide in such trains of research as
are likely to be undertaken by the student on basic substances of
animal origin.

893. Creatine exists ready formed in the juice of the flesh of
almost all animals; at least it has been found in that of the Horse,
Ox, Sheep, Pig, Deer, Hare, Fox, Marten, Fowl, Pigeon, Turkey,
Skate, Haddock, Salmon, Herring, Turbot, Cod, Dog-fish, Pike,
Whale, and Alligator. If, to the chopped flesh of the animal,
water to the extent of the weight of the flesh be added, and the
whole be well pressed, a fluid is obtained which contains the
creatine, but little is obtained on evaporation, because it is de-
composed by the free acid. But if, after heating the juice to
coagulate the albumen, it be filtered, and neutralized by baryta-
water, and then evaporated at about 130° Fahr., a thin jelly is
obtained, from which the creatine crystallizes out in hard brilliant
prismatic crystals*, having the formula $C^8H^9N^3O^4+2HO$. By
weak acid or alkaline liquids it is not altered, but strong acids
convert it into creatinine, another alkaloid, thus:—

$$\underbrace{C^8\,H^9\,N^3\,O^4}_{\text{Creatine.}} = \underbrace{C^8\,H^7\,N^3\,O^2}_{\text{Creatinine.}} + 2HO.$$
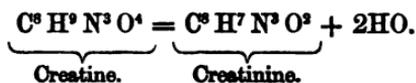
894. We see, therefore, that one alkaloid may, by mere loss
of water, be converted into another. A parallel case is found in
Wertheim's conhydrine, an alkaloid recently extracted from
Conium maculatum. The reaction is precisely analogous, except
that the resulting base contains no oxygen:—

* Fluids of a gelatinous consistency are peculiarly adapted for yielding
well-defined crystals.

$$C^{16} H^{17} NO^3 = C^{16} H^{15} N + 2HO.$$

Conhydrine.   Coniine.
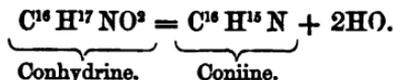
Creatine forms well-defined salts, including hydrochlorate, sulphate, and nitrate. Creatinine yields salts, and also combines with chloride of zinc. The hydrochlorate gives a double salt with bichloride of platinum.

895. *Production of bases by the action of alkalies on the cyanic and cyanuric ethers* *.—This method of obtaining volatile organic bases, discovered by M. Wurtz, has had the most important consequences, in entirely modifying our ideas of basic combinations, and, by leading M. Hofmann to an examination of the action of ammonia on the hydriodic ethers, caused the discovery of a general method by which we are enabled to determine the constitution of all the other natural and artificial alkaloids.

896. Previous to describing the reactions by which the bases are produced, it is necessary to remind the student that the alcohol radicals, regarded as two volume-formulæ, are precisely analogous to hydrogen; they fulfil the same functions, and are capable of replacing it without destroying the original type of the compound. If, therefore, we could replace one of the three equivalents of hydrogen in ammonia by methyl, or, in fact, by any alcohol radical, we might anticipate that the resulting compound would, to a certain extent, resemble the original base. Now, let us see the reaction which takes place between the caustic alkalies and the above-mentioned ethers. In the first place, cyanic acid is decomposed by potash in the following manner:—

$$C^2 NO, HO + 2KO + 2HO = 2(KO, CO^2) + NH^3.$$
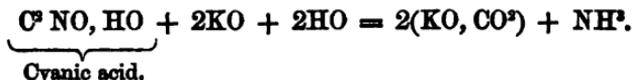
Cyanic acid.

In methylcyanic ether, an equivalent of hydrogen in the cyanic acid is replaced by methyl; if, then, the ether is acted on in the same manner as the acid, we have,—

* WURTZ, 1849. And, *in extenso*, Mémoire sur les ammoniaques composées. Extrait du tome xi. des mémoires présentés par divers savants à l'Académie des Sciences.

$$C^3 NO, C^2 H^3 O + 2KO + 2HO = 2(KO, CO^2) + C^2 H^5 N.$$

Methylcyanic ether.   Methylamine.
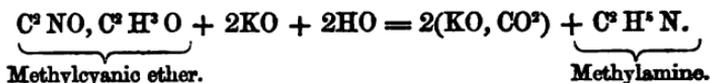
897. If, now, we merely multiply the last equation by three, we obtain the reaction of the alkali on the cyanuric ethers, because the latter are polymeric with the cyanic ethers. The bases are also formed by the action of potash on the compound ureas; but we shall only notice the first method at length.

898. If the formulæ given for ammonia and methylamine in the last equation be examined, it is plain that they might be written thus :—

$$\left. \begin{array}{c} H \\ H \\ H \end{array} \right\} N \qquad \left. \begin{array}{c} C^2 H^3 \\ H \\ H \end{array} \right\} N.$$

Ammonia.   Methylamine.
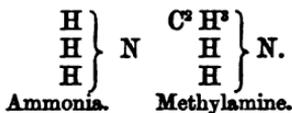
Where we see at once that one of the equivalents of hydrogen in ammonia is replaced by methyl, the type remaining intact.

899. If we now consider what the most obvious properties of ammonia are, and also what are the characteristics of methylamine, we shall see at once the extraordinary resemblances between them. They are both gases, soluble in water, affording solutions of extreme pungency, which fume on approach of a rod dipped in hydrochloric acid; the solution precipitates metallic oxides like ammonia, and affords well-crystallized salts. In fact, methylamine so greatly resembles ammonia in its properties, that it has repeatedly been mistaken for that alkali. One of the best means of distinguishing, and even of separating them when mixed, is by treating the dry hydrochlorate with strong alcohol, which readily dissolves hydrochlorate of methylamine, but scarcely dissolves sal-ammoniac.

900. The idea immediately strikes us, on viewing the formula of methylamine, whether it would not be possible to replace more than one equivalent of hydrogen in ammonia by alcohol radicals; and in the next paragraph we shall study the very simple method by which M. Hofmann has determined this question.

901. *Production of bases by the action of ammonia ·on the hydriodic ethers*[*].—If we consider for a moment what it is that we desire to effect, we shall find that the reagent required, is an alcohol radical in combination with an element having a powerful affinity for hydrogen. The reason for this is very simple; it is because we wish to remove an equivalent of hydrogen from ammonia, and substitute the radical in its place. We shall still use methyl as our illustration. If, then, we place an alcoholic solution of ammonia in contact with excess of iodide of methyl, and after sealing up the mixture in a pressure-tube (§ 303), expose the apparatus for some time to a temperature of 212° Fahr., we shall find that the ammonia disappears, and the solution contains the hydriodate of a new base. We shall disregard secondary reactions, and suppose that the reaction is simply confined to the production of one substance, because the others that are, under certain circumstances, formed simultaneously will be more conveniently studied afterwards. If, now, the excess of iodide of methyl be distilled off, we find, on evaporation of the fluid, that a crystalline salt is deposited having the formula $C^2 H^5 N$, HI, or the hydriodate of methylamine. The salt is formed in accordance with the following equation:—

$$\left.\begin{array}{c} H \\ H \\ H \end{array}\right\} N + C^2 H^3, I = \left.\begin{array}{c} C^2 H^3 \\ H \\ H \end{array}\right\} N, HI.$$

<table>
<tr><td>Ammonia.</td><td>Iodide of methyl.</td><td>Hydriodate of methylamine.</td></tr>
</table>
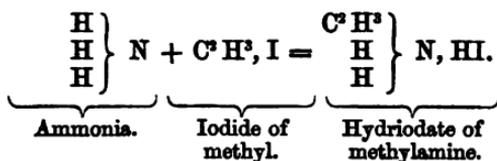
It is plain that there is no reason why the above reaction should not take place equally well with the new base instead of ammonia, and accordingly we find that on distilling the hydriodate of methylamine with an alkali, so as to obtain the free base, and then submitting the latter to the action of iodide of methyl, we obtain the result expressed in the annexed equation:—

[*] HOFMANN.—Phil. Trans. 1850.

$$\left.\begin{array}{c} C^2 H^3 \\ H \\ H \end{array}\right\} N + C^2 H^3, I = \left.\begin{array}{c} C^2 H^3 \\ C^2 H^3 \\ H \end{array}\right\} N, HI.$$

| Methylamine. | Iodide of methyl. | Hydriodate of di-methylamine. |
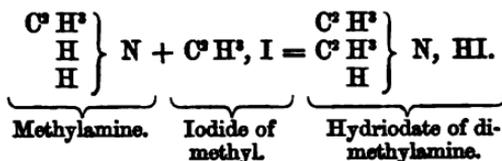
And, again, by proceeding exactly as before :—

$$\left.\begin{array}{c} C^2 H^3 \\ C^2 H^3 \\ H \end{array}\right\} N + C^2 H^3, I = \left.\begin{array}{c} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{array}\right\} N, HI.$$

| Dimethyl-amine. | Iodide of methyl. | Hydriodate of trimethylamine. |
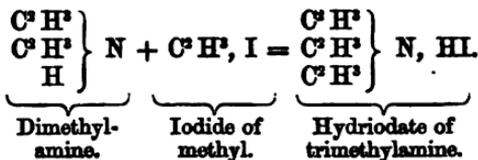
902. All the bases thus formed are powerful alkalies, and it is to be observed that they become less volatile and more oily as the greater number of equivalents of hydrogen in ammonia become replaced.

The question next presents itself, whether, regarding ammonium as the type of basic organic bodies, the fourth equivalent of hydrogen may not be replaced by methyl to form a compound ammonium; and if we repeat the treatment of the base as before, we have—

$$\left.\begin{array}{c} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{array}\right\} N + C^2 H^3, I = \left.\begin{array}{c} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{array}\right\} N, I.$$

| Trimethyl-amine. | Iodide of tetra-methylammonium. |
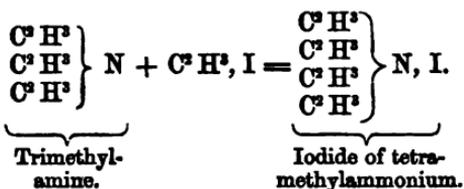
903. The last base is therefore constituted exactly in the same manner as the iodide of ammonium. To obtain the free base, it is necessary to adopt a different method to that which was employed with the first, second, and third bases, because the last is no longer volatile. But if, to the aqueous solution of the iodide of tetramethylammonium, obtained by the last process, we add oxide of silver, a new base is obtained, not volatile without decomposition. The following equation explains the reaction :—

$$N \begin{Bmatrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{Bmatrix} I + AgO + HO = N \begin{Bmatrix} C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \\ C^2 H^3 \end{Bmatrix} O, HO + AgI.$$

Iodide of tetramethyl-   Hydrated oxide of tetra-
ammonium.   methylammonium.
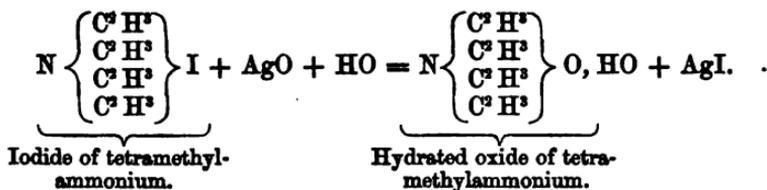
The hydrated oxides thus obtained by the reactions given, and with the iodides of methyl, ethyl, &c., are most powerful alkalies, the solutions of which resemble solutions of caustic potash so perfectly that they might be easily mistaken for that substance by mere qualitative testing.

We have entered thus minutely into the reactions which produce these bodies, because it is essential for the student to comprehend them, in order to follow out the methods of examining alkaloids—to be presently described.

904. *Action of reducing agents on the nitro-compounds of certain hydrocarbons.*—Many hydrocarbons when treated with fuming nitric acid in the manner to be described further on, yield substances retaining the type of the original body, but having one of the equivalents of hydrogen replaced by hyponitric acid. These nitro-compounds, by treatment with reducing agents, yield alkaloids which always belong to the first class, that is to say, they are ammonias in which one equivalent of hydrogen is replaced by a radical. The following represents the nature of the decomposition which takes place when an alcoholic solution of nitrobenzole is treated with sulphuretted hydrogen :—

$$C^{12} H^5 NO^4 + 6HS = C^{12} H^7 N + 4HO + 6S.$$

Nitrobenzole.   Aniline.
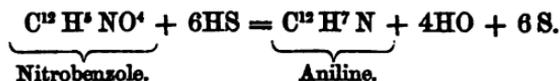
905. This process does not yield the base nearly so easily, or in so pure a state, as the following, given by M. Béchamp[*]. It is founded on the strong tendency of the proto-salts of iron to become oxidized at the expense of the oxygen of any substances with which it may be in contact. An acetate of iron is pre-

[*] BÉCHAMP.—'Chem. Gaz.' March 1855; and 'Ann. de Chim. et de Phys.' [3] xlii. p. 186.

pared, containing three parts of iron to one of the nitro-com-
pound, and the two being mixed, are heated on the water-bath,
in a capacious flask, provided with a tube leading to a well-
cooled recipient. If 100 grammes of nitro-compound are used,
the heating on the water-bath requires about an hour. When
cooled, the mass in the flask has water added to it, and the whole
is filtered; the mass on the filter is to be washed with hot water,
and the united fluids are distilled until nine-tenths have passed
over. The acetate of aniline and acetic acid both distil over. It
is necessary to ensure efficient condensation, as, in presence of
steam, acetate of aniline is so volatile that much would be lost
if this precaution were not taken. The distillate is to have 40
grammes of concentrated oil of vitriol added for every 100 grammes
of nitrobenzole used. On distillation the sulphuric acid displaces
the acetic acid, which accordingly distils over, and when the
greater part has been obtained, the sulphate of aniline is to be
distilled with excess of a strong solution of caustic potash. The
aniline is thus obtained in a very pure condition.

906. A still more convenient process is to mix in a spacious
retort 1 part of nitrobenzole with 1·2 of bright iron-filings and
1 part of commercial acetic acid. In a few minutes a violent
reaction takes place, and unless the receiver be well cooled, all
might be lost. When the action has ceased, and the retort
cooled, the fluids which have distilled over are to be returned to
the retort, and the whole is distilled to dryness. The distillate
merely requires to have excess of potash added to it to separate
the base, which may be removed from the alkaline fluid, and be
digested with sticks of caustic potash to remove moisture. The
following equation explains the reaction which takes place:—

$$\underbrace{C^{12}\,H^5\,NO^4}_{\text{Nitrobenzole.}} + 2HO + 4Fe = 2Fe^2\,O^3 + \underbrace{C^{12}\,H^7\,N.}_{\text{Aniline.}}$$
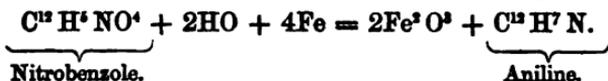
Almost all ordinary nitro-compounds may be decomposed in
the same manner as nitrobenzole, with formation of oily or
crystalline alkaloids. For example, nitronaphthaline yields
naphthalamine, nitrocymol cymidine, &c. To form the last-named

nitro-compound, it is necessary to cool the hydrocarbon and the nitric acid by means of a freezing mixture, before allowing them to react on each other.

907. *Action of reducing agents on the nitro-compounds of oxidized bodies.*—Some oxidized bodies by reduction yield alkaloids. The only example which we shall adduce is coumaramine*. In the case of this substance, neither sulphuretted hydrogen nor nascent hydrogen yield any satisfactory results; but if a mixture of iron filings and dilute acetic acid be used, and the mixture, with the nitrocoumarine, be heated on the water-bath, action soon commences, sesquioxide of iron separates, and on cooling, yellow needles of coumaramine are deposited. This substance is a true alkaloid, forming a crystalline hydrochlorate and a double compound with bichloride of platinum. There are many oxidized natural and artificial alkaloids and proximate principles the nitro-compounds of which have not been studied, and which, under the influence of acetate of iron, would doubtless yield facts of interest. This is more especially the case now that we know the precautions necessary in forming nitro-compounds with substances which decompose with nitric acid if the temperature be allowed to rise. We have previously alluded to this in describing the method of forming trinitrocresylic acid from the hydrate of cresyl, § 853.

908. *Formation of alkaloids by destructive distillation.*—The number of bases formed in this manner is very considerable, and it is probable that no nitrogenized animal or vegetable matters can be submitted to distillation without their appearing in the distillate. The subject has been very fully investigated during the last few years. The first person who took up the subject was, it is believed, Unverdorben, who ascertained the presence in Dippel's oil, or as it is commonly called, bone-oil, of a very peculiar class of substances of decidedly alkaline properties. He merely described their reactions. Runge afterwards followed in the same track, and found that coal-naphtha also contained organic

* FRAPOLLI and CHIOZZA.—'Chem. Gaz.,' Oct. 15, 1855; and Liebig's 'Annalen,' xcv. p. 252.

bases and acids, but he also depended entirely on reactions. Hofmann made an examination of the bases in coal-naphtha, and separated aniline and leukol or chinoline. Anderson subsequently found picoline in coal-naphtha; and still later, he discovered in bone-oil the whole series of which picoline is a member, as well as many of the bases of the alcohol series. I have also been occupied for some years with the subject, and have ascertained several facts, and added a few new bases to the list of those previously known.

909. Several fixed alkaloids found in nature yield oily bases by distillation with alkalies; thus cinchonine yields chinoline, &c. Narcotine yields trimethylamine, and probably other bases *.

910. Nitrogenized non-alkaline bodies also yield bases; indigo for instance affords aniline in a state of purity by careful distillation with hydrate of potash; and it is worthy of remark, that, contrary to what happens generally under similar circumstances, no other base appears to be formed. Recent researches appear to indicate that pure amylamine may be obtained by destructive distillation from horn and also from leucine; my own experiments upon feathers, made some years ago, lead me to believe, however, that the reaction is not so simple.

911. The general mode of extraction of bases from the oils produced by destructive distillation of nitrogenized organic matter, is to agitate the oil with dilute sulphuric acid, and, after allowing the fluids to rest some time, in order to promote the separation of the oil and acid, to siphon off the latter, which contains the bases in solution. The acid solution of the bases is to be boiled in a large open copper vessel for a long time, until no reaction of pyrrol is obtained by exposing to the escaping steam a slip of deal wood moistened with concentrated hydrochloric acid, §§ 373, 445. This procedure also resinifies many tarry matters, which would otherwise cause much trouble in the after processes. The cake of resin which usually appears on the surface

---

* The products of the distillation of narcotine with potash require examination.

of the acid is then to be removed, and the whole fluid filtered through coarsely powdered charcoal. The liquid should now have an excess of slaked lime added, and the whole is to be distilled.

912. The distillation requires care, in order that the more volatile products may not be lost. For this purpose, the end of the condenser should fit into an adapter which is connected with a large tubulated receiver. The tubulature of the receiver should have a tube passing from it into some moderately strong hydrochloric acid, in order to condense any exceedingly volatile bases, such as methylamine, &c.

913. The fluid collected in the receiver should be again submitted to distillation on the water-bath, to separate any very volatile bases; the latter may then be saturated with hydrochloric acid, and the solution is to be evaporated to dryness on the water-bath. The dry mass is to be extracted with very strong alcohol, which will dissolve the volatile bases as hydrochlorates, leaving the sal-ammoniac behind. The alcoholic solution is to be again evaporated to dryness, and the treatment with alcohol is to be repeated. The purified hydrochlorates, freed from any trace of alcohol by exposure for some time to 212° F., are then to be dissolved in water, and treated with bichloride of platinum; the precipitate, if any, being analysed, and the mother-liquid being evaporated over sulphuric acid, the succeeding crops are to be examined to see whether more than one base is present.

914. The fluid containing the less volatile bases is now to have potash in excess added, to separate them. When they have risen to the surface, the alkaline fluid may be removed by a siphon. The bases, as thus procured, retain about a third of their bulk of water, which is to be removed by repeated digestion with sticks of fresh potash.

915. The various bases existing in a mixture obtained in the manner indicated from products of destructive distillation, are to be separated from each other by fractional distillation, § 353.

916. *General remarks on organic alkaloids.*—In order to de-

termine the constitution of organic bases, there are several processes which are more especially necessary.   These are,—

> Analysis of salts.
> Action of alcohol iodides.
> Formation of bodies analogous to urea.
> Vapour density.

917. The metamorphoses which organic alkaloids may be made to undergo are excessively numerous, and cannot be described here; they may be studied in the various papers scattered through the chemical journals.

918. *Some processes and reactions connected with neutral bodies.* —The number of existing organic bodies possessing neither acid nor alkaline properties is so immense, and the processes by which they are separated from others so various, that we shall only touch upon a few of the most important, and even then in a very cursory manner.   Those which we shall consider are,—

> Alcohols.
> Ethers.
> Aldehydes.
> Hydrocarbons.

