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Contributors

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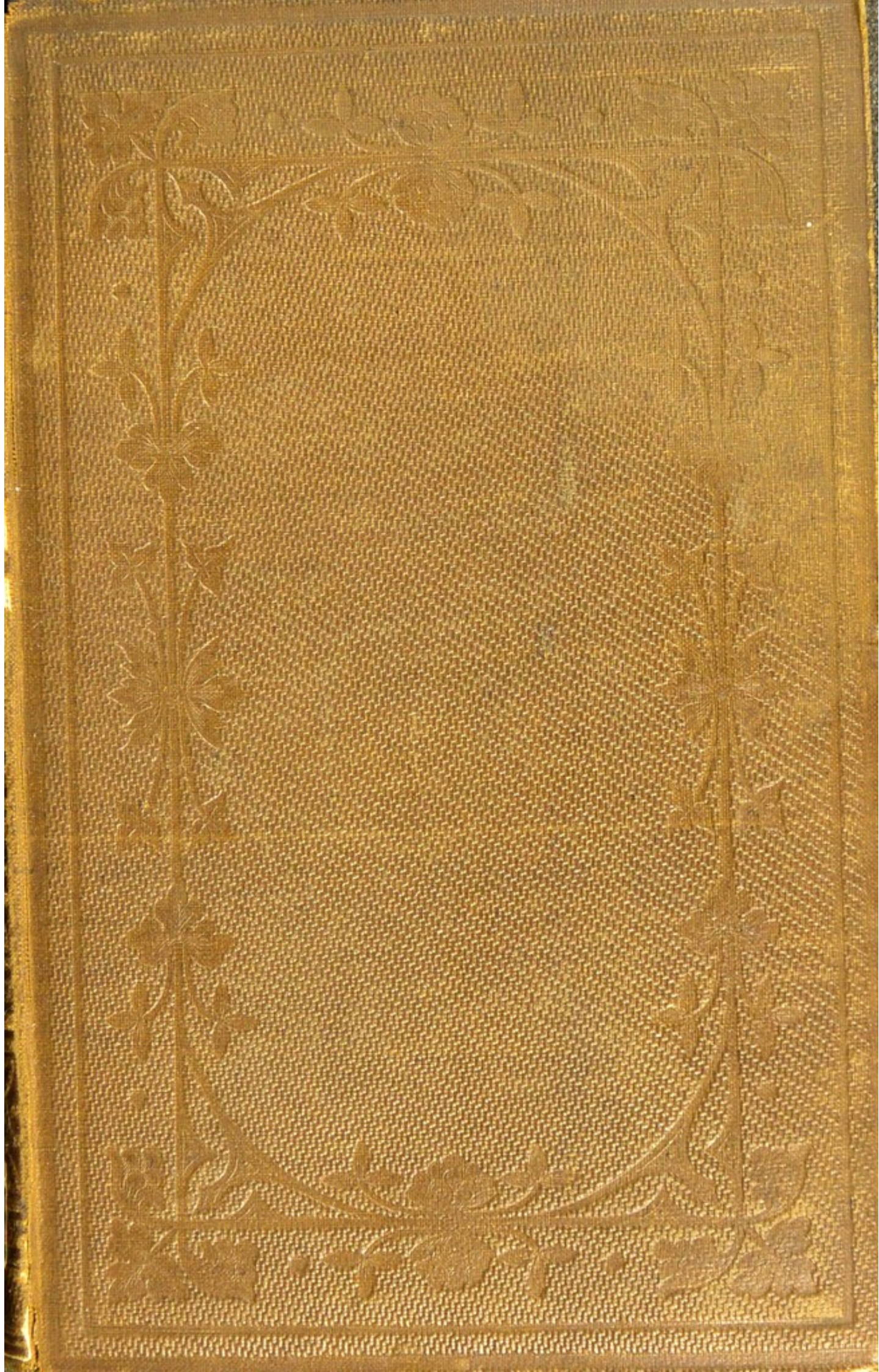
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