

# **Universitäts- und Landesbibliothek Tirol**

## **A handbook of chemical manipulation**

**Williams, Charles Greville**

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Section XXIII. Manipulation Connected with Organic Analysis

## 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  $\frac{3}{4}$ ths 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		
<hr/> 6·25		

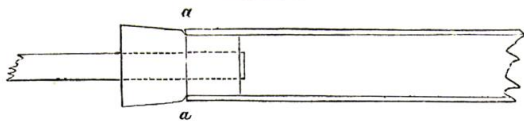
in the manner indicated above, with b.d. attached, indicating “before drying.” This is merely done to enable the operator to remember the weight, so as to save time in the subsequent weighings; when the substance has remained half an hour or more in the bath, it is taken out, and the glass which was 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  $212^{\circ}$ , 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.

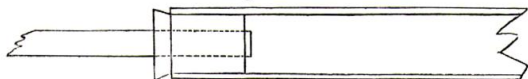
578. *Corks for combustions*.—No trouble should be spared in selecting the very best corks for attaching the chloride-of-calcium apparatus to the combustion-tubes; the latter should be tolerably uniform in size, in order that the same corks may be frequently used; they must be filed somewhat conical, 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.

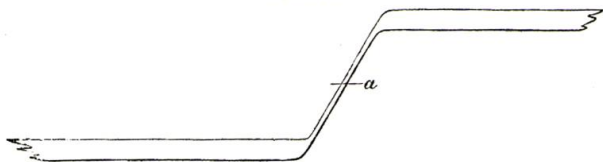
It is very common with beginners to use tubes far larger in diameter than is necessary; but this is improper in more ways than one. In the first place, it is much more difficult to make corks fit tightly into large than small tubes; and in the next, the former require an unnecessarily large quantity 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.

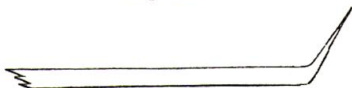
Fig. 281.



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 become very hot; it may then be heated at the edges with

Fig. 282.



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 combustion-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.

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 flattening-mill, and afterwards 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 considerable 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 constructed of sheet-iron, and has had several improvements made in it by different chemists, none of which are, however, of sufficient 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 *ab*, has the form of fig. 284,

Fig. 283.

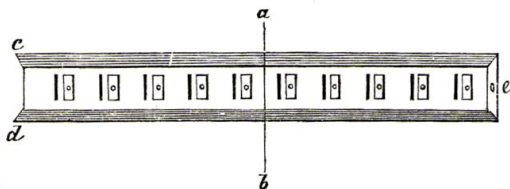


Fig. 284.



from which it will also be seen that the furnace is slightly hollowed 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, *cd*, 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  $212^{\circ}$  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.

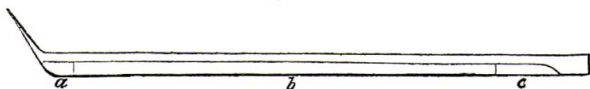
588. *Analysis of substances free from nitrogen.*—The apparatus



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

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.

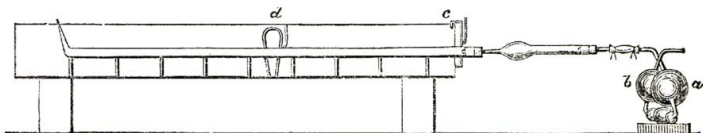


presents the portion of pure chromate first introduced, *b* the mixture with the organic substance, and *c* the rinsings of the mortar.

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 furnace 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 expanded 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 contained 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 previously 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

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
<hr/>	<hr/>	<hr/>
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  $\cdot 1$  to  $\cdot 15$  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  $\cdot 11$  of a per cent. and the excess of hydrogen  $\cdot 03$ .

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 nitrogen 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 difficult, 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



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 analysed 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 immediately 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 condenses, 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 performed 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 during 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 importance, 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 portion 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 centimetres), and then 5 centimetres of asbestos followed by 10 centimetres 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 heating 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.