919. By the term alcohol is understood a substance derived from the type water by the substitution of one atom of an electro-positive radical for an equivalent of hydrogen.   But we must remember, if we use the equivalents ordinarily employed in this country, that the alcoholic group is formed on the type of two equivalents of water; on the other hand, by considering with Gerhardt the atomic weight of oxygen to be 16 and that of carbon 12, we have the alcohols derived from one equivalent of water. The following represents the formulæ according to these views:—

$$\text{Water.} \quad \text{Alcohol.} \qquad \text{Water.} \quad \text{Alcohol.}$$
$$\left.\begin{matrix} H \\ H \end{matrix}\right\} O^2 \quad \left.\begin{matrix} C^4 H^5 \\ H \end{matrix}\right\} O^2 \qquad \left.\begin{matrix} H \\ H \end{matrix}\right\} O \quad \left.\begin{matrix} C^2 H^5 \\ H \end{matrix}\right\} O.$$

$$\underbrace{\qquad\qquad\qquad}_{\text{Ordinary equivalents.}} \qquad \underbrace{\qquad\qquad\qquad}_{\text{Gerhardt's equivalents.}}$$
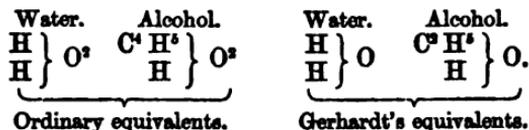
920. Vinic alcohol (common alcohol) is the second member of that great series of bodies of which such an immense number of

derivatives are known, commencing with wood-spirit and ascending to the wax alcohols.

921. Several of these bodies may be obtained by fractional distillation of fusel oil, especially that obtained from the grape-marc.

922. The constitution of an alcohol cannot be satisfactorily demonstrated with the same readiness as that of an acid or a base. Its formula must be substantiated by the study of several of its derivatives. In the first place, the substance when obtained pure must be analysed, and its vapour density be determined. The vapour densities of alcohols do not generally require to be taken at temperatures much above the boiling-point. At 36° above the boiling-point of common alcohol the density comes out 1·65, theory requiring 1·59; at somewhat higher temperatures the experimental value is almost exactly the same as that required by theory. An alcohol should have its conjugate sulphuric acid compound examined; also the acid bearing the same relation to it that the acetic does to common alcohol. It is easy to obtain the volatile acid corresponding to an alcohol, by various processes of oxidation ; the following equation represents the nature of the reaction :—

$$\underbrace{C^4\,H^6\,O^2}_{\text{Alcohol.}} + 4O = \underbrace{C^4\,H^4\,O^4}_{\text{Acetic acid.}} + 2HO.$$
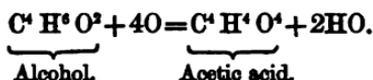
If of the vinic class, it should also have the iodide or bromide of its radical obtained; also the alkaloid derived from ammonia by the substitution of its radical for an atom of hydrogen in ammonia. The simple ether should also be obtained. It will be essential also to determine (if belonging to known series) whether it obeys Kopp's law of boiling-points. Alcohols possess one property which assimilates them to monobasic acids, that is to say, when treated with potassium or sodium they are decomposed with formation of a compound possessing an equivalent of the metal in the place of an equivalent of hydrogen.

923. The aldehyde corresponding to the alcohol should also be studied ; it may be procured by a process of oxidation less energetic than that required to form the acid of the series. The annexed equation illustrates the conversion of common alcohol into aldehyde :—

$$C^4 H^4 O^2 + 2O = C^4 H^4 O^2 + 2HO.$$

Alcohol.   Aldehyde.
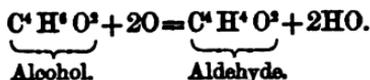
924. Alcohols vary greatly in their physical conditions, even when belonging to the same homologous series; for while methylic alcohol, $C^2 H^4 O^2$, is a colourless mobile fluid, boiling at 66°·5 Cent., the melissic alcohol, $C^{60} H^{62} O^2$, is a crystalline solid, having a fusing-point as high as 85° Cent.

When heated with caustic potash, the alcohols of the vinic class are decomposed, with formation of an acid corresponding to it, hydrogen being disengaged, thus:—

$$C^2 H^4 O^2 + KO, HO = C^2 HO^3 KO + 4H.$$

Wood-spirit.   Formiate of potash.
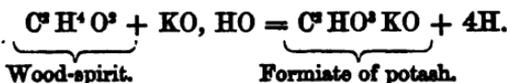
Even when so high up in the series as the melissic alcohol, the reaction is precisely similar, for

$$C^{60} H^{62} O^2 + KO, HO = C^{60} H^{59} O^2, KO + 4H.$$

Melissic alcohol.   Melissate of potash.
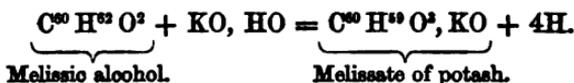
925. Alcohols are obtainable from several sources, and are produced by more than one interesting reaction. The greater number are products of fermentation, such as the ethylic, propylic, amylic, &c. The methylic alcohol, the first of this series, is obtained by the distillation of wood, while the caprylic is a product of metamorphosis of ricinoleic acid at a high temperature, under the influence of hydrate of potash.

$$C^{36} H^{34} O^6 + 2(KO HO) = C^{16} H^{18} O^2 + 2H + C^{20} H^{16} O^6, 2KO.$$

Ricinoleic   Caprylic   Sebate of
acid.   alcohol.   potash.

926. One of the most interesting reactions connected with alcoholic groups, is that by which we are enabled to pass from certain kinds of aldehydes to alcohols of the same class. This happens when bitter-almond oil, otherwise known as benzoic aldehyde, is treated with alcoholic potash.

$$2\,C^{14}H^6O^2 + KO, HO = C^{14}H^5O^2 + C^{14}H^5O^3, KO.$$

Bitter-almond oil.　　　Benzoic alcohol.　　　Benzoate of potash.
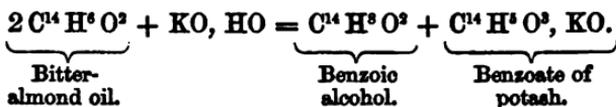
927. It has already been mentioned that the phenylic and cresylic alcohols are products of the destructive distillation of wood and coal (§§ 373, 853, 868). It must not be forgotten that the benzoic is isomeric, not identical, with the cresylic alcohol, the latter being homologous with carbolic acid.

928. The above sketch of the more prominent features in the reactions connected with alcoholic groups, is sufficient to show the extreme interest belonging to the subject; it cannot, however, be pursued further here, as we must now turn our attention to one of the most important derivatives of the alcohols.

929. *Ethers.*—These bodies are either simple or compound. The simple ethers come first in the order of study.

We have seen (§ 919) that an alcohol may be defined as two equivalents of water in which *one* equivalent of hydrogen is replaced by an electro-positive radical. In simple ethers, on the other hand, we have two equivalents of water in which both equivalents of hydrogen are replaced by an electro-positive radical. But numerous ethers exist which contain two different radicals, *i. e.* derived from two equivalents of water, in which both atoms of hydrogen are replaced, but by two different radicals. Nevertheless, if both the replacing radicals belong to alcoholic groups, the ether is still said to be simple. The following are examples of simple ethers placed by the side of their type for the sake of comparison:—

$$\left.\begin{array}{l} H \\ H \end{array}\right\} O^2 \qquad \left.\begin{array}{l} C^4H^5 \\ C^4H^5 \end{array}\right\} O^2 \qquad \left.\begin{array}{l} C^4H^5 \\ C^2H^3 \end{array}\right\} O^2 \qquad \left.\begin{array}{l} C^{12}H^5 \\ C^{12}H^5 \end{array}\right\} O^2.$$

Water.　　　Common ether.　　　Methyl-ethylic ether.　　　Phenylic ether.
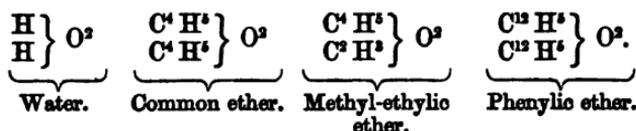
930. The simple ethers may generally be obtained by distillation of the corresponding alcohols with sulphuric acid, or by the action of the alcoholic iodides on the sodium or potassium alcohols. The annexed equation represents the latter reaction:—

$$\left.\begin{array}{c} C^4\,H^5 \\ K \end{array}\right\} O^2 + C^4\,H^5\,I = \left.\begin{array}{c} C^4\,H^5 \\ C^4\,H^5 \end{array}\right\} O^2 + IK.$$

$$\underbrace{\hphantom{xxxxx}}_{\substack{\text{Potassium-}\\\text{alcohol, or}\\\text{ethylate of}\\\text{potash.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Iodide of}\\\text{ethyl.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Common}\\\text{ether.}}}$$
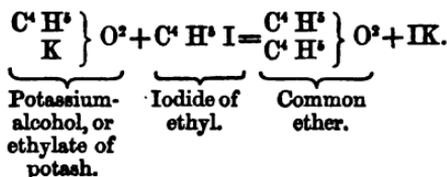
If it be desired to produce an ether containing two different alcoholic radicals, we proceed in the manner indicated by the annexed equation:—

$$\left.\begin{array}{c} C^4\,H^5 \\ K \end{array}\right\} O^2 + C^2\,H^3, I = \left.\begin{array}{c} C^4\,H^5 \\ C^2\,H^3 \end{array}\right\} O^2 + IK.$$

$$\underbrace{\hphantom{xxxxx}}_{\substack{\text{Potassium-}\\\text{alcohol.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Iodide of}\\\text{methyl.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Methyl-}\\\text{ethylic ether.}}}$$
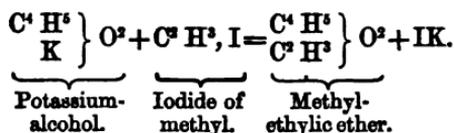
It is plain that by varying the nature of the alcohol containing the potassium, or the alcoholic iodide, we may obtain a great variety of these mixed ethers.

931. *Compound ethers.*—These differ from the mixed ethers mentioned above, inasmuch as the two atoms of hydrogen in the water are replaced, the one by the radical of an acid, and the other by the radical of an alcohol. They are formed by a very considerable number of reactions, among which may be mentioned, the distillation with strong sulphuric acid of a salt of the acid which it is desired shall enter into the ether with the alcohol, the radical of which shall also enter into the ether. Another method very often employed is to pass a current of hydrochloric acid gas into a mixture of the organic acid and alcohol. The reaction of the alcohol iodides on silver salts may be made use of to prepare compound ethers, thus:—

$$\left.\begin{array}{c} C^4\,H^3 \\ Ag \end{array}\right\} O^4 + C^4\,H^5\,I = \left.\begin{array}{c} C^4\,H^3 \\ C^4\,H^5 \end{array}\right\} O^4 + Ag\,I.$$

$$\underbrace{\hphantom{xxxx}}_{\substack{\text{Acetate of}\\\text{silver.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Iodide of}\\\text{ethyl.}}} \quad \underbrace{\hphantom{xxx}}_{\substack{\text{Acetic}\\\text{ether.}}}$$
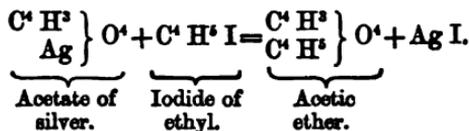
The formula of acetic ether is perhaps more correctly written—

$$\left.\begin{array}{c} C^4\,H^3\,O^2 \\ C^4\,H^5 \end{array}\right\} O^2,$$
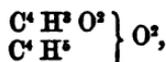
because it is generally considered that the oxidized radical $C^4 H^3 O^2$, known as acetyl or othyl, exists in it.

932. The subject of the compound ethers is one of considerable interest in a theoretical point of view, but it cannot be entered upon here, and for further information the student is referred to works specially devoted to organic chemistry.

933. *Aldehydes.*—The aldehydes are rapidly becoming better known, and are scarcely to be surpassed in the interesting nature of their reactions.

934. The aldehydes, in the present state of our knowledge, may be regarded from several points of view, each of which has certain advantages; the most convenient is perhaps to consider them as derived from the hydrogen type. In this way we look upon ordinary aldehyde as

$$H$$
$$H,$$

in which one of the atoms of hydrogen is replaced by the radical of acetic acid. The duplex character of the free radicals will be made more apparent in treating of the hydrocarbons. The formula of aldehyde is therefore $C^4 H^3 O^2$, H, or hydruret of acetyle.

935. Aldehydes are derived from numerous sources. We have already considered their production by the action of oxidizing agents on the alcohols in § 923.

936. One of the most interesting reactions resulting in the formation of an aldehyde, is that by which the benzoic aldehyde, hydruret of benzoyl or oil of bitter almonds, is produced from amygdaline. The substance which causes the metamorphosis of the last-named body does not, strange to say, enter into the resulting compound. It merely acts as a ferment; it is known as emulsine or synaptase, and exists in the bitter almond together with the amygdaline. The following equation explains the nature of the reaction :—

$$C^{40} H^{27} NO^{22} + 4HO = C^{14} H^6 O^2 + C^2 HN + 2C^{12} H^{12} O^{12}.$$

Amygdaline. Hydruret of   Hydro-   Grape-sugar.
              benzoyl.   cyanic acid.
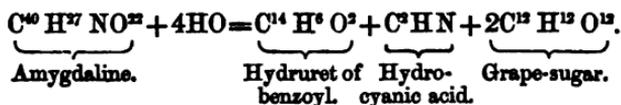
937. The above equation is sometimes written so as to include

2 A

the production of formic acid, but its formation is generally considered to be due to a secondary decomposition of the hydrocyanic acid.

938. The aldehydes are also obtained by destructive distillation; œnanthylic aldehyde is by this means obtained from castor oil. They are also found in nature in plants, such as cinnamic aldehyde in oil of cassia, cuminic aldehyde in oil of cumin, &c. The oil of rue, according to Gerhardt, consists of capric aldehyde mixed with a small quantity of an unknown hydrocarbon[*]. The formation of an aldehyde by fermentation has been mentioned above.

939. The aldehydes are often capable of assuming isomeric conditions. The lime-salts of several acids, moreover, yield isomers of the aldehydes by destructive distillation. One of the most important peculiarities of the aldehydes is their remarkable tendency to combine with the alkaline bisulphites, especially those of soda and ammonia. These compounds are not limited to the aldehydes of the alcohols of the vinic type, for cinnamic aldehyde and its congeners equally possess the property of combining with the alkaline bisulphites.

940. The ammoniacal compounds of this class yield bases by distillation with lime. In this manner triphenylamine is said to be produced from the bisulphite of the ammoniacal cinnamic aldehyde[†].

941. The aldehydes combine with ammonia to form crystalline salts; ordinary aldehyde for instance yields the following compound,—

$$C^4 H^4 O^2, NH^3.$$
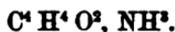
The above, when acted on by sulphuretted hydrogen, gives thialdine in accordance with the annexed equation:—

$$3(\underbrace{C^4 H^4 O^2, NH^3})+4HS=\underbrace{C^{12} H^{13} NS^4}+2NH^3+6HO.$$
Aldehyde-ammonia.   Thialdine.
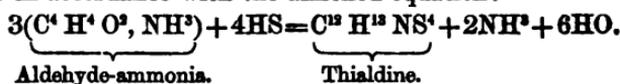
Thialdine is said to yield chinoline when distilled with hydrate of lime; this is, however, most improbable in a theoretic point of view, and some experiments made by myself, although on too

* Some researches of my own now in progress indicate the composition of oil of rue to be more complex than has been hitherto supposed.

† GÖSSMANN.—Liebig's 'Annalen,' c. p. 57.

small a scale to work out the true nature of the decomposition, decidedly indicate the entire absence of chinoline from the products of the reaction.

942. In separating aldehydes from complex mixtures, we must endeavour to obtain a compound with an alkaline bisulphite, and after pressing the latter between folds of bibulous paper until nothing more is extracted, or recrystallizing it from alcohol, distil with water, when the aldehyde will be obtained in a state that merely requires washing and drying previous to analysis.

943. The tendency of the aldehydes to acidify by contact of the air must not be lost sight of in determining their vapour density (§ 479).

944. *Hydrocarbons.*—The number of bodies known to chemists consisting solely of carbon and hydrogen is so great, that a volume would be required to give anything like a complete account of the processes and reactions employed in investigating their constitution.

The methods by which hydrocarbons are obtained are very numerous, but prominent among them stands destructive distillation. Out of the numerous families of them we shall select three, the properties of which are so varied, that a short description of their principal habitudes will illustrate, as fully as falls within the province of this work, the methods adopted for the examination of hydrocarbons; they are the benzole series, the radicals of the alcohols, and the homologues of olefiant gas. We shall also glance slightly at some of the derivatives of naphthaline.

945. *The benzole series.*—This very important group has been as thoroughly investigated as perhaps any other bodies known to chemists, but such is their tendency to form compounds, which in their turn are liable to numerous metamorphoses, that much yet remains to complete their history.

946. The most important member of them is of course the first term benzole, and as the other homologues yield almost exactly analogous derivatives, we shall confine ourselves to it in our formulæ, it being understood by the student that the same reactions in almost all cases apply to the other homologues.

2 A 2

It is to be observed that benzole is regarded with the other hydrocarbons as formed on the hydrogen type, being HH, in which one of the equivalents of H is replaced by phenyl; or, in other words, it is the hydruret of that radical.

947. The hydrocarbons of this class are obtainable in the largest quantity, and with the greatest ease and economy, from coal-naphtha, of which they form the chief bulk.   They are separated by fractional distillation (§ 353), the first member also being capable of further purification by crystallization (§ 419).   The volatility of benzole enables us to obtain it in a tolerably pure state (without the necessity for a great number of fractionations), by means of the double-headed stills represented in § 380.   After two distillations performed in that apparatus, the purification of the benzole may be completed by freezing and draining away the uncrystallizable hydrocarbons.   Although benzole and its homologues combine with sulphuric acid, they do so less readily than the $C^x H^x$ class which coexist with them in coal-naphtha; much advantage is therefore found by treating toluol and its less volatile congeners with sulphuric acid two or three times before proceeding to form new compounds.

948. It has been said that coal-naphtha is the most economical source of benzole; it can, however, be obtained in several ways, and it appears to be almost universally formed during the destructive distillation of highly complex organic matters.   Benzole is produced from benzoic acid by the removal of two, and from phthalic acid by the removal of four equivalents of carbonic acid.   To obtain it from these sources, the acid to be decomposed is mixed with an excess of lime or baryta and distilled.

949. The derivatives of benzole are highly interesting, but their history is as yet by no means complete.   Poured into excess of chlorine, a crystalline compound is obtained, in which six equivalents of the gas have combined with the hydrocarbon without removal of hydrogen.   This new substance, by treatment with alcoholic potash, loses three equivalents of hydrochloric acid with the production of trichlorobenzole.   The reaction may be expressed thus :—

$$C^{12} H^6 Cl^6 + 3KO = \left. \begin{matrix} C^{12} H^3 \\ Cl^3 \end{matrix} \right\} + 3KCl + 3HO.$$

950. The last product is in the form of an oil, and distils without alteration. It would be very interesting to treat it with sodium, with a view to the production of new hydrocarbons.

951. Benzole and its homologues combine directly with sulphuric acid when treated with the latter in a fuming state, forming well defined conjugate acids which yield crystalline salts with bases.

952. The derivatives of benzole with nitric acid are also most interesting. Treated with precaution with fuming nitric acid, it dissolves, and on pouring the solution into water an oil precipitates; this is nitrobenzole, or benzole in which an equivalent of hydrogen is replaced by hyponitric acid. By mixing the nitric with sulphuric acid previous to the addition of the benzole and employing heat, the reaction proceeds further, two equivalents of hydrogen being removed and replaced by hyponitric acid, in accordance with the annexed equations :—

$$\underbrace{C^{12} H^6}_{\text{Benzole.}} + NO^6H = \underbrace{\left. \begin{matrix} C^{12} H^5 \\ (NO^4) \end{matrix} \right\}}_{\text{Nitrobenzole.}} + 2HO,$$

and

$$\underbrace{C^{12} H^6}_{\text{Benzole.}} + 2NO^6H = \underbrace{\left. \begin{matrix} C^{12} H^4 \\ 2(NO^4) \end{matrix} \right\}}_{\text{Binitrobenzole.}} + 4HO.$$
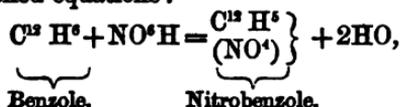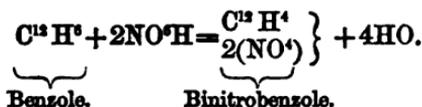
953. The two compounds last described yield new derivatives when treated with reducing agents. The equation expressing the conversion of nitrobenzole into the highly interesting alkaloid aniline, has been given in §§ 469, 906. Binitrobenzole in its turn yields nitraniline, when treated with reducing agents.