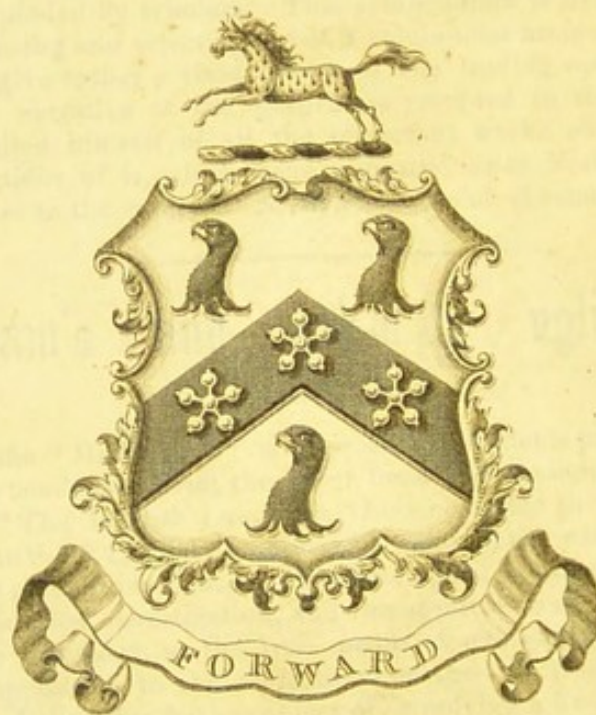
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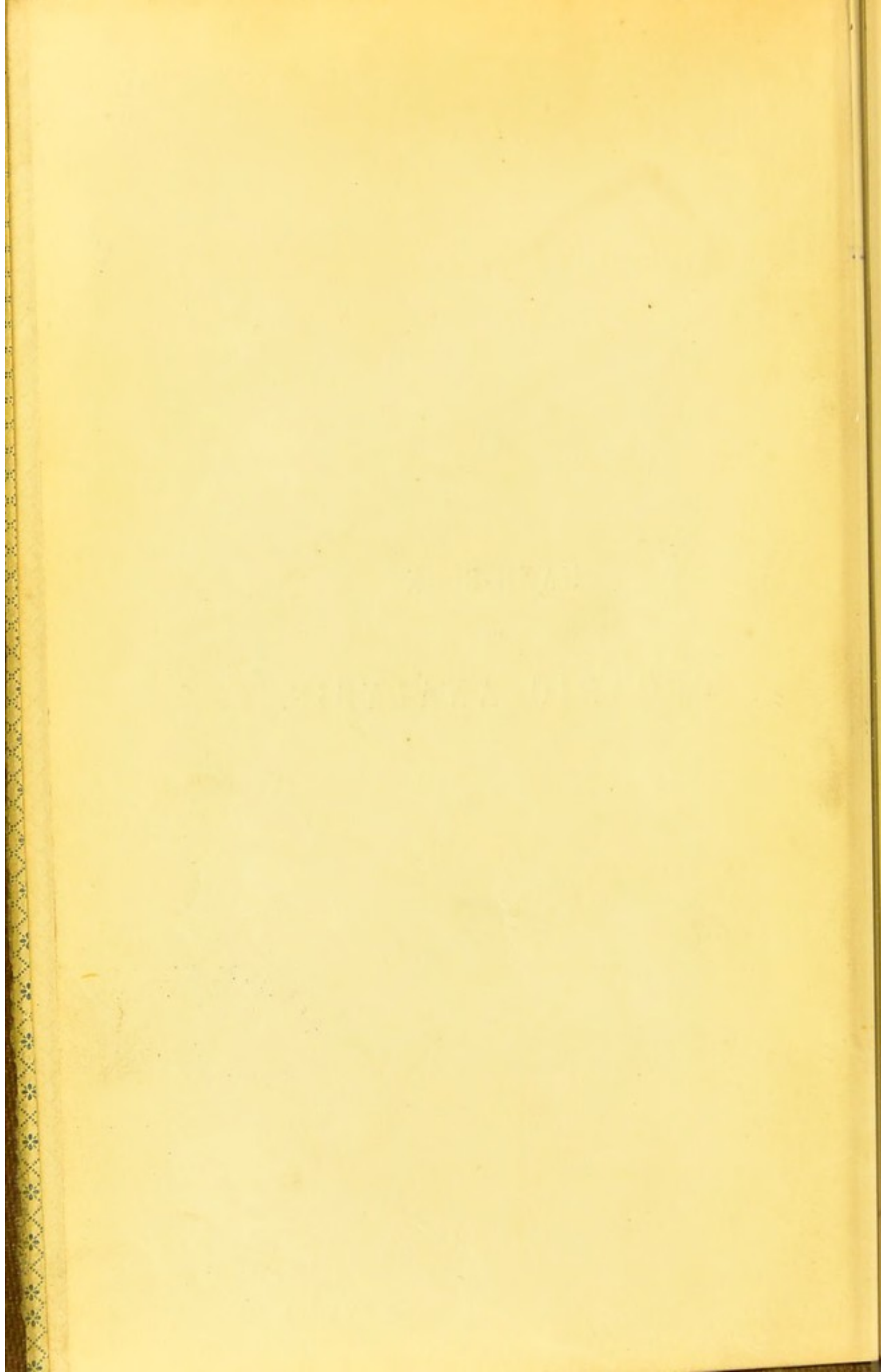
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HAND-BOOK
OF
ORGANIC ANALYSIS.