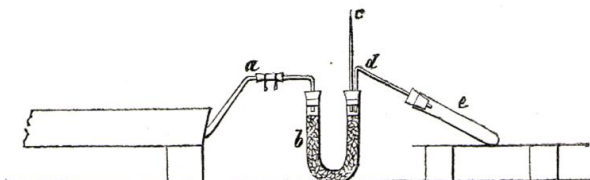
A common method of effecting the combustion of very refractory organic substances, is by passing a current of oxygen gas through the tube, either during the whole time or only at the conclusion of the operation. The manipulation in the former case will be evident from the description of Hofmann's gas-furnace. 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.



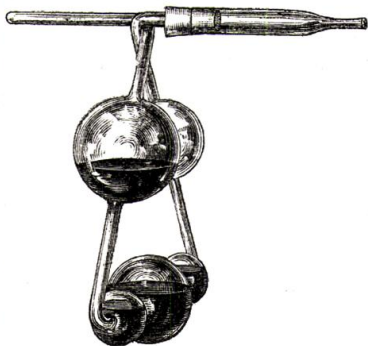
The posterior end of the combustion-tube has its point, *a*, fig. 297, attached by means of a caoutchouc connector with the U-tube, *b*, one limb of which is filled with fragments of caustic potash, and the other with chloride of calcium. The limb furthest from the combustion-furnace has two tubes inserted 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.

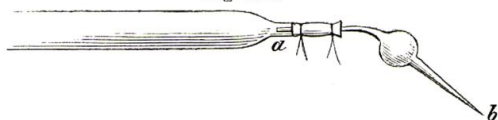
609. Where chlorinated substances are burnt with oxide of copper in a stream of oxygen, it is also necessary to use copper turnings, the current of oxygen being arrested immediately on its being seen that the copper in front of the tube is becoming oxidized.

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.



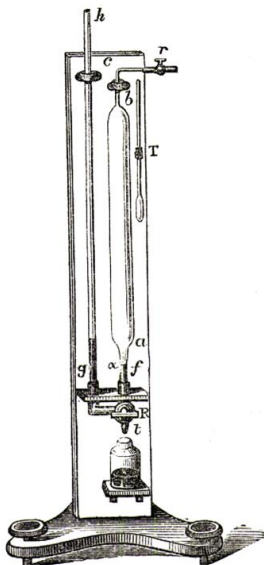
connected by a small caoutchouc tube with the anterior portion of the combustion-tube, which is drawn out for the purpose. It is sealed at both ends when affixed to the combustion-tube, and when the whole of the oxide of copper is heated to redness, the point, *a*, fig. 299, is broken by pressing it 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.

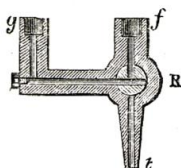


Fig. 302.

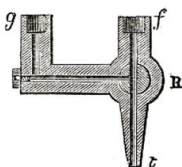
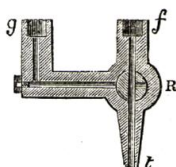


Fig. 303.



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 analysed, mercury is again introduced as before, and the vessel producing 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.

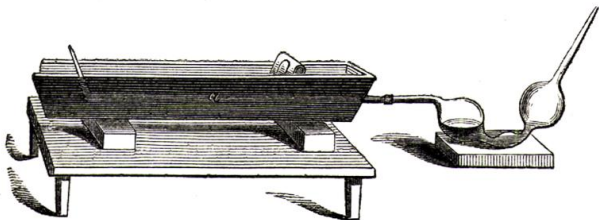
613. The anterior end of the combustion-tube being connected with the stopcock,  $r$ , mercury is to be poured in at  $h$  to expel the gas, which is thus forced over the oxide of copper, the products

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.