Nitrobenzole yields another interesting body, azobenzide ($C^{24} H^{10} N^2$), when distilled with alcoholic potash; azobenzide, by the action of reducing agents, gives the singular alkaloid benzidine ($C^{24} H^{12} N^2$).

954. We are unable to devote more space to the derivatives of benzole; it is true they can hardly be surpassed for interest, whether we regard their beauty or the peculiar reactions by which

they are formed; but we must proceed to the study of hydrocarbons belonging to a different series of organic groups.

955. *The alcohol radicals.*—This very important group has hitherto been obtained by three methods, namely,—

Decomposition of the hydriodic ethers by certain metals.

Electrolysis of the fatty acids.

Destructive distillation of certain kinds of bituminous coal.

956. They are all formed on the hydrogen type, and are regarded by most chemists as H H, in which both equivalents of hydrogen are replaced by alcoholic (electro-positive) radicals.

957. The radicals are all very light, mobile, highly refractive, fragrant hydrocarbons, acted on with some difficulty by acids.

958. To determine the nature of an organic radical, it is necessary to make a most accurate analysis of it, to determine its boiling-point, density in the states of liquid and vapour, and also to try the action of concentrated nitric and sulphuric acids on it.

959. It is more than probable that the organic radicals have, in addition to the marsh-gas series, numerous isomers; but in the present state of our knowledge, it would be difficult to prove by strictly chemical evidence, that a body possessing the same composition, boiling-point, density in the fluid and gaseous states, and acted on with difficulty by acids, was not a radical. We want a general method, like that used by chemists to determine the nature of organic bases, by which we can determine the true constitution of a hydrocarbon. It is certain that this is merely a question of time.

960. *Hydrocarbons homologous with olefiant gas.*—These bodies, of course formed on the hydrogen type (HH), are regarded as the hydrurets of the aldehyde radicals. They are pre-eminently distinguished by their tendency to combine with iodine, bromine, and chlorine. The iodine and bromine compounds of hydrocarbons of this class have become of considerable interest lately, in consequence of the highly important products which have been obtained from them.

961. When hydrocarbons of the formula $C^n H^n$ are treated with chlorine or bromine, it is usual for two equivalents of the latter

to unite to the former, propylene becoming therefore $C^6 H^6 Cl^2$. By treatment with alcoholic potash, HCl is removed, giving rise to the new derivative, $C^6 H^5 Cl$. To remove the last equivalent of the halogen, it is necessary to employ potassium or sodium. The formula represented above corresponds to 4 volumes of vapour; and if the chlorine be removed, we have the same phenomenon as with the hydriodic ethers, namely, the carbon and hydrogen becomes doubled for the same vapour-volume. For example, iodide of allyl, when treated with sodium, acts as represented in the annexed equation:—

$$2C^6 H^5 I + 2Na = C^{12} H^{10} + 2NaI.$$

Iodide of allyl. Allyl.
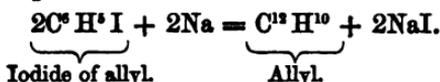
962. The boiling-point of derived hydrocarbons obtained by a reaction of this kind is always greatly above that of the original hydrocarbon from which the halogen compound was procured. Where, however, the number of equivalents of carbon is high, there is a tendency to split up into simpler combinations[*], and this tendency is the greater the higher the temperature at which

[*] As an illustration of this, I may mention that I have found when the naphtha from the Torbane-hill mineral, boiling between 180° and 190° F., is treated with bromine in presence of water, the latter is decolorized in the same manner as happens with turpentine (§ 486). If, to ensure a definite product, a slight excess of bromine be added, which excess is after-wards removed by agitation with mercury, a very dense colourless aromatic oil is obtained. This oil, on keeping for some time, separates into two layers. The upper layer is decomposed by alcoholic potash with great development of heat, bromide of potassium being deposited in large quantity. The whole, on being distilled to dryness, gave a distillate from which, on treatment with water, a heavy oil separated; which, when cohobated repeatedly over sodium, yielded a hydrocarbon, evidently a $C^x H^x$, for it contained,—

	Experiment.		Calcul., $C^x H^x$.
Carbon	85·4	85·7	85·7
Hydrogen	14·3	14·2	14·3
	99·7	99·9	100·0

Its vapour-density was 3·01, which points to the formula $C^{12} H^{12}$, requiring 2·91. The boiling-point was 165° F. During the cohobation the metal acquired a brilliant blue colour.

the sodium acts on the compound. As an illustration of this, let us see what happens when chloride of capryl is treated in the cold with sodium,—

$$2C^{16}H^{17}Cl + 2Na = C^{32}H^{34} + 2NaCl.$$

Chloride of capryl.   Capryl.
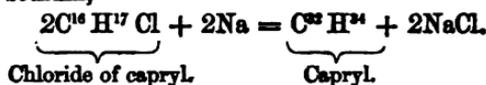
But if heat is employed, we have

$$2C^{16}H^{17}Cl + 2Na = 2NaCl + 2C^{16}H^{16} + 2H.$$

Chloride of capryl.   Caprylene.
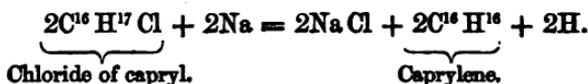
963. *Naphthaline.*—Few substances have been so much studied as this. Laurent, whose researches upon naphthaline alone fill a large volume, has discovered an immense number of bodies, chiefly derived from it, by substitution of chlorine, bromine, or hyponitric acid for hydrogen. By the action of chlorine, a number of most curious bodies are procured, several of which are susceptible of isomeric modifications.

964. The so-called bichloride of naphthaline, $C^{20}H^{16}Cl^4$, is a most beautiful substance; crystallized from benzole, it forms rhombs indistinguishable by the eye from Iceland spar. I find, moreover, that it distinctly possesses the property of double refraction (§ 419).

965. Naphthaline yields numerous acid and basic derivatives; the acids produced from naphthaline are especially interesting, from the fact that oxynaphthalic acid is, perhaps, identical with alizarine, one of the colouring matters of madder.

966. In spite of the immense mass of work which has been done on naphthaline, there are many interesting points in its history which remain to be examined; not the least of these is the as yet untouched field of the action of sodium upon its numerous solid and fluid chlorinated derivatives.

APPENDIX.

967. *Production of high temperatures.*—M. H. Sainte-Claire Deville[*] having been occupied for a considerable time with researches which involve the use of excessively high temperatures, has constructed two sets of apparatus for the purpose of enabling chemists to produce extreme heat with considerable economy of time and material. The first is a peculiar kind of lamp without a wick; the fuel is oil of turpentine; and, in order to effect complete combustion of the very large quantity of carbon contained in it, he sends a blast of air through the burner by means of bellows. The heat obtained is so intense, that a platinum wire of half a millimetre[†] in diameter may be fused in the flame. Felspar becomes perfectly fluid, and even the emerald shows signs of fusion when heated in a small platinum crucible. The engraving, fig. 389, represents the apparatus on a scale of one-fifth the real size.

Fig. 389.
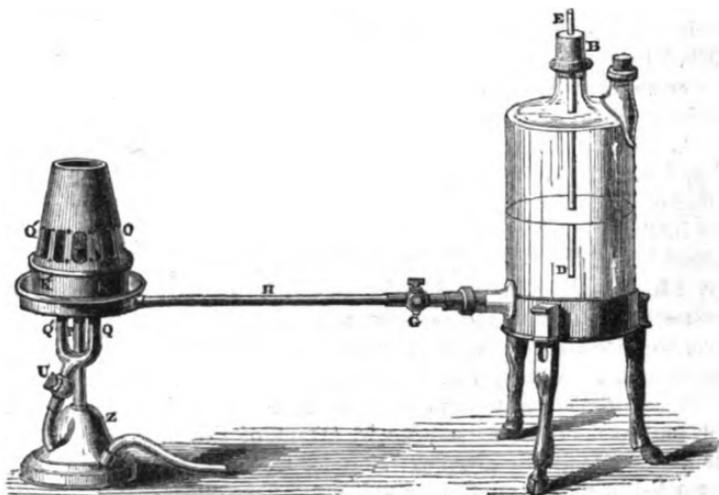
[*] Ann. de Chim. et de Phy . [3] xlvi. 182.
[†] A table for the conversion of millimetres into inches will be found at the end of the volume.

968. The flask, D, is so arranged that by the aid of the tube, E D, the turpentine is retained at a constant level. The section, fig. 390,

represents the burner and the contrivance by which the air is shut in; it consists of a reservoir, K K, of stout copper, which communicates with the turpentine bottle, D, by means of the tube, H. The annular space, K K, is closed at the bottom by a circular copper tray, I I, which is intended to hold water for the purpose to be described presently. The burner, K K, has on the side next the air-tube, P, a row of holes, eight in number, at S S; they may be from 3 to 4 millimetres in diameter. The lamp is surmounted by a loose copper dome, R, which is supported by a depression or groove on the top of the burner. At its upper part it is pierced with an aperture to allow of the egress of the flame. A chimney, 75 millimetres high, and somewhat conical, is cut away at its lower part, so as to form the large apertures

Fig. 390.

seen at O O. These apertures permit a large quantity of air to pass. On the top of the chimney is to be placed the triangle of platinum, which supports the crucible to be heated.
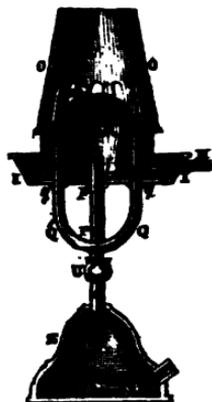
969. The upper extremity of the pipe, P p, has a jet attached, pierced with an aperture two and a quarter millimetres in diameter. This jet may be replaced by others, according to the size of the crucible to be heated. The aperture of the jet is placed 5 millimetres below the holes, S S. The tubes, Q q and Q′ q (which carry the air over the surface of the turpentine in the lamp), are united at their lower extremity into one tube, which is attached to the stopcock, U. The upper extremities of the tubes, Q q and Q′ q, are seen to pass through the tray, I I, ascending in the interior of the burner nearly to the top. The reservoir, Z, communicates with a pair of bellows of sufficient power to force air into the lamp with a pressure equal to that exerted by a column of mercury 7 or 8 centimetres in height.

970. The first operation, preparatory to using the lamp, is to establish the level of the turpentine by means of the tube, D, fig. 389. It is necessary that the lower extremity of D should be exactly 5 millimetres below the level of the apertures, S S, in order to prevent the turpentine in the burner from overflowing and becoming inflamed, which, although not presenting any danger, would cause some trouble.

To set the apparatus at work, water is to be poured into the tray or

cup, I I, which latter is to heated with a lamp until it has boiled for some time, so as to heat the turpentine; the stopcock, U, may then be partly opened and air sent in; at the same time a lamp-flame is brought near the holes, O O, to ignite the inflammable vapour.   When the lighted vapour burns steadily, the stopcock, U, may be further opened, and the bellows are to be worked to their full power.   In a few moments after the ignition of the vapour the stopcock, G, fig. 389. is to be opened.   A few trials must be made to ascertain the conditions necessary for obtaining the maximum temperature.   It is unnecessary to apply a lamp-flame to the water in the tray, I I, during the whole of the operation, as the heat of the combustion is more than sufficient for the purpose.

To extinguish the lamp, it is sufficient to close the stopcocks U and G [*].

971. *Forge for high temperatures.*—M. Deville has also described an apparatus by means of which he has obtained very remarkable results, owing not only to the excessively high temperatures reached, but perhaps still more to the power of resistance to heat possessed by his vessels.   The furnace described by him is, in principle, not very unlike that described by Faraday in his 'Chemical Manipulation.'   It is proper to mention that the last-named philosopher distinctly mentions that it was want of sufficiently refractory vessels that prevented the full powers of his furnace from being employed.   Pure platinum was melted many years ago by the blast-furnace belonging to the Royal Institution.   That used by M. Deville, however, not only melted but even volatilized platinum in such quantity that, according to him, it must have entered into ebullition.

The furnace consists of a baked clay cylinder, E E, fig. 391, 18 centimetres in diameter, placed upon an iron plate, F F, pierced with holes at O O O, fig. 392.   This plate rests upon a hemispherical cavity, B, which is placed in communication with the bellows by means of the tube seen in the engraving.   M. Deville uses small pieces of cinder, free from clinkers, as fuel.   To use the furnace, the crucible is placed on the centre of the iron plate, and is covered with ignited charcoal to the height of about 5 or 6 centimetres; the rest of the furnace is then filled up with pieces of coke or cinders of the size of nuts.   As the heat rises on working the bellows, the descent of the fuel is assisted by means of an iron rod, and more fuel is to be added to keep the furnace full.   During the whole time of the experiment the coals on the upper part of the furnace remain cold.   The highest tem-

* These lamps may be obtained of M. Wiesnegg of Paris, who has made several for the Normal School.

perature commences about 2 or 3 centimetres above the plate F, and
extends upwards about 7 or 8 centimetres. Above this zone of elevated

Fig. 391.
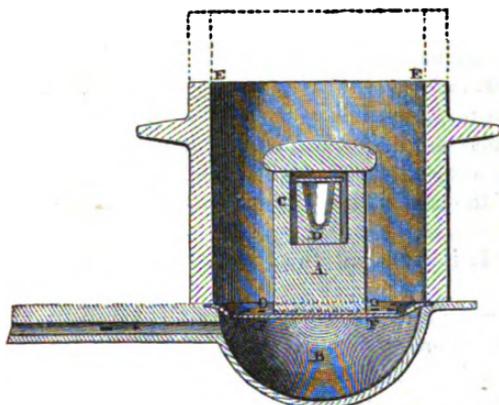
Fig. 392.
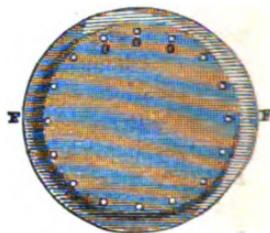
temperature the heat decreases with excessive rapidity, the cooling
being due to the transformation of carbonic acid into carbonic oxide,
which gas, in M. Deville's apparatus, burns with a flame 2 metres long.

972. *Crucibles for high temperatures.*—M. Deville uses three kinds
of crucibles for his blast-furnace, namely, lime, carbon, or alumina.
The lime-crucibles are simply pieces of well-burned slightly hydraulic
lime, A, fig. 391, shaped with a saw or knife into a prism 8 or 10
centimetres wide, and 12 or 15 centimetres high. If the utmost de-
gree of heat is not required, the crucible containing the assay may
be placed within another, D, fig. 391. Both the concentric crucibles
have covers also made of lime. The bottom of the inner crucible
should be 5 or 6 centimetres above that of the outer one. They are
placed at once on the plate of the furnace, without the intervention
of a piece of baked earth or tile as is usually recommended.

973. If the utmost degree of heat is required, only one crucible is to
be used, the aperture made in it not exceeding 2 or 3 centimetres in
diameter, and 5 or 6 deep.

974. In some experiments M. Deville uses crucibles made by means
of the lathe from the graphite of gas-retorts. They must not exceed
1 decimetre in height, because the zone of maximum temperature does
not reach above 8 centimetres.

When it becomes necessary to remove the sulphur, iron, silica, and
alumina from these crucibles, they are to be placed in one made of
clay, through the bottom of which a porcelain tube passes, and is well

luted with fire-clay softened with water and mixed with cow-hair. The crucible being heated to redness, a stream of chlorine is passed through to remove the impurities.

These carbon crucibles, B, fig. 393, are not heated directly, but are to be enclosed inside one of lime, A A, the space, C C, between the two being tightly packed with alumina which has previously been heated to whiteness. The lime crucible has a cover, D, fitted to it.

Fig. 393.

975. M. Deville also uses crucibles made of alumina. To make them, he takes some ammonia-alum, and, after exposing it to a temperature only just sufficient to expel the volatile matters, kneads the alumina so prepared with water and some alumina which has been heated to whiteness for a long time. The pasty mass is to be moulded into a shape, dried and burnt.

976. It is somewhat curious that platinum which has been melted by means of the furnace described, when hammered into foil does not effect the combination of hydrogen with oxygen.

If red oxide of manganese is mixed with charcoal from sugar, but in quantity insufficient for complete reduction, and the whole be heated in a lime-crucible, the metal is obtained in a single brittle button of a reddish colour like bismuth. The pulverulent metal, when heated a little above the ordinary atmospheric temperature, decomposed water, as has also been observed by M. Regnault. The button of metal was accompanied by crystals apparently of the formula $Mn^2 O^3$, CaO.

977. Oxide of chromium, heated with a quantity of carbon insufficient for complete reduction to a temperature sufficiently high to volatilize platinum, gave a melted mass, but not a button. The chromium thus prepared is so hard that it cut glass like a diamond, and if it were less brittle might be used for that purpose. Hydrochloric acid attacks chromium with facility, dilute sulphuric acid but slightly, and nitric acid, either strong or diluted, does not act upon it at all.

978. Nickel, when obtained in a pure button, was found to possess extraordinary ductility, and a tenacity greater than that of iron.

An iron and a nickel wire of the same diameter were tried with weights, and it was found that while 60 kilogrammes ruptured the first, it took 90 to break the second. See also § 780.

979. Cobalt prepared from the oxalate and well fused was examined as to its physical properties, and it was ascertained that a wire of the same diameter as the iron and nickel ones mentioned above, required
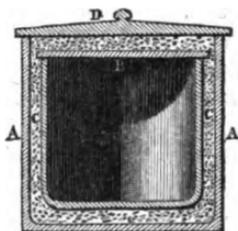
115 kilogrammes to break it, consequently it is nearly twice as tenacious as iron.

Silica was partially, but not perfectly, fused in the furnace.

Fig. 394.

980. *Determination of vapour-densities at varying pressures.*—In endeavouring to ascertain the constitution of certain hydrocarbons, I was led to determine the amount of influence exerted by pressure on the volumes of vapours. M. Regnault has occupied himself with the same subject, but the only notice I have seen of his experiments is in the extended memoir of M. Wurtz, "Sur les Ammoniaques composées." In that paper he gives tables of the vapour-densities of methylamine and ethylamine at varying temperatures and pressures. The experiments were made by M. Izarn, in Regnault's laboratory, with an apparatus not yet described, but made on the model of the eudiometer described at p. 325.

981. The instrument used by me is of the simplest character, and, when once constructed, is even easier to use than the ordinary apparatus of M. Gay-Lussac. A determination of a vapour-density at the pressure of the atmosphere can be made in half an hour, and at three pressures in one hour.

982. For this purpose the gas-jar, $a\,b$, fig. 394, is accurately graduated, and cemented at its lower extremity into a steel cap ending in a screw. The jar is only half the diameter at the lower end that it is at the upper; this is in order to make the effect of small pressures on the bulk of the gas more evident. The jar is to be filled with hot mercury, the air-bubbles removed with a wire, and then inverted in the mercurial trough. The small glass globule containing the fluid is then passed underneath the edge of the jar, and rises to the top of the mercury. The steel foot, $c\,d$, fig. 394, must now be held under the surface of the metal in the trough, while the lower end of the jar, $a\,b$, is screwed into its place. The pressure-tube, $e\,f$, is now inserted, and then the rod, $i\,k$, which is merely intended to enable the arrangement to be plunged into the water in the cylinder. A jet of steam from a small boiler is to be sent to the bottom of the water in the cylinder, until the desired temperature is attained. The exact degree can easily be maintained by more or less opening the tap of the steam-pipe. The

temperature is observed by two thermometers at g and l. As soon as the heat has risen a little, the bulb containing the fluid (the density of the vapour of which is to be determined) bursts, and the mercury slowly falls in $a\,b$, and of course rises in the pressure-tube, $e\,f$. By means of a rod carrying a deep notch at one end, the tap, h, is now to be opened, so as to allow the mercury to run out of the pressure-tube until it stands at or nearly the same level in both limbs. The difference of level is to be read off with a cathetometer. By a very simple calculation the vapour-density may now be found at, or very nearly, the atmospheric pressure. If it be desired to take the vapour-density at a pressure less than that of the atmosphere, it is merely necessary to use only sufficient substance to partly fill $a\,b$ with vapour.