HAND-BOOK
OF
ORGANIC ANALYSIS;

CONTAINING A
DETAILED ACCOUNT OF THE VARIOUS METHODS USED IN DETERMINING
THE
ELEMENTARY COMPOSITION
OF
ORGANIC SUBSTANCES.

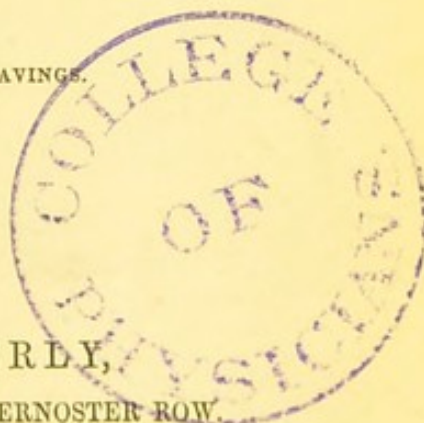
BY JUSTUS LIEBIG,
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF MUNICH.

EDITED
BY A. W. HOFMANN, PH.D., F.R.S.,
PROFESSOR IN THE ROYAL COLLEGE OF CHEMISTRY.

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PREFATORY REMARKS.

IN publishing the Second Edition of my "Instructions in Organic Analysis," I have been kindly assisted by Dr. Strecker, in Christiana, and Dr. A. W. Hofmann, in London, and I believe that the co-operation of my friends, who possess so much experience in that department of chemical analysis, has conferred a peculiar value upon this little work. Since the publication of the first edition, a great variety of new apparatus and many new methods have been proposed, but only such have been adopted and described in the following pages, as have stood the test of a rigorous experimental examination.

DR. JUSTUS LIEBIG.

The Editor of the English Translation has but little to add to the prefatory remarks of Baron Liebig. Entrusted with the supervision of the German Edition, and thus compelled to institute a close comparison of the present methods of analysis with those in use at the time the first edition was published, he was struck with the great progress in this department of chemical analysis—a pro-

gress apt to be overlooked, consisting as it does of the gradual addition of many little improvements. Impressed moreover, with the want of such a hand-book by the laboratory-student who wishes to engage in organic investigations, he was led to undertake the publication of the English Edition. He may state that the English work is a faithful representation of the German, with the exception of the last chapter, which contains a description by the Editor of an arrangement for using coal-gas as fuel, in the combustion of organic bodies, instead of charcoal or spirits of wine, hitherto exclusively employed.