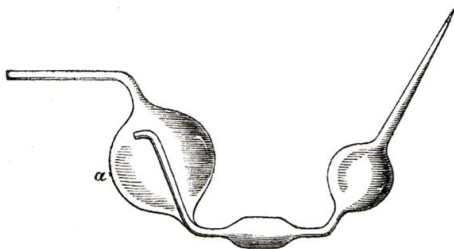
the fluid to enter the combustion-tube. It is advisable always to add a little starch or sugar, because if the organic matter is small in quantity the gases evolved from the starch carry the ammonia

forward into the bulbs. Where hydrochloric acid is used to condense the ammonia, it is usual to convert the latter into the platinum-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 impossible; its mode of action is seen by reference to fig. 305. It

Fig. 305.

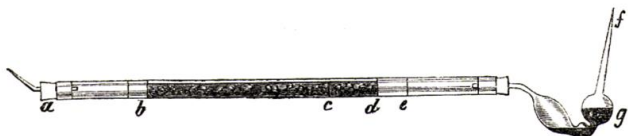


is plain that if regurgitation should take place, the acid merely enters the bulb,  $\alpha$ , without finding its way into the combustion-tube. The acid for condensation is chiefly contained in the smaller bulb, a little being, however, allowed to enter the other. On the 5th of the same month, Mr. Warren 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.

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  $\frac{5}{8}$ ths to  $\frac{3}{4}$ ths 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

Fig. 307.



Fig. 308.



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.

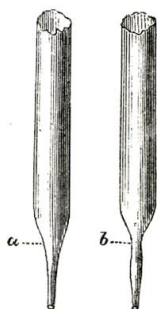
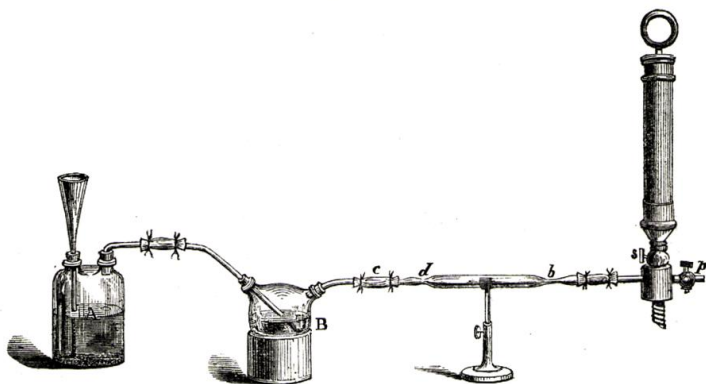


Fig. 311.

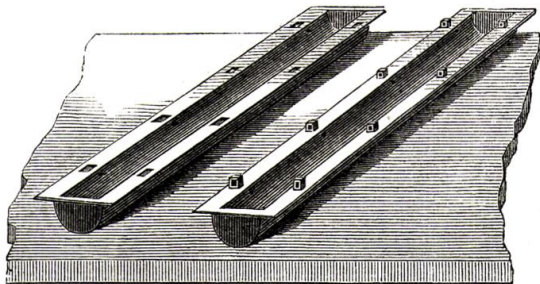


render it tight. A slight vacuum is produced by making a stroke of the piston, and the tap, *s*, is to be turned off. A strong blowpipe-flame is now made to play upon the parts *d* and *b* which are to be closed, the operation being greatly facilitated by the vacuum.

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

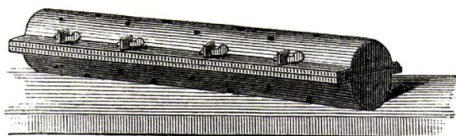
disperse the air-bubbles by stirring. The tube containing the substance is now imbedded in the plaster, and the other half placed

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.



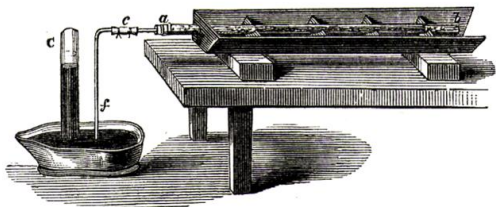
From *a* to *b* is bicarbonate of soda; *b* to *c*, oxide of copper; *c* to *d*, the mixture of the substance with oxide; *d* to *e*, coarse grains of the oxide; and *e* to *f*, metallic copper. The temperature required in the combustion, combined with the pressure of the mercury,

\* The measurement will be far more accurate if a cathetometer is employed.