983. If, on the other hand, it be desired to make the experiment at a pressure greater than that of the atmosphere, it suffices to pour mercury into $f\,e$ to the desired extent.

984. The steel foot into which the tubes, $a\,b$, $e\,f$, and the rod, $i\,k$, are inserted, is shown on a larger scale in fig. 395; the lettering is the same in both engravings.

985. The results of the experiments made with this instrument belong to my paper which is not yet published, but I may quote the following values obtained with a specimen of propyl extracted from the products of the destructive distillation of the Torbane-hill mineral.

Fig. 395.
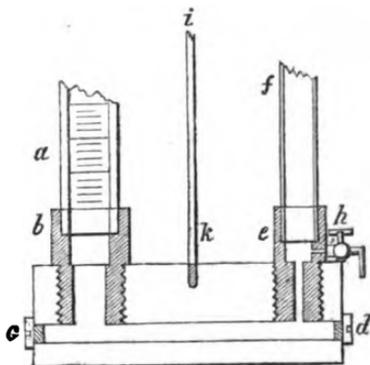
VAPOUR-DENSITY OF PROPYL AT VARYING PRESSURES.

Theory $2\cdot976 = 4$ volumes.

Temperature, Centigrade.	Pressure, millimetres.	Density.
100°	772·1	2·963
97°	870·6	3·005
97°	943·8	3·022
98°·7	1013·0	3·032

986. From the above Table, it is plain that the density augments with the pressure, although I am of opinion that the difference between the first two determinations is too great. It will be necessary to repeat the experiments several times before considering the amount of increase of density established; I merely therefore give the above as an illustration of the method of proceeding.

987. *Lines divided into equal parts.*—It constantly happens in laboratories where gas analyses are made, that it becomes necessary to accurately and rapidly divide a line into a given number of equal parts. Among the methods which may be adopted, there are two which more especially possess the requisites of simplicity and accuracy. The first is as follows :—From one end, A, of the given line, A B, draw the line A C, making any angle with A B. From the other end, B, draw the

Fig. 396.
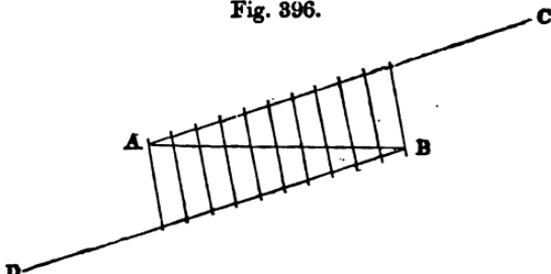
line B D, making A B D the same angle as A B C. The length to which the lines A C and B D are drawn is immaterial. Then point off on the line A C as many equal spaces (commencing from A) as the line A B is to be divided into. In the same manner point off an equal number of spaces on the line B D. Then draw parallel lines joining the spaces marked off, taking care to connect the last point on A C with the first point on B D. In this manner the line A B will be accurately divided into the desired number of equal parts.

988. Another method is that used by Bunsen. On a plate of glass is drawn with a writing-diamond a line A B divided into a greater number of equal parts than is likely to be required in practice. From the divisions on this line other lines are drawn, all converging to a point, as in fig. 397.

989. Then supposing it be required to divide an inch into 17 equal parts, find that portion of the system of lines where seventeen are required to make up an inch; in the case cited this will be at C D. In the same manner it is always possible to find some portion of the scale where the desired number of parts will be found to occupy the required space.

Fig. 397.
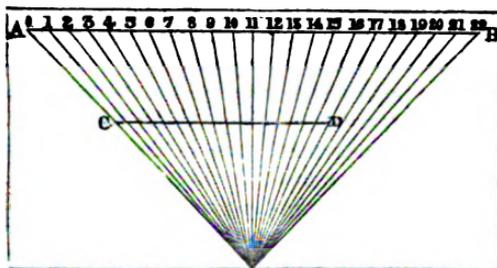
990. *Stills for destructive distillation and other purposes.*—One of the most convenient pieces of distillatory apparatus for operations requiring either high or low temperatures, may be made from a common glue-pot. The contrivance is, moreover, especially useful in distilling organic matters at high temperatures with caustic potash, as, for example, the preparation of aniline from indigo, chinoline and its associated bases from cinchonine, &c.

Fig. 398.

In fig. 398, *a* represents a copper head made to slip tightly into the aperture of the glue-pot, *b*. A small tubulature, *c*, permits the passage of a thermometer, or the addition of any substance during the progress of the distillation. The seams in the head are all brazed. The juncture of the head with the pot is luted with almond and linseed-meal.

991. If it be desired to distil with a glass tube to carry the products into the condenser, or, on the other hand, to cohobate in the manner shown in fig. 208, I have the copper cover, fig. 399, attached to the pot. It is to be luted in the same manner as the head, fig. 398.
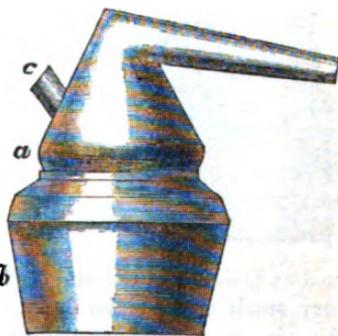
Fig. 399.
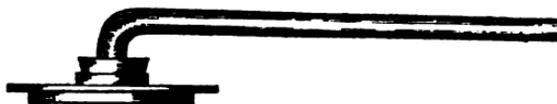
992. Supposing it be required to distil at a very gentle heat, such

as that of boiling water, I attach another head, somewhat smaller than that shown in fig. 398, to the water-bath of the glue-pot. The arrangement with this mode of distilling, is seen in section in fig. 400.

It is very desirable to observe the precautions mentioned in §§ 351, 378, regarding the proper angle of "dip" for the beak of the still.

993. *Supports for U-tubes.*—In supporting these useful pieces of apparatus I use the arrangement seen in fig. 401. A small wooden screw (made with the instrument described in § 689) presses against a piece of wood, *a*, which in its turn clamps the U-tube to the upright board, *b c*, which is mortised into a wooden foot, *c d*.

994. Dr. Anderson adopts a plan for supporting U-tubes, when required for lecture illustration, which has a very neat appearance; it is not, however, so well adapted for experiments of research as the last, owing to its being less steady. Two stout brass wires, *a b* and *c d*, fig. 402, are
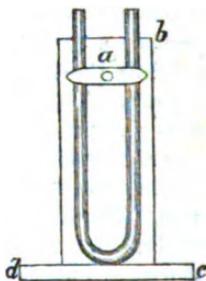
Fig. 400.	Fig. 401.	Fig. 402.
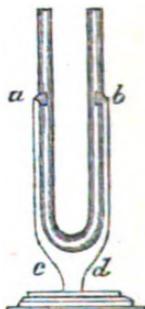
fixed at their lower extremities into a foot. On their upper ends they carry small semicircular brass pieces, *a b*, which hold the U-tube. The wires are somewhat nearer together than the width of the tube, so that a little force is required to insert it in its place, thus giving greater firmness to the apparatus.

995. *Compression pipettes.*—Some of my experiments rendering it frequently necessary to separate small quantities of hydrocarbons from fuming nitric acid, with which they had been treated, I found it very inconvenient to draw them off with a pipette in the usual manner, owing to the unpleasant effect of inhaling the fumes of the acid. I then adopted the plan, common in Continental laboratories, of using a pipette having a vulcanized india-rubber ball attached to its upper extremity. If the orifice of the pipette is sufficiently small, no diffi-

culty will be found in adjusting the smallest quantities with the greatest accuracy.

996. *Simple decanting apparatus.*—In making researches, it constantly happens that crops of crystals are obtained in the bottoms of beakers, and it is equally often required to drain the mother-liquid off without disturbing the deposit. The methods usually adopted in the laboratory to meet this end are most imperfect. It is a common proceeding to place the beaker (containing the crystals) in a sloping position on the top of another beaker; but it not unfrequently happens that a vibration of the table causes it to slip, and much delay and annoyance are thus caused. To avoid this, I made the little apparatus represented in figs. 403, 404, and 405. The beaker, *a*, fig. 403, is

Fig. 403.
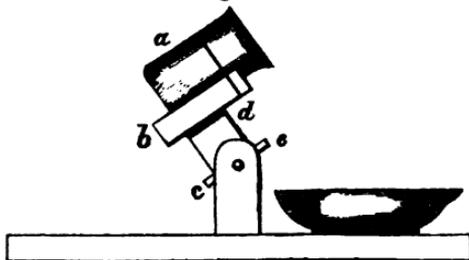
Fig. 404.
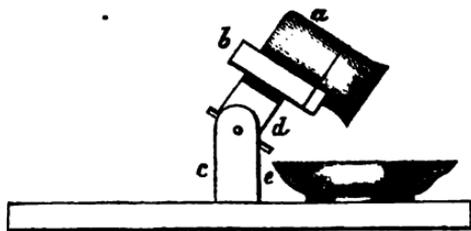
Fig. 405.
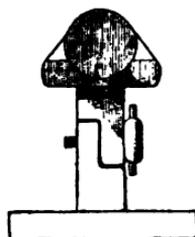
fastened by a strong vulcanized india-rubber ring to a deeply-grooved table, *b*. The circular groove in *b* is made of long radius, so as to hold steadily variously-sized beakers. The table is supported by a square rod, *d*, having its lower end jointed to another rod, *c*, in such a manner that it permits of a circular motion, which can be arrested in any position by the screw, *e*. This joint is precisely on the same principle as that in the arm of the support for vapour-densities shown in fig. 141, § 247. The figures 403 and 404 show the beaker in the

two principal positions, while fig. 405 gives a front view, illustrating the position of the two pieces of which the joint is composed. The screw is only cut on half the rod attached to the handle, e, the other part passing smoothly through one of the pieces of wood, like fig. 141, § 247. The entire apparatus can easily be made by any person with the tools described in §§ 688 and 689.

997. *Small press for squeezing fluids out of preparations.*—In organic chemistry, the substances produced during experiments are often contaminated with oily or other kinds of fluid impurities which are usually removed by pressure between folds of filtering-paper. A small screw press can easily be made, which, by permitting greater pressure to be applied than could be given by the hands, will greatly facilitate the purification of substances. It frequently happens, that a steady pressure for a long time is the best way of removing the impurities, as, if sufficient paper be used, it becomes gradually but perfectly absorbed; and by this mode of operating there is less danger of introducing organic matter from the paper than when repeated pressure with the fingers is employed, especially as in the latter mode of proceeding the papers require more frequent renewal.

998. *Cement for glass and metal for temperatures up to 212°.*—For cementing glass tubes, necks of balloons, &c. into metal mountings, where the apparatus is to be exposed to heat, a mixture of equal parts of red- and white-lead is preferable to white-lead alone. If the cemented pieces, after the junctures are made, be placed for a few days on the sand-bath, the mixture becomes extremely hard. If possible, the glass should be roughened, and a little tow wrapped round the part where it is to be applied.

999. *Apparatus for obtaining the electric spark in damp rooms.*—The precautions necessary for obtaining an electric spark of sufficient power to inflame gaseous mixtures, have been alluded to in §§ 551 and 555. The electrophorus, which possesses certain advantages over the electrical machine, has been described in § 657. If, however, the room in which the experiments are made is both cold and damp (and such rooms are best adapted for researches on gases), we must adopt a different method of obtaining the spark[*]. For this purpose, a large porcelain tube, 3 feet long and 1½ inch thick, is used as the substitute for an electrical machine. It is to be excited by rubbing with a piece of the best silk covered with amalgam. Only half of that portion of the silk in contact with the tube has amalgam on it.

1000. The Leyden jar is made from a small cylinder about 3 inches high and 1 inch in diameter; the inside is covered with tinfoil in the

[*] BUNSEN.—Gasometry, p. 46.

usual manner, but the outer coating is made of platinum-foil to prevent amalgamation. To charge the jar, it is merely necessary to hold the porcelain tube in front of the iron wire with which it is mounted, and employ brisk friction with the silk and amalgam. Only a few seconds are required to obtain a sufficient charge. The amalgam is made by heating two parts of mercury with one part of thin zinc-foil, to which one part of zinc is added while stirring. It is to be melted, and stirred several times before being applied to the silk.

1001. *Explanation of figs.* 406 *and* 407.—Fig. 406 represents a plan

Fig. 406.
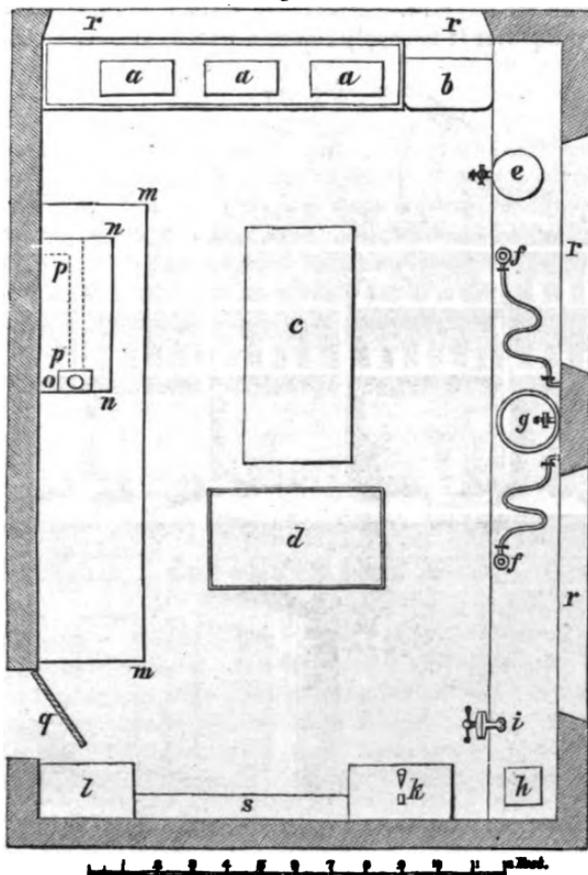
of a small laboratory, where only one room is available. It corresponds

in most points with the description given in § 1. One or two differences will be found, but these arise from the fact of the arrangement in the plan having been found more practically convenient. The three balances, *a a a*, are protected in the manner described in § 6. The desk, *b*, is placed close beside them, as that has been ascertained to be a more advantageous position than that alluded to in § 7. A large and heavy table, *c*, occupies a central position, while another, *d*, has a beading round it, to adapt it for experiments with the mercurial trough. The stoneware barrel, *e*, serves to hold distilled water (§ 8). Two gas-lights, *f f*, are attached by means of vulcanized india-rubber tubing with the gas-pipe. A porcelain basin, *g*, is sunk in the bench, and has a tap over it to supply common water. The basin has a plug

Fig. 407.
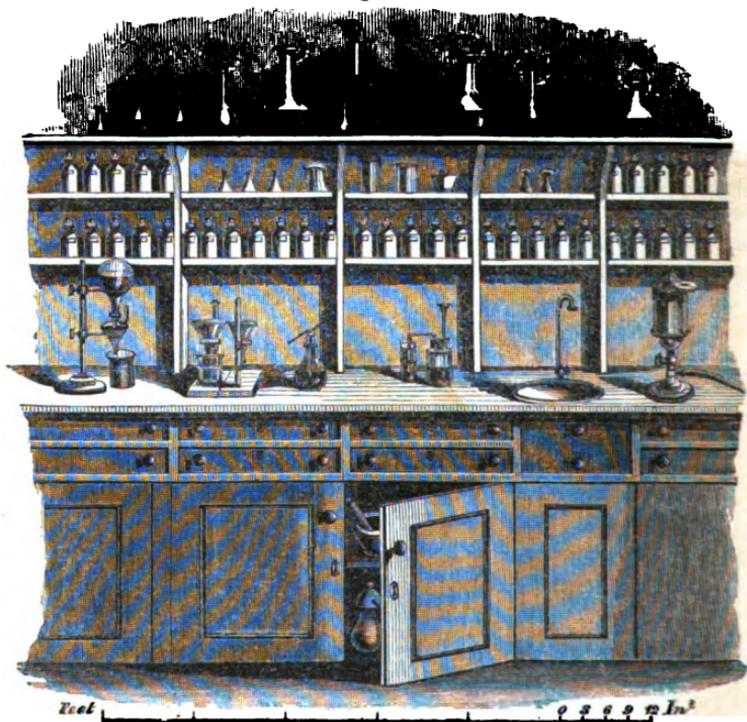
at the bottom, to enable the water to run away. The position of the water-bath (§ 12) is seen at *h*. A strong vice, *i*, is screwed to the

bench close to the blowpipe-table, *k.* A vapour or sulphuretted hydrogen closet is placed at *l.*

1002. A large hood, *m m,* covers a slightly raised brick flooring (§ 11), on which is placed a table-furnace *n n* ; *p p* shows the direction of the flue beneath the sand-bath. .The fireplace, and its rings (§ 29), are seen at *o.* The arrangement of the table-furnace is somewhat different from that seen in fig. 1, because the latter is intended to be adapted to a common fireplace. The entrance is seen at *q.* The windows are represented at *r r r r.*

Where the laboratory is attached to a University School of Medicine, or other place where the science is taught, a very different arrangement must be adopted. The room must be much larger; there must be a special chamber appropriated to the balances, and the working-benches should be fitted up in an entirely different manner. It will be proper to have the working places for the students at right angles to the windows, instead of parallel to them: each place should have a gas-light and a basin, with its tap for supplying water. It is convenient to have the tap rise a distance of about a foot from the table, and then bend down again in the manner seen in fig. 407, such an arrangement affording great facility for the filling of beakers, tall cylinders, &c. with water. The disposition of shelves, &c. in a student's working-bench, may be gathered from an inspection of fig. 407.

TABLE L—For the Conversion of Degrees on the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
− 50	−58·0	− 6	21·2	38	100·4	82	179·6
− 49	−56·2	− 5	23·0	39	102·2	83	181·4
− 48	−54·4	− 4	24·8	40	104·0	84	183·2
− 47	−52·6	− 3	26·6	41	105·8	85	185·0
− 46	−50·8	− 2	28·4	42	107·6	86	186·8
− 45	−49·0	− 1	30·2	43	109·4	87	188·6
− 44	−47·2	0	32·0	44	111·2	88	190·4
− 43	−45·4	+1	33·8	45	113·0	89	192·2
− 42	−43·6	2	35·6	46	114·8	90	194·0
− 41	−41·8	3	37·4	47	116·6	91	195·8
− 40	−40·0	4	39·2	48	118·4	92	197·6
− 39	−38·2	5	41·0	49	120·2	93	199·4
− 38	−36·4	6	42·8	50	122·0	94	201·2
− 37	−34·6	7	44·6	51	123·8	95	203·0
− 36	−32·8	8	46·4	52	125·6	96	204·8
− 35	−30·0	9	48·2	53	127·4	97	206·6
− 34	−29·2	10	50·0	54	129·2	98	208·4
− 33	−27·4	11	51·8	55	131·0	99	210·2
− 32	−25·6	12	53·6	56	132·8	100	212·0
− 31	−23·8	13	55·4	57	134·6	101	213·8
− 30	−22·0	14	57·2	58	136·4	102	215·6
− 29	−20·2	15	59·0	59	138·2	103	217·4
− 28	−18·4	16	60·8	60	140·0	104	219·2
− 27	−16·6	17	62·6	61	141·8	105	221·0
− 26	−14·8	18	64·4	62	143·6	106	222·8
− 25	−13·0	19	66·2	63	145·4	107	224·6
− 24	−11·2	20	68·0	64	147·2	108	226·4
− 23	− 9·4	21	69·8	65	149·0	109	228·2
− 22	− 7·6	22	71·6	66	150·8	110	230·0
− 21	− 5·8	23	73·4	67	152·6	111	231·8
− 20	− 4·0	24	75·2	68	154·4	112	233·6
− 19	− 2·2	25	77·0	69	156·2	113	235·4
− 18	− 0·4	26	78·8	70	158·0	114	237·2
− 17	+ 1·4	27	80·6	71	159·8	115	239·0
− 16	3·2	28	82·4	72	161·6	116	240·8
− 15	5·0	29	84·2	73	163·4	117	242·6
− 14	6·8	30	86·0	74	165·2	118	244·4
− 13	8·6	31	87·8	75	167·0	119	246·2
− 12	10·4	32	89·6	76	168·8	120	248·0
− 11	12·2	33	91·4	77	170·6	121	249·8
− 10	14·0	34	93·2	78	172·4	122	251·6
− 9	15·8	35	95·0	79	174·2	123	253·4
− 8	17·6	36	95·8	80	176·0	124	255·2
− 7	19·4	37	98·6	81	177·8	125	257·0

TABLE I. (continued.)