A. W. H.

ROYAL COLLEGE OF CHEMISTRY,
AUGUST 18, 1853.

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HANDBOOK
OF
ORGANIC ANALYSIS.

THE analysis of organic substances has for its object the determination of the nature and quantity of their elements, and constitutes one of the most important departments of analytical chemistry. The course which was formerly pursued in order to obtain an insight into the chemical composition of organic compounds, bears not the least similarity to the present method of analysis. The substances to be examined were subjected to dry distillation, and the difference in their composition was inferred from the nature of the products so obtained.

It is only within the last forty years that this department of chemistry has been perfected upon scientific principles, and all the later methods of analysis differ only in the manner in which these principles are carried out.

The simplest method of determining the proportions of the elements of an organic compound appears to consist in obtaining these in a separate state; but it is evident that if,

instead of the individual elements, we obtain compounds of these with other elements, of known composition, we shall be enabled to determine their amount with equal precision.

Most organic substances contain carbon, hydrogen, and oxygen; a smaller number contain also nitrogen, and others, sulphur, chlorine, bromine, iodine, and phosphorus. Of these, nitrogen is the only element which can be separated, in the pure state, from organic compounds; if, however, the whole of the carbon be converted into carbonic acid, and the whole of the hydrogen into water, we are enabled, from the weight of these compounds, to determine, with the greatest accuracy, the amount of carbon and hydrogen present in the substance. Even in cases where the elements of organic compounds could be separated in a state of purity, preference would be accorded to the methods of analysis now in use, on account of their superior accuracy.

The process then by which an accurate knowledge of the amount of carbon and hydrogen in an organic compound is arrived at, consists in the conversion of a known weight of the substance into carbonic acid and water; the success of the analysis depending upon the extent to which the apparatus allows these products to be collected without loss. When nitrogen is contained in the substance, it may either be separated in a pure state, or may be converted into ammonia, the quantity of which is determined; the sulphur is converted into sulphuric acid, phosphorus into phosphoric acid; chlorine, bromine, and iodine are weighed in combination with silver. The oxygen is usually determined by difference.

Gay-Lussac and Thénard, who originated organic analysis, employed chlorate of potassa for the combustion of organic compounds. The substance was mixed with the chlorate, made into small pellets, and introduced, in small

portions, into a vertical glass tube heated to redness. The evolved gases were conducted, by a lateral tube, into a bell-jar standing over mercury.

The whole of the gaseous mixture was accurately measured, and, after correction for temperature and barometric pressure, brought in contact with caustic potassa. After the absorption of the carbonic acid, there remained either pure oxygen, or a mixture of this gas with nitrogen. The relative quantity of the latter was determined by means of the eudiometer. The weights of the organic substance and of the chlorate of potassa being known, as also the quantities of carbonic acid and of uncombined oxygen, the analyst was possessed of all the data for calculating the composition of the substance. The difference between the amount of oxygen contained in the gaseous mixture, and that known to be evolved from the chlorate of potassa, must have been consumed in the conversion of the hydrogen of the substance into water.

The apparatus of Gay-Lussac and Thénard had no fault but that of making the accuracy of the results to depend, in too great a degree, upon the dexterity of the operator. The analysis of nitrogenised bodies, by burning with chlorate of potassa, was inaccurate, in consequence of the formation of nitrous acid; moreover, it was impossible to analyse a liquid or volatile substance by this method.

Berzelius succeeded, by employing horizontal combustion-tubes, and collecting the water produced in the analysis, in rendering this method more easy of execution, and in divesting it of the numerous calculations. He employed the chlorate of potassa mixed with a large quantity of common salt, which had the advantage of rendering the combustion more gradual, and of permitting the introduc-

tion of the whole of the substance, at one time, into the combustion-tube.