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-

Fig. 315.



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.

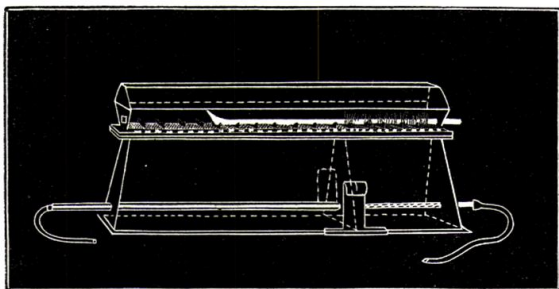
The bicarbonate of soda may be replaced with advantage by carbonate of manganese\*.

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-

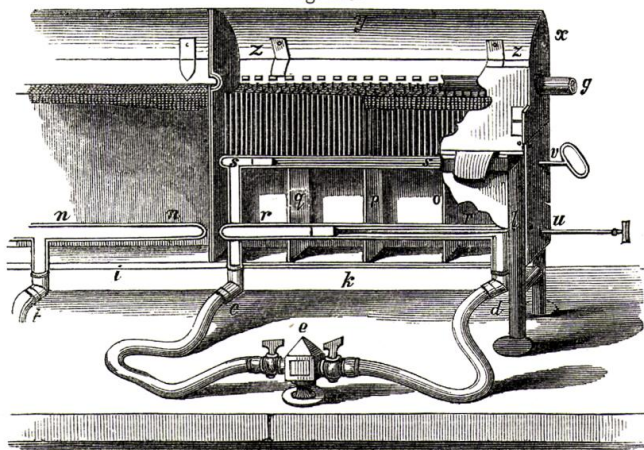




moreover, as a bubble-gauge for measuring the rapidity of the current.

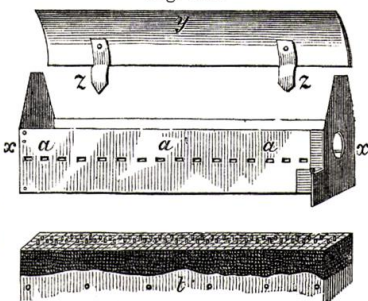
“The furnace consists of three separate compartments of strong iron plate, *h*, *i* and *k*, which are supported by a stout iron stand, *lm*. The arrangement of these compartments requires a few explanations; their construction is evident from figs. 318 and 319:

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, *nn*, 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, *rr*, resembles in every respect the gas-pipe, *nn*,

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-

stance' may now be commenced. For this purpose the gas is admitted, by means of the flexible tube, *d*, to the lower gas-pipe, *rr*, and the piston, *u*, pushed so far from the inlet as to supply the gas to the chamber, *ol*, 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, *ss*, 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.

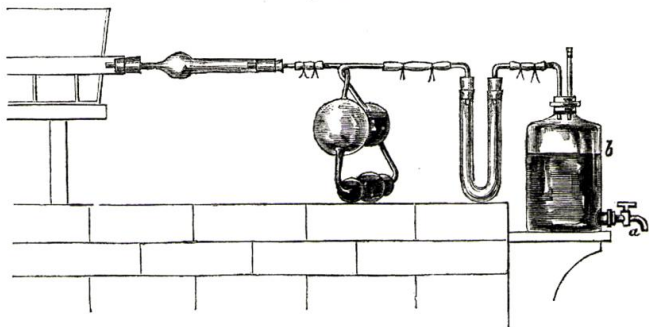
629. "The furnace given in the above illustrations is composed of three distinct divisions, which may be separately fixed upon the support. By this provision the apparatus becomes adapted to a variety of operations, especially to nitrogen determinations, which require a shorter tube. This separation, 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.