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
126	258·8	175	347·0	224	435·2	273	523·4
127	260·6	176	348·8	225	437·0	274	525·2
128	262·4	177	350·6	226	438·8	275	527·0
129	264·2	178	352·4	227	440·6	276	528·8
130	266·0	179	354·2	228	442·4	277	530·6
131	267·8	180	356·0	229	444·2	278	532·4
132	269·6	181	357·8	230	446·0	279	534·2
133	271·4	182	359·6	231	447·8	280	536·0
134	273·2	183	361·4	232	449·6	281	537·8
135	275·0	184	363·2	233	451·4	282	539·6
136	276·8	185	365·0	234	453·2	283	541·4
137	278·6	186	366·8	235	455·0	284	543·2
138	280·4	187	368·6	236	456·8	285	545·0
139	282·2	188	370·4	237	458·6	286	546·8
140	284·0	189	372·2	238	460·4	287	548·6
141	285·8	190	374·0	239	462·2	288	550·4
142	287·6	191	375·8	240	464·0	289	552·2
143	289·4	192	377·6	241	465·8	290	554·0
144	291·2	193	379·4	242	467·6	291	555·8
145	293·0	194	381·2	243	469·4	292	557·6
146	294·8	195	383·0	244	471·2	293	559·4
147	296·6	196	384·8	245	473·0	294	561·2
148	298·4	197	386·6	246	474·8	295	563·0
149	300·2	198	388·4	247	476·6	296	564·8
150	302·0	199	390·2	248	478·4	297	566·6
151	303·8	200	392·0	249	480·2	298	568·4
152	305·6	201	393·8	250	482·0	299	570·2
153	307·4	202	395·6	251	483·8	300	572·0
154	309·2	203	397·4	252	485·6	301	573·8
155	311·0	204	399·2	253	487·4	302	575·6
156	312·8	205	401·0	254	489·2	303	577·4
157	314·6	206	402·8	255	491·0	304	579·2
158	316·4	207	404·6	256	492·8	305	581·0
159	318·2	208	406·4	257	494·6	306	582·8
160	320·0	209	408·2	258	496·4	307	584·6
161	321·8	210	410·0	259	498·2	308	586·4
162	323·6	211	411·8	260	500·0	309	588·2
163	325·4	212	413·6	261	501·8	310	590·0
164	327·2	213	415·4	262	503·6	311	591·8
165	329·0	214	417·2	263	505·4	312	593·6
166	330·8	215	419·0	264	507·2	313	595·4
167	332·6	216	420·8	265	509·0	314	597·2
168	334·4	217	422·6	266	510·8	315	599·0
169	336·2	218	424·4	267	512·6	316	600·8
170	338·0	219	426·2	268	514·4	317	602·6
171	339·8	220	428·0	269	516·2	318	604·4
172	341·6	221	429·8	270	518·0	319	606·2
173	343·4	222	431·6	271	519·8	320	608·0
174	345·2	223	433·4	272	521·6		

2 B

TABLE II.—Elastic Force of Aqueous Vapour in inches of Mercury for Fahrenheit's Thermometer.

Temp. Fahr.	Force. Inches of Mercury.	Temp. Fahr.	Force. Inches of Mercury.	Temp. Fahr.	Force. Inches of Mercury.	Temp. Fahr.	Force. Inches of Mercury.
0	0·051	32	0·186	63	0·570	94	1·562
1	0·053	33	0·193	64	0·590	95	1·610
2	0·056	34	0·200	65	0·611	96	1·660
3	0·058	35	0·208	66	0·632	97	1·712
4	0·060	36	0·216	67	0·654	98	1·764
5	0·063	37	0·224	68	0·676	99	1·819
6	0·066	38	0·233	69	0·699	100	1·874
7	0·069	39	0·242	70	0·723	101	1·931
8	0·071	40	0·251	71	0·748	102	1·990
9	0·074	41	0·260	72	0·773	103	2·050
10	0·078	42	0·270	73	0·799	104	2·112
11	0·081	43	0·280	74	0·826	105	2·176
12	0·084	44	0·291	75	0·854	106	2·241
13	0·088	45	0·302	76	0·882	107	2·307
14	0·092	46	0·313	77	0·911	108	2·376
15	0·095	47	0·324	78	0·942	109	2·447
16	0·099	48	0·336	79	0·973	110	2·519
17	0·103	49	0·349	80	1·005	111	2·593
18	0·107	50	0·361	81	1·036	112	2·669
19	0·112	51	0·375	82	1·072	113	2·747
20	0·116	52	0·389	83	1·106	114	2·826
21	0·121	53	0·402	84	1·142	115	2·908
22	0·126	54	0·417	85	1·179	116	2·992
23	0·131	55	0·432	86	1·217	117	3·078
24	0·136	56	0·447	87	1·256	118	3·166
25	0·142	57	0·463	88	1·296	119	3·257
26	0·147	58	0·480	89	1·337	120	3·349
27	0·153	59	0·497	90	1·380	121	3·444
28	0·159	60	0·514	91	1·423	122	3·542
29	0·165	61	0·532	92	1·468	123	3·641
30	0·172	62	0·551	93	1·514	124	3·743
31	0·179						

TABLE V.—According to Magnus.

Degrees of the Mercurial Thermometer.	Degrees of the Air-thermometer.	Degrees of the Mercurial Thermometer.	Degrees of the Air-thermometer.
100	100·00	250	245·39
150	148·74	300	294·51
200	196·49	330	320·92

TABLE III.—Elastic Force of Aqueous Vapour in Millimetres of Mercury for Centigrade Thermometer.

Tempe-rature. Cent.	Force of the Aqueous Vapour in Milli-metres.	Tempe-rature. Cent.	Force of the Aqueous Vapour in Milli-metres.	Tempe-rature. Cent.	Force of the Aqueous Vapour in Milli-metres.	Tempe-rature. Cent.	Force of the Aqueous Vapour in Milli-metres.
0	4·525	11	9·751	22	19·675	33	37·473
1	4·867	12	10·421	23	20·909	34	39·630
2	5·231	13	11·130	24	22·211	35	41·893
3	5·619	14	11·882	25	23·582	36	44·268
4	6·032	15	12·677	26	25·026	37	46·758
5	6·471	16	13·519	27	26·547	38	49·368
6	6·939	17	14·409	28	28·148	39	52·103
7	7·436	18	15·351	29	29·832	40	54·969
8	7·964	19	16·345	30	31·602		
9	8·525	20	17·396	31	33·464		
10	9·126	21	18·505	32	35·419		

TABLE IV.—Comparison of the Degrees of the Mercurial with those of the Air-thermometer.—According to Regnault.

Air-thermo-meter.	Mercurial Thermometer.	Air-thermo-meter.	Mercurial Thermometer.
0	0	250	250·0
50	50·2	300	301·2
100	100·0	325	326·9
150	150·0	350	353·3
200	200·0		

[TABLE V.—*See* opposite page.]

TABLE VI.—According to Dulong and Petit.

Degrees of the Mer-curial Thermometer.	Degrees of the Air-thermometer.	Degrees of the Mer-curial Thermometer.	Degrees of the Air-thermometer.
105	104·8	220	216·2
110	109·6	230	225·9
120	119·5	240	235·4
130	129·2	250	245·0
140	139·0	260	254·6
150	148·7	270	264·0
160	158·4	280	273·5
170	168·0	290	283·2
180	177·7	300	292·7
190	187·4	320	311·6
200	197·0	340	330·5
210	206·7	350	340·0

TABLE VII.—Correction to be applied to Barometers with *brass scales*, extending from the cistern to the top of the mercurial column, to reduce the observation to 32° Fahrenheit.

Inches.

Temp.	20	20·5	21	21·5	22	22·5	23	23·5	24	24·5	25	25·5	26	26·5	27	27·5	Temp.
0	+·051	+·053	+·054	+·055	+·056	+·058	+·059	+·060	+·061	+·063	+·064	+·065	+·067	+·068	+·069	+·071	0
1	·049	·051	·052	·053	·054	·056	·057	·058	·059	·061	·062	·063	·064	·065	·067	·068	1
2	·048	·049	·050	·051	·052	·054	·055	·056	·057	·058	·060	·061	·062	·063	·064	·066	2
3	·046	·047	·048	·049	·050	·052	·053	·054	·055	·056	·057	·059	·060	·061	·062	·063	3
4	·044	·045	·046	·047	·048	·050	·051	·052	·053	·054	·055	·056	·057	·058	·059	·061	4
5	·042	·043	·044	·045	·046	·048	·049	·050	·051	·052	·053	·054	·055	·056	·057	·058	5
6	·040	·042	·042	·044	·044	·046	·047	·048	·049	·050	·051	·052	·053	·054	·055	·056	6
7	·039	·040	·041	·042	·042	·044	·044	·046	·046	·047	·048	·049	·050	·051	·052	·053	7
8	·037	·038	·039	·040	·041	·041	·042	·043	·044	·045	·046	·047	·048	·049	·050	·051	8
9	·035	·036	·037	·038	·039	·039	·040	·041	·042	·043	·044	·045	·046	·046	·047	·048	9
10	·033	·034	·035	·036	·037	·037	·038	·039	·040	·041	·042	·042	·043	·044	·045	·046	10
11	·031	·032	·033	·034	·035	·035	·036	·037	·038	·039	·039	·040	·041	·042	·042	·043	11
12	·030	·030	·031	·032	·033	·033	·034	·035	·036	·036	·037	·038	·039	·039	·040	·041	12
13	·028	·029	·029	·030	·031	·031	·032	·033	·033	·034	·035	·036	·036	·037	·038	·038	13
14	·026	·027	·027	·028	·029	·029	·030	·031	·031	·032	·033	·033	·034	·035	·035	·036	14
15	·024	·025	·026	·026	·027	·027	·028	·029	·029	·030	·030	·031	·032	·032	·033	·033	15
16	·022	·023	·024	·024	·025	·025	·026	·026	·027	·028	·028	·029	·029	·030	·030	·031	16
17	·021	·021	·022	·022	·023	·023	·024	·024	·026	·025	·026	·026	·027	·027	·028	·028	17
18	·019	·019	·020	·020	·021	·021	·022	·022	·023	·023	·024	·024	·025	·025	·026	·026	18
19	·017	·018	·018	·018	·019	·019	·020	·020	·021	·021	·021	·022	·023	·023	·024	·024	19
20	·015	·016	·016	·016	·017	·017	·018	·018	·018	·019	·019	·020	·020	·020	·021	·021	20

	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
21	·016	·016	·016	·015	·015	·015	·014	·010	·010	·015	·015	·015	·015	·014	·014	·014													
22	·014	·013	·013	·013	·013	·013	·012	·014	·014	·013	·013	·013	·013	·012	·012	·012													
23	·011	·011	·011	·011	·010	·010	·010	·012	·012	·011	·011	·011	·011	·010	·010	·010													
24	·009	·009	·008	·008	·008	·008	·008	·010	·010	·009	·009	·009	·009	·009	·008	·008													
25	·006	·006	·006	·006	·006	·006	·006	·008	·007	·007	·007	·007	·007	·007	·007	·006													
26	·004	·004	·004	·004	·003	·003	·003	·005	·005	·005	·005	·005	·005	·005	·003	·003													
27	·001	·001	·001	·001	·001	·001	·001	·003	·003	·003	·003	·003	·003	·001	·001	·001													
28	—	—	—	—	—	—	—	·001	·001	·001	·001	·001	·001	·001	·001	—													
29	·001	·001	·001	·001	·001	·001	·001	—	—	·001	·001	·001	·001	·001	·001	·001													
30	·004	·004	·004	·004	·004	·003	·003	·001	·001	·003	·003	·003	·003	·003	·003	·003													
31	·006	·006	·006	·006	·006	·006	·006	·003	·003	·005	·005	·005	·005	·005	·006	·005													
32	·009	·008	·008	·008	·008	·008	·008	·005	·005	·007	·007	·007	·007	·008	·008	·008													
33	·011	·011	·011	·011	·010	·010	·010	·008	·007	·009	·009	·009	·009	·010	·010	·010													
34	·014	·013	·013	·013	·013	·012	·012	·010	·010	·011	·011	·011	·011	·012	·012	·012													
35	·016	·016	·015	·015	·015	·015	·014	·012	·012	·013	·013	·013	·013	·014	·014	·015													
36	·019	·018	·018	·017	·017	·017	·017	·016	·016	·015	·015	·015	·014	·014	·013	·013													
37	·021	·021	·020	·020	·019	·019	·019	·018	·018	·017	·017	·017	·016	·016	·015	·015													
38	·023	·023	·023	·022	·022	·021	·021	·020	·020	·019	·019	·019	·018	·018	·017	·017													
39	·026	·025	·025	·024	·024	·024	·023	·023	·022	·021	·021	·021	·020	·020	·019	·019													
40	·028	·028	·027	·027	·026	·026	·025	·025	·024	·023	·023	·023	·022	·021	·021	·021													
41	·031	·030	·030	·029	·029	·028	·028	·027	·026	·025	·025	·025	·024	·023	·023	·022													
42	·033	·033	·032	·031	·031	·030	·030	·029	·028	·027	·027	·027	·026	·025	·025	·024													
43	·036	·035	·034	·034	·033	·032	·032	·031	·031	·029	·029	·029	·028	·027	·027	·026													
44	·038	·037	·037	·036	·035	·035	·034	·033	·033	·031	·031	·031	·030	·029	·029	·028													
45	·041	·040	·039	·038	·038	·037	·036	·035	·035	·033	·033	·033	·032	·031	·030	·030													
46	·043	·042	·042	·041	·040	·039	·038	·038	·037	·035	·035	·035	·034	·033	·032	·031													
47	·046	·045	·044	·043	·042	·041	·040	·040	·039	·037	·036	·036	·036	·035	·034	·033													
48	·048	·047	·046	·045	·045	·044	·043	·042	·041	·039	·038	·038	·037	·037	·036	·035													
49	·050	·050	·049	·048	·047	·046	·045	·044	·043	·041	·040	·040	·039	·039	·038	·037													
50	·053	·052	·051	·050	·049	·048	·047	·046	·045	·043	·042	·041	·041	·040	·039	·038													

TABLE VII. (*continued.*)

Inches.

Temp.	27·5	27	26·5	26	25·5	25	24·5	24	23·5	23	22·5	22	21·5	21	20·5	20	Temp.
51	·055	·054	·053	·052	·051	·050	·049	·048	·047	·046	·045	·044	·043	·042	·041	·040	51
52	·058	·057	·056	·055	·054	·053	·052	·050	·049	·048	·047	·046	·045	·044	·043	·042	52
53	·060	·059	·058	·057	·056	·055	·054	·053	·052	·050	·049	·048	·047	·046	·045	·044	53
54	·063	·062	·060	·059	·058	·057	·056	·055	·054	·052	·051	·050	·049	·048	·047	·046	54
55	·065	·064	·063	·062	·060	·059	·058	·057	·056	·055	·053	·052	·051	·050	·049	·047	55
56	·068	·066	·065	·064	·063	·061	·060	·059	·058	·057	·055	·054	·053	·052	·050	·049	56
57	·070	·069	·068	·066	·065	·064	·062	·061	·060	·059	·057	·056	·055	·054	·052	·051	57
58	·073	·071	·070	·069	·067	·066	·065	·063	·062	·061	·059	·058	·057	·055	·054	·053	58
59	·075	·074	·072	·071	·070	·068	·067	·065	·064	·063	·061	·060	·059	·057	·056	·055	59
60	·077	·076	·075	·073	·072	·070	·069	·068	·066	·065	·063	·062	·061	·059	·058	·056	60
61	·080	·078	·077	·075	·074	·073	·071	·070	·068	·067	·065	·064	·062	·061	·060	·058	61
62	·082	·081	·079	·078	·076	·075	·073	·072	·070	·069	·067	·066	·064	·063	·061	·060	62
63	·085	·083	·082	·080	·079	·077	·076	·074	·072	·071	·069	·068	·066	·065	·063	·062	63
64	·087	·086	·084	·082	·081	·079	·078	·076	·075	·073	·071	·070	·068	·067	·065	·063	64
65	·090	·088	·086	·085	·083	·082	·080	·078	·077	·075	·073	·072	·070	·068	·067	·065	65
66	·092	·090	·089	·087	·085	·084	·082	·080	·079	·077	·076	·074	·072	·070	·069	·067	66
67	·095	·093	·091	·089	·088	·086	·084	·083	·081	·079	·077	·076	·074	·072	·071	·069	67
68	·097	·095	·094	·092	·090	·088	·086	·085	·083	·081	·079	·078	·076	·074	·072	·071	68
69	·100	·098	·096	·094	·092	·090	·089	·087	·085	·083	·081	·080	·078	·076	·074	·072	69
70	·102	·100	·098	·096	·095	·093	·091	·090	·087	·086	·083	·082	·080	·078	·076	·074	70

71	·105	·103	·101	·099	·097	·095	·093	·091	·089	·087	·085	·083	·082	·080	·078	·076	71
72	·107	·105	·103	·101	·099	·097	·095	·093	·091	·089	·087	·085	·084	·082	·080	·078	72
73	·109	·107	·105	·103	·099	·099	·097	·095	·093	·091	·089	·087	·085	·084	·081	·079	73
74	·112	·110	·108	·106	·101	·101	·099	·097	·095	·093	·091	·089	·087	·085	·083	·081	74
75	·114	·112	·110	·108	·104	·104	·102	·100	·097	·095	·093	·091	·089	·087	·085	·083	75
76	·117	·114	·112	·110	·108	·106	·104	·102	·100	·097	·095	·093	·091	·089	·087	·085	76
77	·119	·117	·115	·112	·110	·108	·106	·104	·102	·100	·097	·095	·093	·091	·089	·087	77
78	·122	·119	·117	·115	·113	·110	·108	·106	·104	·102	·099	·097	·095	·093	·091	·088	78
79	·124	·122	·119	·117	·115	·113	·110	·108	·106	·104	·101	·099	·097	·095	·092	·090	79
80	·126	·124	·122	·119	·117	·115	·113	·111	·108	·106	·103	·101	·099	·096	·094	·092	80
81	·129	·126	·124	·122	·119	·117	·115	·112	·110	·108	·105	·103	·101	·098	·096	·094	81
82	·131	·129	·126	·124	·122	·119	·117	·114	·112	·110	·107	·105	·103	·100	·098	·095	82
83	·134	·131	·129	·126	·124	·121	·119	·117	·114	·112	·109	·107	·105	·102	·100	·097	83
84	·136	·134	·131	·129	·126	·124	·121	·119	·116	·114	·111	·109	·106	·104	·101	·099	84
85	·139	·136	·133	·131	·128	·126	·123	·121	·118	·116	·113	·111	·108	·106	·103	·101	85
86	·141	·138	·136	·133	·131	·128	·126	·123	·120	·118	·115	·113	·110	·108	·105	·103	86
87	·143	·141	·138	·136	·133	·130	·128	·125	·123	·120	·117	·115	·112	·109	·107	·104	87
88	·146	·143	·141	·138	·135	·133	·130	·127	·125	·122	·119	·117	·114	·111	·109	·106	88
89	·148	·146	·143	·140	·137	·135	·132	·129	·127	·124	·121	·119	·116	·113	·111	·108	89
90	·151	·148	·145	·142	·140	·137	·134	·131	·129	·126	·123	·121	·118	·115	·113	·110	90
91	·153	·150	·148	·145	·142	·139	·136	·134	·131	·128	·125	·123	·120	·117	·114	·111	91
92	·156	·153	·150	·147	·144	·141	·138	·136	·133	·130	·127	·125	·122	·119	·116	·113	92
93	·158	·155	·152	·149	·147	·144	·141	·138	·135	·132	·129	·127	·124	·121	·118	·115	93
94	·161	·157	·155	·152	·149	·146	·143	·140	·137	·134	·131	·129	·125	·122	·120	·117	94
95	·163	·160	·157	·154	·151	·148	·145	·142	·139	·136	·133	·130	·127	·124	·121	·118	95
96	·165	·162	·159	·156	·153	·150	·147	·144	·141	·138	·135	·132	·129	·126	·123	·120	96
97	·168	·165	·162	·159	·156	·152	·149	·146	·143	·140	·137	·134	·131	·128	·125	·122	97
98	·170	·167	·164	·161	·158	·155	·152	·148	·145	·142	·139	·136	·133	·130	·127	·124	98
99	·173	·169	·166	·163	·160	·157	·154	·151	·147	·144	·141	·138	·135	·132	·129	·125	99
100	·175	·172	·169	·165	·162	·159	·156	·153	·150	·146	·143	·140	·137	·134	·130	·127	100