A great and very essential improvement has been made in these forms of apparatus, which could be applied to the analysis of only a limited class of substances, in consequence of the employment of oxide of copper instead of chlorate of potassa, a change first proposed by Gay-Lussac, and applied by him in the combustion of uric acid. At present, the advantages of this method over the use of chlorate of potassa are so well appreciated, that the latter has been almost entirely abandoned. Chromate of lead and bichromate of potassa are also employed for the combustion of many organic substances very rich in carbon.

Saussure and Prout have also described apparatus for the analysis of organic substances, differing from those originally recommended by Gay-Lussac and Thénard only in their form, and in the substitution of oxygen gas and oxide of copper for chlorate of potassa.

Prout's apparatus is arranged in such a manner that the substance to be analysed is burnt, either alone or in the state of mixture, in a measured quantity of oxygen, and the volume of this gas remaining after the combustion is compared with its original volume. This method is founded upon the circumstance, that when carbon is burnt in oxygen, the carbonic acid formed occupies exactly the same space as the oxygen which has been consumed, and therefore no alteration of volume takes place: that, moreover, when hydrogen combines with oxygen, $\frac{1}{2}$ volume of the latter disappears, for every volume of hydrogen, in the condensation of the water which is produced.

Hence it follows, that when the substance to be burnt consists only of carbon, hydrogen, and nitrogen, the result

may be one of three cases: either the original volume of the oxygen remains unaltered after the combustion (and in this case the substance analysed contained oxygen and hydrogen in the proportions to form water), or the volume of the oxygen is diminished, or it is augmented: in the two last cases, either the substance contained more hydrogen, and therefore less oxygen, than was requisite for the formation of water, or the reverse. The quantity by which the original volume of oxygen had been increased or diminished could be accurately measured, and, the volume of the carbonic acid produced being also known, it was easy to express numerically the composition of the substance.

For the analysis of nitrogenised substances, and of a number of others, however, this apparatus was not applicable. Another form of apparatus, upon a similar principle, has been recently constructed by Brunner. All these, however, have been used only by their inventors, and since they possess no advantage over those ordinarily employed, it would be superfluous here to describe them in detail.

GENERAL METHOD OF PROCEEDING.

We are now about to describe the apparatus and processes which are at present employed by the majority of chemists, in organic analysis, and this is the place for a few preliminary general remarks upon the operations.

It will be observed that all the apparatus employed in the analysis of organic substances is very simple, and requires no particular dexterity in its manipulation. The chief points which must be attended to in order to ensure the success of the analysis are—the greatest accuracy in weighing the apparatus, and the strictest scrupulousness in

executing all the preliminary operations. The analyst must not flatter himself that he will obtain an accurate result when he has omitted anything which he might have secured; on the contrary, all the care and time employed in the experiment are lost, when the operator omits to fulfil one of the prescribed conditions.

Every chemist, after acquiring some experience in organic analysis, will be enabled to alter the apparatus here described, in particular cases, according to his own views, so as to adapt it to the object which he desires to attain; but he goes too far who regards this deviation, on a special occasion, as an improvement upon the general method of proceeding, and recommends it as such.

Innate in the human mind is a longing after perfection; hence the endeavours to improve present methods and to invent new ones for the attainment of a proposed end. Here, men, for the most part, fall into the prevalent error of omitting to test the applicability of the known method, or even to acquaint themselves with it; they take another course from the first, and when their efforts are crowned with success, the satisfaction of their spirit of discovery causes them to overlook the obstacles, and the circuitous paths by which they have been surmounted, though these would have been avoided had they kept the beaten track.

We adhere, in the following pages, to the rule of Berzelius, the most experienced chemist of our own, and probably of all times; and where there are two processes equally good, prefer the simpler to the more complicated one.

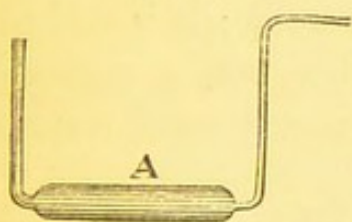
The first problem which must be solved in organic analysis, is to obtain the substance in the highest degree

of purity, and the analyst should neglect no means by which he may assure himself of the absence of foreign matters.