TABLE VII. (*continued.*)

Temp.	Inches.						
	28	28·5	29	29·5	30	30·5	31
51	·056	·057	·058	·069	·060	·061	·062
52	·059	·060	·061	·062	·063	·064	·065
53	·061	·063	·064	·065	·065	·067	·068
54	·064	·065	·066	·067	·068	·070	·071
55	·066	·068	·069	·070	·071	·072	·073
56	·069	·070	·071	·073	·074	·075	·076
57	·071	·073	·074	·075	·076	·078	·079
58	·074	·075	·077	·078	·079	·081	·082
59	·076	·078	·079	·080	·082	·083	·085
60	·079	·080	·082	·083	·085	·086	·087
61	·081	·083	·084	·086	·087	·089	·090
62	·084	·085	·087	·088	·090	·091	·093
63	·086	·088	·090	·091	·093	·094	·096
64	·089	·090	·092	·094	·095	·097	·098
65	·091	·093	·095	·096	·098	·100	·101
66	·094	·096	·097	·099	·101	·102	·104
67	·096	·098	·100	·102	·103	·105	·107
68	·099	·101	·102	·104	·105	·108	·109
69	·101	·103	·105	·107	·109	·110	·112
70	·104	·106	·108	·109	·111	·113	·116

Temp.	Inches.						
	28	28·5	29	29·5	30	35·5	31
0	+·072	+·073	+·074	+·076	+·077	+·078	+·060
1	·069	·071	·072	·073	·074	·076	·077
2	·067	·068	·069	·070	·072	·073	·074
3	·064	·065	·067	·068	·069	·070	·071
4	·062	·063	·064	·065	·066	·067	·068
5	·059	·060	·061	·062	·063	·065	·066
6	·057	·058	·059	·060	·061	·062	·063
7	·054	·055	·056	·057	·058	·059	·060
8	·052	·053	·054	·054	·055	·056	·057
9	·049	·050	·051	·052	·053	·054	·054
10	·047	·047	·048	·049	·050	·051	·052
11	·044	·045	·046	·046	·047	·048	·049
12	·042	·042	·043	·044	·045	·045	·046
13	·039	·040	·040	·041	·042	·043	·043
14	·037	·037	·038	·038	·039	·040	·040
15	·034	·036	·035	·036	·036	·037	·038
16	·032	·032	·033	·033	·034	·034	·035
17	·029	·030	·030	·031	·031	·032	·032
18	·026	·027	·027	·028	·028	·029	·030
19	·024	·024	·025	·025	·026	·026	·027
20	·021	·022	·022	·023	·023	·023	·024

Upper table (argument $n = 72$–100; values to be read as decimals, e.g. ·120):

n							
72	·120	·119	·117	·115	·113	·111	·109
73	·123	·121	·119	·117	·115	·113	·111
74	·126	·124	·122	·120	·118	·116	·114
75	·129	·127	·125	·122	·120	·118	·116
76	·131	·129	·127	·125	·123	·121	·119
77	·134	·132	·130	·128	·126	·123	·121
78	·137	·135	·133	·130	·128	·126	·124
79	·140	·137	·135	·133	·131	·128	·126
80	·143	·140	·138	·136	·133	·131	·129
81	·145	·143	·141	·138	·136	·134	·131
82	·148	·146	·143	·141	·138	·136	·134
83	·151	·148	·146	·143	·141	·139	·136
84	·154	·151	·149	·146	·144	·141	·139
85	·156	·154	·151	·149	·146	·144	·141
86	·159	·156	·154	·151	·149	·146	·144
87	·162	·159	·157	·154	·151	·149	·146
88	·165	·162	·159	·157	·154	·151	·149
89	·167	·165	·162	·159	·156	·154	·151
90	·170	·167	·164	·162	·159	·156	·153
91	·173	·170	·167	·165	·162	·159	·156
92	·175	·172	·170	·167	·164	·161	·158
93	·178	·175	·172	·170	·167	·164	·161
94	·180	·177	·175	·172	·169	·166	·163
95	·183	·180	·178	·175	·172	·169	·166
96	·186	·183	·181	·178	·174	·171	·168
97	·189	·186	·183	·180	·177	·174	·171
98	·191	·188	·186	·183	·179	·176	·173
99	·194	·191	·188	·185	·182	·179	·176
100	·197	·194	·191	·188	·184	·181	·178

Lower table (argument $n = 21$–50; values to be read as decimals, e.g. ·018):

n							
21	·018	·018	·018	·017	·017	·017	·016
22	·015	·015	·015	·015	·014	·014	·014
23	·013	·012	·012	·012	·012	·012	·011
24	·010	·010	·009	·009	·009	·009	·009
25	·007	·007	·007	·007	·007	·006	·006
26	·004	·004	·004	·004	·004	·004	·004
27	·001	·001	·001	·001	·001	·001	·001
28	—	—	—	—	—	—	—
29	·001	·001	·001	·001	·001	·001	·001
30	·004	·004	·004	·004	·004	·004	·004
31	·007	·007	·007	·007	·007	·008	·008
32	·010	·010	·009	·009	·009	·009	·009
33	·012	·012	·012	·012	·012	·012	·011
34	·015	·015	·015	·015	·014	·014	·014
35	·018	·018	·018	·017	·017	·017	·016
36	·021	·021	·020	·020	·020	·019	·019
37	·024	·023	·023	·022	·022	·022	·021
38	·026	·026	·026	·025	·025	·024	·024
39	·029	·029	·028	·028	·027	·027	·026
40	·032	·031	·031	·030	·030	·029	·029
41	·035	·034	·034	·033	·033	·032	·031
42	·037	·037	·036	·036	·035	·034	·034
43	·040	·040	·039	·038	·038	·037	·036
44	·043	·042	·042	·041	·040	·040	·039
45	·046	·045	·044	·044	·043	·042	·041
46	·049	·048	·047	·046	·045	·045	·044
47	·051	·051	·050	·049	·048	·047	·046
48	·054	·053	·052	·052	·051	·050	·049
49	·057	·056	·055	·054	·053	·052	·051
50	·060	·059	·058	·057	·056	·055	·054

TABLE VIII.—Correction to be applied to Barometers, the scales of which are engraved on *glass*, to reduce the observations to 32° Fahr.

Temp.	Inches. 28·0.	Inches. 28·5.	Inches. 29·0.	Inches. 29·5.	Inches. 30·0.	Inches. 30·5.	Inches. 31·0.	Inches. 31·5.
25	+·017	+·017	+·017	+·018	+·018	+·018	+·019	+·019
30	+·005	+·005	+·005	+·005	+·005	+·005	+·005	+·005
35	—·007	—·007	—·007	—·008	—·008	—·008	—·008	—·008
40	—·019	—·020	—·020	—·020	—·021	—·021	—·021	—·022
45	—·031	—·032	—·032	—·033	—·033	—·034	—·035	—·036
50	—·043	—·044	—·045	—·046	—·046	—·047	—·048	—·049
55	—·055	—·056	—·057	—·058	—·059	—·060	—·061	—·062
60	—·067	—·068	—·069	—·071	—·072	—·074	—·075	—·076
65	—·079	—·081	—·082	—·083	—·085	—·086	—·088	—·089
70	—·091	—·093	—·094	—·096	—·098	—·100	—·101	—·103
75	—·103	—·105	—·106	—·109	—·111	—·114	—·116	—·118

TABLE IX.—Correction to be added to Barometers for Capillary Action.

Diameter of Tube.	Correction for	
	Unboiled Tubes.	Boiled Tubes.
inch.	inch.	inch.
0·60	0·004	0·002
0·50	0·007	0·003
0·45	0·010	0·005
0·40	0·014	0·007
0·35	0·020	0·010
0·30	0·028	0·014
0·25	0·040	0·020
0·20	0·060	0·029
0·15	0·088	0·044
0·10	0·142	0·070

TABLE X.

Grms.	Grains.	Deci-grms.	Grains.
1	15·4346	1	1·5434
2	30·8692	2	3·0669
3	46·3038	3	4·6304
4	61·7384	4	6·1738
5	77·1730	5	7·7173
6	92·6076	6	9·2607
7	108·0422	7	10·8042
8	123·4768	8	12·3476
9	138·9114	9	13·8911

TABLE XI.

Centi-grammes.	Grains.	Milli-grammes.	Grains.
1	·1543	1	·0154
2	·3086	2	·0308
3	·4630	3	·0463
4	·6173	4	·0617
5	·7717	5	·0771
6	·9260	6	·0926
7	1·0804	7	·1080
8	1·2347	8	·1234
9	1·3891	9	·1389

TABLE XII.—For conversion of millimetres into inches, and inches into millimetres.

	1	2	3	4	5	6	7	8	9
Inches into millimetres.	25·39954	50·79908	76·19862	101·5982	126·9977	152·3972	177·7968	203·1963	228·5959
Millimetres into inches.	·03937079	·07874158	·11811237	·15748316	·19685395	·23622474	·27559553	·31496632	·35433711

TABLE XIII.

One kilogramme	15434	grains.
One cubic centimetre . . .	0·0610	cubic inch.
One litre	61·0271	cubic inches.
One pound avoirdupois . .	7000	grains.
One ounce avoirdupois . .	437·5	grains.
One pound troy	5760·0	grains.
One ounce troy	480·0	grains.

TABLE XIV.—Boiling-points of water at different pressures.

Boiling-point °Fahr.	Barometer. Inches.	Boiling-point °Fahr.	Barometer. Inches.	Boiling-point °Fahr.	Barometer. Inches.
184	16·676	195	21·124	206	26·529
185	17·047	196	21·576	207	27·068
186	17·421	197	22·030	208	27·614
187	17·803	198	22·498	209	28·183
188	18·196	199	22·965	210	28·744
189	18·593	200	23·454	211	29·331
190	18·992	201	23·937	212	29·922
191	19·407	202	24·441	213	30·516
192	19·822	203	25·014	214	31·120
193	20·254	204	25·468	215	31·730
194	20·687	205	25·992		

TABLE XV.—Expansion of gases by heat (Regnault). Between 0° and 212° F. 1000 parts become

Hydrogen	1366·13
Carbonic oxide . . .	1366·88
Atmospheric air . . .	1367·06
Nitrogen	1366·82
Hydrochloric acid . .	1368·12
Carbonic acid . . .	1370·99
Protoxide of nitrogen .	1371·95
Cyanogen	1387·67
Sulphurous acid . .	1390·28

XVI.

TABLES showing the Specific Gravity of Liquids at the temperature of 55° F., corresponding to the degrees of Beaumé's Hydrometer.

For Liquids lighter than water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
10 =	1·000	17 =	0·949	23 =	0·909	29 =	0·874	35 =	0·842
11	0·990	18	0·942	24	0·903	30	0·867	36	0·837
12	0·985	19	0·935	25	0·897	31	0·861	37	0·832
13	0·977	20	0·923	26	0·892	32	0·856	38	0·827
14	0·970	21	0·922	27	0·886	33	0·852	39	0·822
15	0·963	22	0·915	28	0·880	34	0·847	40	0·817
16	0·955								

For Liquids heavier than water.

Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.	Deg.	Sp. Gr.
0 =	1·000	15 =	1·114	30 =	1·261	45 =	1·455	60 =	1·717
3	1·020	18	1·140	33	1·295	48	1·500	63	1·779
6	1·040	21	1·170	36	1·333	51	1·547	66	1·848
9	1·064	24	1·200	39	1·373	54	1·594	69	1·920
12	1·089	27	1·230	42	1·414	57	1·659	72	2·000

TABLE XVII.—Weight of one cubic centimetre of atmospheric air at different temperatures from 0° to 300° C. (grammes).

0°	0·001293						
1	0·001288	21°	0·001201	41°	0·001124	61°	0·001057
2	0·001284	22	0·001197	42	0·001121	62	0·001053
3	0·001279	23	0·001193	43	0·001118	63	0·001050
4	0·001275	24	0·001189	44	0·001114	64	0·001047
5	0·001270	25	0·001185	45	0·001111	65	0·001044
6	0·001266	26	0·001181	46	0·001108	66	0·001041
7	0·001261	27	0·001177	47	0·001105	67	0·001038
8	0·001257	28	0·001173	48	0·001102	68	0·001035
9	0·001252	29	0·001169	49	0·001098	69	0·001032
10	0·001248	30	0·001165	50	0·001095	70	0·001029
11	0·001243	31	0·001161	51	0·001091	71	0·001026
12	0·001239	32	0·001157	52	0·001088	72	0·001023
13	0·001234	33	0·001154	53	0·001084	73	0·001020
14	0·001230	34	0·001150	54	0·001081	74	0·001017
15	0·001225	35	0·001146	55	0·001077	75	0·001014
16	0·001221	36	0·001142	56	0·001074	76	0·001011
17	0·001217	37	0·001138	57	0·001070	77	0·001008
18	0·001213	38	0·001134	58	0·001067	78	0·001005
19	0·001209	39	0·001131	59	0·001063	79	0·001002
20	0·001205	40	0·001128	60	0·001060	80	0·001000

TABLE XVII. (*continued.*)

81	0·000997	126	0·000684	171	0·000794	216	0·000721
82	0·000994	127	0·000682	172	0·000793	217	0·000719
83	0·000992	128	0·000680	173	0·000791	218	0·000718
84	0·000989	129	0·000678	174	0·000789	219	0·000716
85	0·000986	130	0·000676	175	0·000788	220	0·000715
86	0·000983	131	0·000674	176	0·000786	221	0·000713
87	0·000980	132	0·000671	177	0·000784	222	0·000712
88	0·000977	133	0·000669	178	0·000782	223	0·000710
89	0·000974	134	0·000667	179	0·000781	224	0·000709
90	0·000972	135	0·000665	180	0·000779	225	0·000708
91	0·000969	136	0·000663	181	0·000777	226	0·000706
92	0·000967	137	0·000660	182	0·000776	227	0·000705
93	0·000964	138	0·000658	183	0·000774	228	0·000703
94	0·000962	139	0·000656	184	0·000772	229	0·000702
95	0·000959	140	0·000654	185	0·000770	230	0·000701
96	0·000956	141	0·000652	186	0·000769	231	0·000699
97	0·000953	142	0·000650	187	0·000767	232	0·000698
98	0·000951	143	0·000648	188	0·000765	233	0·000697
99	0·000948	144	0·000646	189	0·000763	234	0·000695
100	0·000946	145	0·000644	190	0·000762	235	0·000694
101	0·000943	146	0·000642	191	0·000760	236	0·000692
102	0·000941	147	0·000640	192	0·000758	237	0·000691
103	0·000938	148	0·000638	193	0·000757	238	0·000690
104	0·000936	149	0·000636	194	0·000755	239	0·000689
105	0·000933	150	0·000634	195	0·000754	240	0·000688
106	0·000931	151	0·000632	196	0·000752	241	0·000686
107	0·000928	152	0·000630	197	0·000751	242	0·000685
108	0·000926	153	0·000628	198	0·000749	243	0·000683
109	0·000923	154	0·000626	199	0·000748	244	0·000682
110	0·000921	155	0·000624	200	0·000746	245	0·000681
111	0·000919	156	0·000622	201	0·000744	246	0·000679
112	0·000916	157	0·000621	202	0·000743	247	0·000678
113	0·000914	158	0·000619	203	0·000740	248	0·000677
114	0·000911	159	0·000617	204	0·000739	249	0·000675
115	0·000909	160	0·000615	205	0·000737	250	0·000674
116	0·000907	161	0·000613	206	0·000736	251	0·000673
117	0·000905	162	0·000611	207	0·000734	252	0·000672
118	0·000903	163	0·000609	208	0·000733	253	0·000670
119	0·000900	164	0·000607	209	0·000731	254	0·000669
120	0·000898	165	0·000606	210	0·000730	255	0·000668
121	0·000896	166	0·000604	211	0·000728	256	0·000666
122	0·000894	167	0·000602	212	0·000727	257	0·000665
123	0·000891	168	0·000600	213	0·000725	258	0·000664
124	0·000889	169	0·000598	214	0·000724	259	0·000663
125	0·000887	170	0·000596	215	0·000722	260	0·000662

TABLE XVII. (*continued.*)

261	0·000660	271	0·000648	281	0·000636	291	0·000625
262	0·000659	272	0·000647	282	0·000635	292	0·000624
263	0·000658	273	0·000646	283	0·000634	293	0·000623
264	0·000657	274	0·000645	284	0·000633	294	0·000622
265	0·000655	275	0·000643	285	0·000631	295	0·000621
266	0·000654	276	0·000642	286	0·000630	296	0·000620
267	0·000653	277	0·000641	287	0·000629	297	0·000619
268	0·000652	278	0·000640	288	0·000628	298	0·000618
269	0·000651	279	0·000639	289	0·000627	299	0·000617
270	0·000650	280	0·000638	290	0·000626	300	0·000616

TABLE XVIII.—Specific Gravity and Absolute Weight of several Gases.

	Specific gravity : atmospheric air =1·0000.	One litre (1000 cubic centimetres) of gas at 0° C. and 0·76 metre bar. pressure weight. Grammes.
Atmospheric air	1·0000	1·29363
Oxygen	1·10563	1·43028
Hydrogen	0·06910	0·08939
Water, vapour of	0·62192	0·80453
Carbon, vapour of	0·82922	1·07270
Carbonic acid	1·52024	1·96663
Carbonic oxide	0·96743	1·25150
Phosphorus, vapour of	4·33452	5·60727
Sulphur, vapour of	6·63378	8·58165
Hydrosulphuric acid	1·17475	1·51969
Iodine, vapour of	8·76760	11·34203
Bromine, vapour of	5·52605	7·14866
Chlorine	2·45052	3·17007
Nitrogen	0·96776	1·25192
Ammonia	0·58753	0·76005

TABLE XIX.—Showing the Quantity of Absolute Alcohol in Spirits of different Specific Gravities, according to Lowitz.

100 Parts.		Specific Gravity.		100 Parts.		Specific Gravity.	
Alcohol.	Water.	At 68°.	At 60°.	Alcohol.	Water.	At 68°.	At 60°.
100	0	0·791	0·796	95	5	0·805	0·809
99	1	0·794	0·798	94	6	0·808	0·812
98	2	0·797	0·801	93	7	0·811	0·815
97	3	0·800	0·804	92	8	0·813	0·817
96	4	0·803	0·807	91	9	0·816	0·820

TABLE XIX. (*continued.*)

100 Parts.		Specific Gravity.		100 Parts.		Specific Gravity.	
Alcohol.	Water.	At 68°.	At 60°.	Alcohol.	Water.	At 68°.	At 60°.
90	10	0·818	0·822	44	56	0·927	0·930
89	11	0·821	0·825	43	57	0·930	0·933
88	12	0·823	0·827	42	58	0·932	0·935
87	13	0·826	0·830	41	59	0·934	0·937
86	14	0·828	0·832	40	60	0·936	0·939
85	15	0·831	0·835	39	61	0·938	0·941
84	16	0·834	0·838	38	62	0·940	0·943
83	17	0·836	0·840	37	63	0·942	0·945
82	18	0·839	0·843	36	64	0·944	0·947
81	19	0·842	0·846	35	65	0·946	0·949
80	20	0·844	0·848	34	66	0·948	0·951
79	21	0·847	0·851	33	67	0·950	0·953
78	22	0·849	0·853	32	68	0·952	0·955
77	23	0·851	0·855	31	69	0·954	0·957
76	24	0·853	0·857	30	70	0·956	0·958
75	25	0·856	0·860	29	71	0·957	0·960
74	26	0·859	0·863	28	72	0·959	0·962
73	27	0·861	0·865	27	73	0·961	0·963
72	28	0·863	0·867	26	74	0·963	0·965
71	29	0·866	0·870	25	75	0·965	0·967
70	30	0·868	0·872	24	76	0·966	0·968
69	31	0·870	0·874	23	77	0·968	0·970
68	32	0·872	0·875	22	78	0·970	0·972
67	33	0·875	0·879	21	79	0·971	0·973
66	34	0·877	0·881	20	80	0·973	0·974
65	35	0·880	0·883	19	81	0·974	0·975
64	36	0·882	0·886	18	82	0·976	0·977
63	37	0·885	0·889	17	83	0·977	0·978
62	38	0·887	0·891	16	84	0·978	0·979
61	39	0·889	0·893	15	85	0·980	0·981
60	40	0·892	0·896	14	86	0·981	0·982
59	41	0·894	0·898	13	87	0·983	0·984
58	42	0·896	0·900	12	88	0·985	0·986
57	43	0·899	0·902	11	89	0·986	0·987
56	44	0·901	0·904	10	90	0·987	0·988
55	45	0·903	0·906	9	91	0·988	0·989
54	46	0·905	0·908	8	92	0·989	0·990
53	47	0·907	0·910	7	93	0·991	0·991
52	48	0·909	0·912	6	94	0·992	0·992
51	49	0·912	0·915	5	95	0·994	
50	50	0·914	0·917	4	96	0·995	
49	51	0·917	0·920	3	97	0·997	
48	52	0·919	0·922	2	98	0·998	
47	53	0·921	0·924	1	99	0·999	
46	54	0·923	0·926	0	100	1·000	
45	55	0·925	0·928				

TABLE XX.—Showing the Quantity of Absolute Alcohol by Weight in Mixtures of Alcohol and Water of different Specific Gravities, according to Mr. Drinkwater.

Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.	Sp. Gr. at 60° Fahr.	Alcohol per cent. by weight.
1·0000	0·00	·9959	2·22	·9918	4·64	·9877	7·30
·9999	0·05	·9958	2·28	·9917	4·70	·9876	7·37
·9998	0·11	·9957	2·34	·9916	4·76	·9875	7·43
·9997	0·16	·9956	2·37	·9915	4·82	·9874	7·50
·9996	0·21	·9955	2·45	·9914	4·88	·9873	7·57
·9995	0·26	·9954	2·51	·9913	4·94	·9872	7·64
·9994	0·32	·9953	2·57	·9912	5·01	·9871	7·71
·9993	0·37	·9952	2·62	·9911	5·07	·9870	7·78
·9992	0·42	·9951	2·68	·9910	5·13	·9869	7·85
·9991	0·47	·9950	2·74	·9909	5·20	·9868	7·92
·9990	0·53	·9949	2·79	·9908	5·26	·9867	7·99
·9989	0·58	·9948	2·85	·9907	5·32	·9866	8·06
·9988	0·64	·9947	2·91	·9906	5·39	·9865	8·13
·9987	0·69	·9946	2·97	·9905	5·45	·9864	8·20
·9986	0·74	·9945	3·02	·9904	5·51	·9863	8·27
·9985	0·80	·9944	3·08	·9903	5·58	·9862	8·34
·9984	0·85	·9943	3·14	·9902	5·64	·9861	8·41
·9983	0·91	·9942	3·20	·9901	5·70	·9860	8·48
·9982	0·96	·9941	3·26	·9900	5·77	·9859	8·55
·9981	1·02	·9940	3·32	·9899	5·83	·9858	8·62
·9980	1·07	·9939	3·37	·9898	5·89	·9857	8·70
·9979	1·12	·9938	3·43	·9897	5·96	·9856	8·77
·9978	1·18	·9937	3·49	·9896	6·02	·9855	8·84
·9977	1·23	·9936	3·55	·9895	6·09	·9854	8·91
·9976	1·29	·9935	3·61	·9894	6·15	·9853	8·98
·9975	1·34	·9934	3·67	·9893	6·22	·9852	9·05
·9974	1·40	·9933	3·73	·9892	6·29	·9851	9·12
·9973	1·45	·9932	3·78	·9891	6·35	·9850	9·20
·9972	1·51	·9931	3·84	·9890	6·42	·9849	9·27
·9971	1·56	·9930	3·90	·9889	6·49	·9848	9·34
·9970	1·61	·9929	3·96	·9888	6·55	·9847	9·41
·9969	1·67	·9928	4·02	·9887	6·62	·9846	9·49
·9968	1·73	·9927	4·08	·9886	6·69	·9845	9·56
·9967	1·78	·9926	4·14	·9885	6·75	·9844	9·63
·9966	1·83	·9925	4·20	·9884	6·82	·9843	9·70
·9965	1·89	·9924	4·27	·9883	6·89	·9842	9·78
·9964	1·94	·9923	4·33	·9882	6·95	·9841	9·85
·9963	1·99	·9922	4·39	·9881	7·02	·9840	9·92
·9962	2·05	·9921	4·45	·9880	7·09	·9839	9·99
·9961	2·11	·9920	4·51	·9879	7·16	·9838	10·07
·9960	2·17	·9919	4·57	·9878	7·23		

INDEX.

2 c

CATALOGUE OF BOOKS

PUBLISHED BY MR. VAN VOORST.

ZOOLOGY.

MAMMALIA.

History of British Quadrupeds, including the Cetacea.
By THOMAS BELL, F.R.S., P.L.S., Professor of Zoology in
King's College, London. Illustrated by nearly 200 Engravings,
comprising portraits of the animals, and vignette tail-pieces.
8vo. New Edition in preparation.

Natural History of the Sperm Whale, and a Sketch of a
South Sea Whaling Voyage. By THOMAS BEALE. Post 8vo,
12s. cloth.

BIRDS.

History of British Birds. By WILLIAM YARRELL, V.P.L.S.,
F.Z.S., &c. This work contains a history and a picture por-
trait, engraved expressly for the work, of each species of the Birds
found in Britain. Three volumes, containing 550 Illustrations.
Third Edition, demy 8vo, £4 14s. 6d.

Coloured Illustrations of the Eggs of British Birds, with
Descriptions of their Nests and Nidification. By WILLIAM C.
HEWITSON. Third Edition, 2 vols. 8vo, £4 14s. 6d. The
figures and descriptions of the Eggs in this edition are from dif-
ferent specimens to those figured in the previous editions.

Systematic Catalogue of the Eggs of British Birds,
arranged with a View to supersede the use of Labels for Eggs.
By the Rev. S. C. MALAN, M.A., M.A.S. On writing-paper.
8vo, 8s. 6d.

Ornithological Rambles in Sussex. By A. E. KNOX, M.A.,
F.L.S. Third Edition. Post 8vo, with Four Illustrations by
Wolf, 7s. 6d.

Falconry in the Valley of the Indus. By R. F. BURTON,
Author of 'Goa and the Blue Mountains,' &c. Post 8vo, with
Four Illustrations, 6s.

**Monograph of the Birds forming the Tanagrine Genus
CALLISTE;** illustrated by Coloured Plates of all the known
species. By P. L. SCLATER, M.A., Fellow of Corpus Christi
College, Oxford, F.Z.S., &c. 8vo, £2 2s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Birds of Jamaica. By P. H. GOSSE, F.R.S., Author of the 'Canadian Naturalist,' &c.   Post 8vo, 10s.

The Dodo and its Kindred; or the History, Affinities and Osteology of the Dodo, Solitaire, and other Extinct Birds of the Islands Mauritius, Rodrigues, and Bourbon. By H. E. STRICKLAND, M.A., F.G.S., F.R.G.S., and R. G. MELVILLE, M.D. Edin., M.R.C.S.   Royal 4to, with 18 Plates and other Illustrations, £1 1s.

Geographical and Comparative List of the Birds of Europe and North America. By CHARLES LUCIEN BONAPARTE, Prince of Musignano.   8vo, 5s.

Ornithological Synonyms. By the late HUGH EDWIN STRICKLAND, M.A., F.R.S., &c.   Edited by Mrs. HUGH EDWIN STRICKLAND and SIR WILLIAM JARDINE, Bart., F.R.S.E., &c. 8vo, Vol. I. containing the Order Accipitres, 12s. 6d.

REPTILES.

History of British Reptiles. By THOMAS BELL, F.R.S., President of the Linnean Society, V.P.Z.S., &c., Professor of Zoology in King's College, London. Second Edition, with 50 Illustrations, 12s.

FISHES.

Production and Management of Fish in Fresh Waters, by Artificial Spawning, Breeding, and Rearing. By GOTTLIEB BOCCIUS. 8vo, 5s.

History of British Fishes. By WILLIAM YARRELL, V.P.L.S., F.Z.S., &c.   Third Edition.   Edited by SIR JOHN RICHARDSON, M.D. Two vols. demy 8vo, illustrated by more than 500 Engravings.   Nearly ready.

Yarrell.—Growth of the Salmon in Fresh Water. With Six Coloured Illustrations of the Fish of the natural size, exhibiting its structure and exact appearance at various stages during the first two years.   12s. sewed.

Heraldry of Fish. By THOMAS MOULE.   Nearly six hundred families are noticed in this work, and besides the several descriptions of fish, fishing-nets, and boats, are included also mermaids, tritons, and shell-fish.   Nearly seventy ancient seals are described, and upwards of twenty subjects in stained glass.   The engravings, two hundred and five in number, are from stained glass, tombs, sculpture and carving, medals and coins, rolls of arms, and pedigrees.   8vo, 21s.; a few on large paper (royal 8vo) for colouring, £2 2s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Fly-Fishing in Salt and Fresh Water. With Six Coloured
Plates, representing Artificial Flies, &c. 8vo, 7s. 6d.

An Angler's Rambles. By EDWARD JESSE, F.LS., Author
of 'Gleanings in Natural History.' Contents:—Thames Fishing
—Trolling in Staffordshire—Perch Fishing Club—Two Days'
Fly-fishing on the Test — Luckford Fishing Club — Grayling
Fishing—A Visit to Oxford —The Country Clergyman. Post 8vo,
10s. 6d.

INVERTEBRATA.

Introduction to Conchology; or, Elements of the Natural
History of Molluscous Animals. By GEORGE JOHNSTON,
M.D., LL.D., Fellow of the Royal College of Surgeons of Edin-
burgh, author of 'A History of the British Zoophytes.' 8vo, 102
Illustrations, 21s.

> "The book is a convincing proof that there is no subject, however dry and
> unpromising, that may not be made interesting by a man of taste, genius,
> and learning. Dr. Johnston's object has been to present the concholo-
> gist with a view of the economical, physiological, and systematical rela-
> tions of molluscous animals to each other and to other created beings;
> and this he has done in a style so elegant and captivating, and with such
> a happy facility of illustrating his theories by learned references and
> curious anecdotes, that it is not easy to decide whether his work is most
> valuable as a scientific, or interesting as a literary composition."—
> *Morning Post.*

History of British Mollusca and their Shells. By Pro-
fessor ED. FORBES, F.R.S., &c. and SYLVANUS HANLEY,
B.A., F.L.S. Illustrated by a figure of each known Animal and
of all the Shells, engraved on 203 copper-plates. 4 vols. 8vo,
£6 10s.; royal 8vo, with the plates coloured, £13.

Synopsis of the Mollusca of Great Britain. Arranged
according to their Natural Affinities and Anatomical Structure.
By W. A. LEACH, M.D., F.R.S., &c. &c. Post 8vo, with 13
Plates, 14s.

History of the British Marine Testaceous Mollusca,
described in their Natural Order, on the Basis of the Organiza-
tion of the Animals, with References and Notes on every British
species. By WILLIAM CLARK. 8vo, 15s.

Thesaurus Conchyliorum. By G. B. SOWERBY. Imp. 8vo,
Eighteen Parts, £1 5s. each.

Malacologia Monensis. A Catalogue of the Mollusca inhabiting
the Isle of Man and the neighbouring Sea. By EDWARD
FORBES. Post 8vo, 3s., Edinburgh, 1838.

History of British Star-fishes, and other Animals of the
Class Echinodermata. By EDWARD FORBES, M.W.S., Pro-
fessor of Botany in King's College, London. 8vo, with more than
120 Illustrations, 15s., or royal 8vo, 30s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Genera of Recent Mollusca; arranged according to their Organization. By HENRY AND ARTHUR ADAMS. This work contains a description and a figure engraved on steel of each genus, and an enumeration of the species. 3 vols. 8vo, £4 10s.; or royal 8vo, with the plates coloured, £9.

Elements of Entomology: an Outline of the Natural History and Classification of British Insects. By WILLIAM S. DALLAS, F.L.S. Post 8vo, 8s. 6d.

The Entomologist's Annual for 1855 to 1858. Duodecimo, boards, 2s. 6d. each.

History of British Stalk-eyed Crustacea (Lobsters, Crabs, Prawns, Shrimps, &c.). By THOMAS BELL, President of the Linnean Society, F.G.S., F.Z.S., Professor of Zoology in King's College, London. The volume is illustrated by 174 Engravings of Species and tail-pieces. 8vo, £1 5s.; royal 8vo, £2 10s.

History of the British Zoophytes. By GEORGE JOHNSTON, M.D., LL.D. Second Edition, in 2 vols. 8vo, with an illustration of every species. £2 2s.; or on large paper, royal 8vo, £4 4s.

Manual of the Sea-Anemones commonly found on the English Coast. By the Rev. GEORGE TUGWELL, Oriel College, Oxford. Post 8vo, with Coloured Illustrations, 7s. 6d.

Natural History of Animals. By Professor T. RYMER JONES. Vol. II. Insects, &c., with 104 Illustrations, post 8vo, 12s.

Familiar Introduction to the History of Insects; being a Second and greatly Improved Edition of the Grammar of Entomology. By EDWARD NEWMAN, F.L.S., Z.S., &c. With nearly 100 Illustrations, 8vo, price 12s.

The World of Insects; a Guide to its Wonders. By J. W. DOUGLAS, Secretary to the Entomological Society of London. This work contains rambling observations on the more interesting members of the Insect World to be found in the House, the Garden, the Orchard, the Fields, the Hedges, on the Fences, the Heaths and Commons, the Downs, in the Woods, the Waters, or on the Sea Shore, or on Mountains. 12mo, stiff-paper wrapper, 3s. 6d.

Siebold on True Parthenogenesis in the Honey-Bee and Silk-Worm Moth. Translated from the German by W. S. DALLAS, F.L.S. 8vo, 5s.

Practical Hints respecting Moths and Butterflies, with Notices of their Localities; forming a Calendar of Entomological Operations throughout the Year, in pursuit of Lepidoptera. By RICHARD SHIELD. 12mo, stiff-paper wrapper, 3s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Hewitson's Exotic Butterflies. Vol. I., containing 398 Coloured Figures of new or rare species, Five Guineas.

> "In this work there is a truthfulness of outline, an exquisite delicacy of pencilling, a brilliancy and transparency of colouring, that has rarely been equalled and probably never surpassed."—*The President in his Address to the Entomological Society, 1856.*

Of Vol. II., Eight Parts (21 to 28 of the entire work) are at this time published, 5s. each.

Manual of British Butterflies and Moths. By H. T. STAINTON, Editor of 'The Entomologist's Annual.' 12mo. To be completed in 30 Numbers at 3d. each; 23 at this time published.

Natural History of the Tineina. By H. T. STAINTON, Coloured Plates. Vol. I. to III. 8vo, cloth, each 12s. 6d.

Entomologist's Companion (to the Tineina). By H. T. STAINTON. Second Edition, 12mo, 3s.

Geodephaga Britannica: a Monograph of the Carnivorous Ground-Beetles Indigenous to the British Isles. By J. F. DAWSON, LL.B. 8vo, with Three Coloured Plates, 12s.

Insecta Maderensia; being an Account of the Insects of the Islands of the Madeiran Group. By T. VERNON WOLLASTON, M.A., F.L.S. 4to, with Thirteen Coloured Plates of Beetles, £2 2s.

BOTANY.

Weeds and Wild Flowers. By LADY WILKINSON. Post 8vo, with Coloured Engravings and Woodcuts. 10s. 6d.

Manual of British Botany; containing the Flowering Plants and Ferns, arranged according to their Natural Orders. By C. C. BABINGTON, M.A., F.R.S., F.L.S., &c. 12mo, the Fourth Edition, with many additions and corrections, 10s. 6d., cloth.

Elementary Course of Botany; Structural, Physiological, and Systematic. With a brief Outline of the Geographical and Geological Distribution of Plants. By ARTHUR HENFREY, F.R.S., L.S., &c., Professor of Botany in King's College, London, Examiner in Natural Science to the Royal Military Academy and to the Society of Arts. Illustrated by upwards of 500 Woodcuts. Post 8vo, 12s. 6d.

Also by Professor Henfrey.

Vegetation of Europe, its Conditions and Causes. Foolscap 8vo, 5s.

Principles of the Anatomy and Physiology of the Vegetable Cell. By HUGO VON MOHL. Translated, with the author's permission, by ARTHUR HENFREY, F.R.S., &c. 8vo, with an Illustrative Plate and numerous Woodcuts, 7s. 6d.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Rudiments of Botany. A Familiar Introduction to the Study of Plants. With Illustrative Woodcuts. Second Edition, foolscap 8vo, 3s. 6d.

A Set of Six Coloured Diagrams illustrative of the Rudiments of Botany; for Schools and Lectures. 15s.

History of British Forest-Trees. By PRIDEAUX JOHN SELBY, F.R.S.E., F.L.S., &c. Each species is illustrated by a portrait of some well-known or fine specimen, as a head-piece; the leaf, florification, seed-vessels, or other embellishments tending to make the volume ornamental or useful, are embodied in the text or inserted as tail-pieces. 8vo, with nearly 200 Illustrations, £1 8s.

Manual Flora of Madeira and the adjacent Islands of Porto Santo and the Dezertas. By R. T. LOWE, M.A. 12mo. Part I. Thalamiflorae, 3s. 6d.

Primitiae et Novitiae Faunae et Florae Maderae et Portus Sancti. Two Memoirs on the Ferns, Flowering Plants, and Land Shells of Madeira and Porto Santo. By R. T. LOWE, M.A. 12mo, 6s. 6d., boards (150 copies printed).

Growth of Plants in closely Glazed Cases. By N. B. WARD, F.R.S., F.L.S. Second Edition, Illustrated. Post 8vo, 6s.

The Sea-Weed Collector's Guide; containing plain Instructions for Collecting and Preserving; and a List of all the known Species and Localities in Great Britain. By J. COCKS, M.D. Foolscap 8vo, 2s. 6d.

Manual of the British Marine Algae, containing Generic and Specific Descriptions of all the known British Species of Sea-Weeds, with Plates to illustrate all the Genera. By W. H. HARVEY, M.D., M.R.I.A., Keeper of the Herbarium of the University of Dublin, and Professor of Botany to the Royal Dublin Society. 8vo, £1 1s.; Coloured Copies, £1 11s. 6d.

Nereis Boreali-Americana; or, Contributions towards a History of the Marine Algae of the Atlantic and Pacific Coasts of North America. By W. H. HARVEY, M.D., M.R.I.A., &c. Royal 4to, with 50 Coloured Plates, £3 3s.

Terra Lindisfarnensis. The Natural History of the Eastern Borders. By GEORGE JOHNSTON, M.D., &c., &c. This volume embraces the Topography and Botany; and gives the popular Names and Uses of the Plants, and the Customs and Beliefs which have been associated with them. The chapter on the Fossil Botany of the district is contributed by GEORGE TATE, F.G.S. Illustrated with a few Woodcuts and 15 Plates, 8vo, 10s. 6d.

History of British Ferns. By EDWARD NEWMAN. Comprising under each Species, Figures, detailed Descriptions, an ample List of Localities, and minute Instructions for Cultivating. 8vo, 18s.

Walks after Wild Flowers; or the Botany of the Bohereens. By RICHARD DOWDEN. Foolscap 8vo, 4s. 6d.

Synopsis of the British Diatomaceæ; with Remarks on their Structure, Functions, and Distribution; and Instructions for Collecting and Preserving Specimens. By the Rev. WILLIAM SMITH. The Plates by TUFFEN WEST. In 2 vols. royal 8vo; Vol. I. 21s.; Vol. II. 30s.

CHEMISTRY, MINERALOGY, GEOLOGY.

A Manual of Chemical Analysis (Qualitative). By A. B. NORTHCOTE, F.C.S., and ARTHUR H. CHURCH, F.C.S. Post 8vo, 10s. 6d.

Handbook of Chemical Manipulation. By C. GREVILLE WILLIAMS, Principal Assistant in the Laboratory of the University of Edinburgh. Post 8vo, with very numerous Woodcut Illustrations, 15s.

Elementary Course of Geology, Mineralogy, and Physical Geography. By DAVID T. ANSTED, M.A., F.R.S., F.G.S., &c., Consulting Mining Engineer, Honorary Fellow of King's College, London, Lecturer on Mineralogy and Geology at the H.E.I.C. Mil. Sem. at Addiscombe, late Fellow of Jesus College, Cambridge. A Second Edition, post 8vo, with many Illustrations, 12s.

The Ancient World. By Professor ANSTED. Second Edition, post 8vo, 10s. 6d., with 149 Illustrations.

"The work may be described as an outline of the history of vegetable and animal life upon the globe, from the early age when there were only sea-weeds and marine invertebrates as yet in existence, down to the era when the mammals received among them the king of species, Man. By his intimate acquaintance with the subject, and power of arrangement and description, Professor Ansted succeeds in producing a narration, which tells in its entire range like a romance."—*Manchester Examiner.*

Gold-Seeker's Manual. By Professor ANSTED. Foolscap 8vo, 3s. 6d.

Geologist's Text-Book. Chiefly intended as a Book of Reference for the Geological Student. By Professor ANSTED. Foolscap 8vo, 3s. 6d.

The Ground beneath us; its Geological Phases and Changes. Three Lectures on the Geology of Clapham and the neighbourhood of London generally. By JOSEPH PRESTWICH, F.R.S., F.G.S. &c   8vo, 3s. 6d. sewed.

Manual of the Mineralogy of Great Britain and Ireland.
By ROBERT PHILIPS GREG, F.G.S., and WILLIAM G.
LETTSOM.   8vo, with numerous Woodcuts, 15s.

History of British Fossil Mammals and Birds. By Pro-
fessor OWEN.   This volume is designed as a companion to that
by Professor Bell on the (Recent Mammalia) ' British Quadru-
peds and Cetacea.'   8vo, with 237 Illustrations, £1 11s. 6d., or
large paper (royal 8vo), £3 3s.

Description of the Skeleton of an Extinct Gigantic Sloth
(Mylodon robustus).   With Observations on the Osteology,
Natural Affinities, and probable Habits of the Megatherioid Qua-
drupeds in general. By RICHARD OWEN, F.R.S., &c.   4to.
£1 12s. 6d.

Geological Inquiry respecting the Water-bearing Strata
of the Country around London, with reference especially to the
Water Supply of the Metropolis, and including some Remarks
on Springs.   By JOSEPH PRESTWICH, Jun., F.G.S., &c.
8vo, with a Map and Woodcuts, 8s. 6d.

Memoirs of Hugh E. Strickland, M.A., Deputy Reader of
Geology in the University of Oxford.   By SIR WILLIAM
JARDINE, Bart.; with a selection from his Printed and other
Scientific Papers.   One Vol. Royal 8vo, 36s., Illustrated by Maps,
Geological Sections, Plates and Woodcuts.

Omphalos. An Attempt to Untie the Geological Knot. By P. H.
GOSSE, F.R.S.   In this work the author aims to overthrow the
received conclusions of geologists as to the remote antiquity of
the earth, by the enunciation and illustration of a grand physical
law, hitherto unrecognized, the law of Prochronism in organic
creation.   Post 8vo, pp. 376, with 56 Illustrations on wood.
10s. 6d.

WORKS ON GENERAL NATURAL
HISTORY, &c.

The Aquarian Naturalist: a Manual for the Sea-side. By Pro-
fessor T. RYMER JONES, F.R.S.   Post 8vo, 544 pp., with
8 Coloured Plates, price 18s.

Humble Creatures: the Earthworm and the Common
Housefly. In Eight Letters. By JAMES SAMUELSON, as-
sisted by J. A. HICKS, M.D. Lond., F.L.S.   With Microscopic
Illustrations by the Authors.   Post 8vo, price 3s. 6d.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

The Micrographic Dictionary: a Guide to the Examination and Investigation of the Structure and Nature of Microscopic Objects. By Dr. GRIFFITH and Professor HENFREY. Illustrated by 41 Plates, each with numerous Figures, some coloured, and 816 Woodcuts, 777 pages, 8vo, £2 5s.

Observations in Natural History; with a Calendar of Periodic Phenomena. By the Rev. LEONARD JENYNS, M.A., F.L.S. Post 8vo, 10s. 6d.

Observations in Meteorology; relating to Temperature, the Winds, Atmospheric Pressure, the Aqueous Phenomena of the Atmosphere, Weather Changes, &c.; being chiefly the results of a Meteorological Journal kept for 19 years at Swaffham Bulbeck, in Cambridgeshire, and serving as a guide to the climate of that part of England. By the Rev. LEONARD JENYNS, M.A., F.L.S., &c., late Vicar of Swaffham Bulbeck. Post 8vo, 10s. 6d.

Practical Meteorology. By JOHN DREW, Ph.D., F.R.A.S., Corresponding Member of the Philosophical Institute of Bâle. Foolscap 8vo, with 10 Illustrative Plates, 5s.

Natural History of Animals: being the substance of Three Courses of Lectures delivered before the Royal Institution of Great Britain. By T. RYMER JONES, F.R.S., Professor of Zoology in King's College, London. Post 8vo. Vol. I. with 105 Illustrations; Vol. II. with 104 Illustrations, 12s. each.

General Outline of the Organization of the Animal Kingdom, and Manual of Comparative Anatomy. By T. RYMER JONES, F.R.S., Professor of Comparative Anatomy in King's College, London; late Fullerian Professor of Physiology to the Royal Institution of Great Britain, &c. &c. Second Edition, 8vo, 884 pages, 400 Woodcuts, £1 11s. 6d.

First Steps to Anatomy. By JAMES L. DRUMMOND, M.D., Professor of Anatomy and Physiology in the Belfast Royal Institution. With 12 Illustrative Plates. 12mo, 5s.

Great Artists and Great Anatomists: a Biographical and Philosophical Study. By R. KNOX, M.D., F.R.S.E. Post 8vo, 6s. 6d.

Anatomical Manipulation; or, The Methods of pursuing Practical Investigations in Comparative Anatomy and Physiology. Also an Introduction to the Use of the Microscope, &c. By ALFRED TULK, M.R.C.S., M.E.S.; and ARTHUR HENFREY, F.L.S., M.Micr.S. With Illustrative Diagrams. Foolscap 8vo, 9s.

Familiar Introduction to the Study of Polarized Light. By CHARLES WOODWARD, F.R.S. 8vo, Illustrated, 3s. Second Edition.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Illustrations of Instinct, deduced from the Habits of British Animals. By JONATHAN COUCH, F.L.S., Member of the Royal Geological Society, and of the Royal Institution of Cornwall, &c. Post 8vo, 8s. 6d.

The Powers of the Creator Displayed in the Creation; or, Observations on Life amidst the various forms of the Humbler Tribes of Animated Nature; with Practical Comments and Illustrations. By Sir JOHN GRAHAM DALYELL, Knt. and Bart. In 3 vols. 4to, containing numerous Plates of living subjects, finely coloured, £10 10s.

Rare and Remarkable Animals of Scotland, with Practical Observations on their Nature. By Sir JOHN GRAHAM DALYELL, Knt. and Bart. In 2 vols. 4to, containing 110 Coloured Plates, drawn from the living subjects, £6 6s.

On the Variation of Species, with especial reference to the Insecta; followed by an Inquiry into the Nature of Genera. By T. VERNON WOLLASTON, M.A., F.L.S. Post 8vo, 5s.

> " No compound of this earthly ball
> Is like another, all in all."—*Tennyson.*

Manual of Natural History for the Use of Travellers; being a Description of the Families of the Animal and Vegetable Kingdoms, with Remarks on the Practical Study of Geology and Meteorology. To which are appended Directions for Collecting and Preserving. By ARTHUR ADAMS, M.R.C.S.; W. BALFOUR BAIKIE, M.D.; and CHARLES BARRON, Curator of the Royal Naval Museum at Haslar. Post 8vo, 12s.

Letters of Rusticus on Natural History. Edited by EDWARD NEWMAN, F.L.S., F.Z.S., &c. 8vo, 8s. 6d.

Descriptive Ethnology. By ROBERT GORDON LATHAM, M.D., F.R.S., Fellow of King's College, Cambridge; Vice-President of the Ethnological Society of London; Corresponding Member of the Ethnological Society of New York. 2 vols. 8vo.

Other Works on Ethnology, by Dr. Latham.

Natural History of the Varieties of Man. 8vo, Illustrated, £1 1s.

Ethnology of Europe. Foolscap 8vo, 5s.

Ethnology of the British Islands. Foolscap 8vo, 5s.

Ethnology of the British Colonies and Dependencies. Foolscap 8vo, 5s.

Man and his Migrations. Foolscap 8vo, 5s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

The Sea-side Book: an Introduction to the Natural History of the British Coasts. By W. H. HARVEY, M.D., M.R.I.A., &c. With a Chapter on Fish and Fish Diet, by YARRELL. Foolscap 8vo, with 83 Woodcut Illustrations, 4th Edition, 5s.

Handbook to the Marine Aquarium: containing Practical Instructions for Constructing, Stocking, and Maintaining a Tank, and for Collecting Plants and Animals. By P. H. GOSSE, F.R.S. Foolscap 8vo, Second Edition, 2s. 6d.

Mr. Gosse's Manual of Marine Zoology of the British Isles. Parts I. and II., price 7s. 6d. each.

A Naturalist's Rambles on the Devonshire Coast. By P. H. GOSSE, F.R.S. With 28 Lithographic Plates, some coloured, post 8vo, One Guinea.

The Aquarium; an Unveiling of the Wonders of the Deep Sea. By P. H. GOSSE, F.R.S. Post 8vo, Illustrated, Second Ed. 17s.

The Canadian Naturalist. By P. H. GOSSE, F.R.S. With 44 Illustrations of the most remarkable Animal and Vegetable productions. Post 8vo, 12s.

Tenby; a Seaside Holiday. By P. H. GOSSE, F.R.S. Post 8vo, 400 pages, with 24 Coloured Plates, 21s.

The Isle of Man; its History, Physical, Ecclesiastical and Legendary. By J. G. CUMMING, M.A., F.G.S. Post 8vo, 12s. 6d.

Natural History of the County of Stafford; comprising its Geology, Zoology, Botany, and Meteorology: also its Antiquities, Topography, Manufactures, &c. By ROBERT GARNER, F.L.S. 8vo, with a Geological Map and other Illustrations, 21s.

The Natural History of Selborne. By the late Rev. GILBERT WHITE, M.A. A New Edition, with Notes by the Rev. LEONARD JENYNS, M.A., F.L.S., &c.; with 26 Illustrations, foolscap 8vo, 7s. 6d.

Travels in Lycia, Milyas, and the Cibyratis, in company with the late Rev. E. T. Daniell. By Lieut. SPRATT, R.N., and Professor EDWARD FORBES. Two vols. 8vo, with numerous Illustrations, including Views of the Scenery, Plans of Ancient Cities and Buildings, Plates of Coins and Inscriptions, Cuts of Rock Tombs, Fossils, and Geological Sections, and an original Map of Lycia. 36s.

Healthy Respiration. By STEPHEN H. WARD, M.D. Foolscap 8vo, 1s. 6d.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Tobacco and its Adulterations. By HENRY P. PRESCOTT, of the Inland Revenue Department. With upwards of 250 Illustrations drawn and engraved on Forty Steel Plates. 8vo, 12s. 6d.

A Life of Linnæus. By Miss BRIGHTWELL of Norwich. Foolscap 8vo, 3s. 6d.

Scenery, Science, and Art; being Extracts from the Notebook of a Geologist and Mining Engineer. By Professor D. T. ANSTED, M.A., F.R.S., &c. 8vo, with Woodcuts and Four Views in tinted lithography, 10s. 6d.

Evening Thoughts. By a PHYSICIAN. Post 8vo, Second Edition, 4s. 6d.

> "We cannot help expressing a wish that these 'Evening Thoughts' may not be the only contributions to general literature that we may have from a mind so powerful, so cultivated, and so gentle as that of the Physician whose pages we now close."—*Guardian.*

Illustrations of Arts and Manufactures; being a Selection from a Series of Papers read before the Society for the Encouragement of Arts, Manufactures, and Commerce. By ARTHUR AIKIN, F.L.S., F.G.S., &c., late Secretary to that Institution. Foolscap 8vo, 8s.

The Poor Artist; or, Seven Eye-Sights and One Object. "SCIENCE IN FABLE." Foolscap 8vo, with a Frontispiece, 5s.

Sunday Book for the Young; or, Habits of Patriarchal Times in the East. With Woodcuts, 2s. 6d. By ANNE BULLAR.

Other Books for Young Persons, by Anne Bullar.

Domestic Scenes in Greenland and Iceland. With Woodcuts, 2s. Second Edition.

Every-Day Wonders; or, Facts in Physiology which all should know. With Woodcuts, 2s. 6d.

England before the Norman Conquest. 2s. 6d.

Elements of Practical Knowledge; or, The Young Inquirer Answered. Explaining in Question and Answer, and in familiar language, what most things daily used, seen, or talked of, are; what they are made of, where found, and to what uses applied. Including articles of food and aliment; miscellanies in common use; metals, gems, jewellery; and some account of the principal inventions and most interesting manufactures. Second Edition, 18mo, with Illustrations, 3s. cloth.

Notes on the Geology and Chemical Composition of the various Strata in the Isle of Wight. By CAPTAIN L. L. BOSCAWEN IBBETSON. With a Map in Relief, coloured Geologically, 8vo, 7s. 6d.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

ARCHITECTURE AND THE FINE ARTS, &c.

Instrumenta Ecclesiastica; a Series of Working Designs, engraved on 72 Plates, for the Furniture, Fittings, and Decorations of Churches and their Precincts. Edited by the Ecclesiological, late Cambridge Camden Society. 4to, £1 11s. 6d.

The Second Series contains a Cemetery Chapel, with Sick-house and Gateway Tower—A Wooden Church—A Chapel School—Schools and School-houses—A Village Hospital—An Iron Church—And Designs for Funeral Fittings, for Timber Belfries, and for a Variety of Works in Metal, Wood, and Stone. Price also £1 11s. 6d.

Manual of Gothic Architecture. By F. A. PALEY, M.A. With a full Account of Monumental Brasses and Ecclesiastical Costume. Foolscap 8vo, with 70 Illustrations, 6s. 6d.

> "To the student of the architecture of old English churches this beautiful little volume will prove a most acceptable manual. The two chapters on * * * form an epitome of the whole subject, so lucid, concise, and complete, that it may be regarded as a model of succinct and clear exposition. Both in description and analysis, Mr. Paley is remarkable for neatness and perspicuity; his style is terse and precise, yet withal easy and elegant. The examples, engraved by Thurston Thompson, are the perfection of wood engraving, as applied to architecture: exact in detail, picturesque in effect, and cut with equal firmness and delicacy."— *Spectator.*

Baptismal Fonts. A Series of 125 Engravings, examples of the different periods, accompanied with Descriptions; and with an Introductory Essay. By F. A. PALEY, M.A., Honorary Secretary of the Cambridge Camden Society. 8vo, One Guinea.

Treatise on the Rise and Progress of Decorated Window Tracery in England. By EDMUND SHARPE, M.A., Architect. 8vo, Illustrated with 97 Woodcuts and Six Engravings on steel, 10s. 6d. And a

Series of Illustrations of the Window Tracery of the Decorated Style of Ecclesiastical Architecture. Edited, with descriptions, by Mr. SHARPE. Sixty Engravings on steel, 8vo, 21s.

Heraldry of Fish. By THOMAS MOULE. The Engravings, 205 in number, are from Stained Glass, Tombs, Sculpture, and Carving, Medals and Coins, Rolls of Arms, and Pedigrees. 8vo, 21s. A few on large paper (royal 8vo) for colouring, £2 2s.

Shakspeare's Seven Ages of Man. Illustrated by WM. MULREADY, R.A.; J. CONSTABLE, R.A.; SIR DAVID WILKIE, R.A.; W. COLLINS, R.A.; A. E. CHALON, R.A.; A. COOPER, R.A.; SIR A. W. CALLCOTT, R.A.; EDWIN LANDSEER, R.A.; W. HILTON, R.A. Post 8vo, 6s. A few copies of the First Edition in 4to remain for sale.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

Manual of Gothic Moldings. A Practical Treatise on their formations, gradual development, combinations, and varieties; with full directions for copying them, and for determining their dates. Illustrated by nearly 600 examples. By F. A. PALEY, M.A. Second Edition, 8vo, 7s. 6d.

> "Mouldings are the scholarship of architecture. The present is a most learned work, and displays an amount of practical knowledge which those who know the difficulties of the subject alone can appreciate."— *Christian Remembrancer.*

Gray's Elegy in a Country Church-Yard. Each Stanza illustrated with an engraving on wood, from 33 original drawings. Elegantly printed, in post 8vo, 9s. cloth. (Small edition, 2s. 6d.)

A Polyglot Edition of this volume, with interpaged Translations in the Greek, Latin, German, Italian, and French languages. 12s.

Gray's Bard. With Illustrations by the Hon. Mrs. JOHN TALBOT. Post 8vo, 7s.

The Vicar of Wakefield. With 32 Illustrations by WILLIAM MULREADY, R.A.; engraved by JOHN THOMPSON. First reprint. Square 8vo, 10s. 6d.

> "And there are some designs in the volume in which art may justly boast of having added something to even the exquisite fancy of Goldsmith." —*Examiner.*

The Farmer's Boy and other Rural Tales and Poems. By ROBERT BLOOMFIELD. Foolscap 8vo, 7s. 6d. A few copies on large paper, to correspond with the edition of 'The Vicar of Wakefield,' lately illustrated by WILLIAM MULREADY, R.A. With 13 Illustrations by Sidney Cooper, Horsley, Frederick Tayler, and Thomas Webster, A.R.A.

Watts's Divine and Moral Songs. With 30 Illustrations by C. W. COPE, A.R.A.; engraved by JOHN THOMPSON. Square 8vo, 7s. 6d.; copies bound in morocco, One Guinea.

The Economy of Human Life. In Twelve Books. By R. DODSLEY. With Twelve Plates, engraved on steel, from original designs, by Frank Howard, Harvey, Williams, &c. 18mo, gilt edges, 5s.

Bibliographical Catalogue of Privately Printed Books. By JOHN MARTIN, F.S.A. Second Edition, 8vo, 21s.

The Currency under the Act of 1844; together with Observations on Joint Stock Banks, and the Causes and Results of Commercial Convulsions. From the City Articles of "The Times." 8vo, 6s.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

NATURAL HISTORY OF THE BRITISH ISLES.

*This Series of Works is Illustrated by many Hundred Engravings;
every Species has been Drawn and Engraved under the immediate
inspection of the Authors; the best Artists have been employed, and
no care or expense has been spared.*

A few Copies have been printed on Larger Paper.

QUADRUPEDS, by Professor BELL. A New Edition preparing.

BIRDS, by Mr. YARRELL. Third Edition, 3 vols. £4 14s. 6d.

COLOURED ILLUSTRATIONS OF THE EGGS OF BIRDS, by Mr. HEWITSON. Third Edition, 2 vols., £4 14s. 6d.

REPTILES, by Professor BELL. Second Edition, 12s.

FISHES, by Mr. YARRELL. Third Edition, edited by Sir JOHN RICHARDSON, 2 vols., nearly ready.

CRUSTACEA, by Professor BELL. 8vo, £1 5s.

STAR-FISHES, by Professor EDWARD FORBES. 15s.

ZOOPHYTES, by Dr. JOHNSTON. Second Edition, 2 vols., £2 2s.

MOLLUSCOUS ANIMALS AND THEIR SHELLS, by Professor EDWARD FORBES and Mr. HANLEY. 4 vols. 8vo, £6 10s. Royal 8vo, Coloured, £13.

FOREST TREES, by Mr. SELBY. £1 8s.

FERNS, by Mr. NEWMAN. Third Edition, 18s.

FOSSIL MAMMALS AND BIRDS, by Prof. OWEN. £1 11s. 6d.

Students' Class-Books.

MANUAL OF CHEMICAL QUALITATIVE ANALYSIS. By A. B. NORTHCOTE, F.C.S., and ARTHUR H. CHURCH, F.C.S. Post 8vo, 10s. 6d.

HANDBOOK OF CHEMICAL MANIPULATION. By C. GREVILLE WILLIAMS. 15s.

ELEMENTARY COURSE OF GEOLOGY, MINERALOGY, AND PHYSICAL GEOGRAPHY. By DAVID T. ANSTED, M.A. &c. Second Edition, 12s.

ELEMENTARY COURSE OF BOTANY: Structural, Physiological, and Systematic. By ARTHUR HENFREY. 12s. 6d.

MANUAL OF BRITISH BOTANY. By C. C. BABINGTON, M.A. &c. Fourth Edition, 10s. 6d.

GENERAL OUTLINE OF THE ORGANIZATION OF THE ANIMAL KINGDOM, by Professor T. RYMER JONES. 8vo, Second Edition, £1 11s. 6d.

JOHN VAN VOORST, 1 PATERNOSTER ROW.

INDEX.