Supposing that the substance is pure, another source of uncertainty in the results of the analysis, and of the differences between the numbers obtained in several operations, is found in the difficulty of determining accurately the weight of the substance to be analysed. All organic substances absorb water from the air with great avidity, and suffer a consequent increase of weight; they must be freed from all hygroscopic moisture previously to analysis, and must be weighed in such a manner as to preclude the possibility of absorption of moisture during the process.

When it is remembered that the presence of water in the substance is equivalent to a loss of carbonic acid, the importance of attending most carefully to the correct determination of the weight of the dry substance will be at once perceived.

FIG. 1.



There are several methods for the attainment of this object. The following apparatus allows complete certainty in this respect; it consists of the tube *A*, FIG. 1, the inferior and wider portion of which is about $\frac{1}{2}$ inch in diameter; the two tubes connected with it are barometer tubes, being respectively $\frac{1}{8}$ and $\frac{1}{4}$ inch in diameter. The

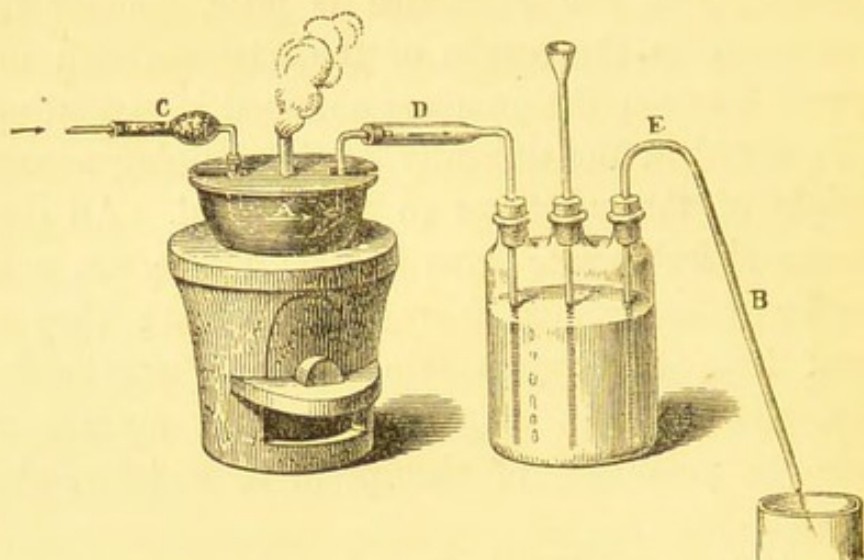
FIG. 2.



substance is introduced through the wider of the two, which is then connected by means of a cork with the chloride-of-calcium-tube *C*, FIG. 2, while the other tube is in connection with the tube *D*,

FIG. 3. *E* is an ordinary syphon; the tube *D* is about an inch shorter than the outer limb *B* of the syphon.

FIG. 3.



It is obvious that by this arrangement, a perfectly uniform efflux of water will be produced, and since the air which replaces the escaping water, enters the bottle from the opening of the tube *D*, it will be immediately seen whether all the joints are perfectly tight.

The three-necked bottle is filled with water; it is evident that when the water is allowed to flow out, a constant stream of dry air will pass over the substance and remove all its moisture.

The horizontal part of the drying tube is placed in a sand-bath, water-bath, chloride-of-calcium-bath, &c., according to the temperature which the substance is capable of supporting without decomposition. If it be desired to estimate the amount of water, the apparatus *A* is weighed, when empty, and again after introducing the substance; it is then placed in the water-bath, chloride-of-calcium-bath, &c., and air allowed to pass over it as long as any water

condenses in the tube *D*. The apparatus *A* is now weighed at intervals, to ascertain if it still loses; when this is no longer the case, a small quantity of the substance is transferred

FIG. 4.

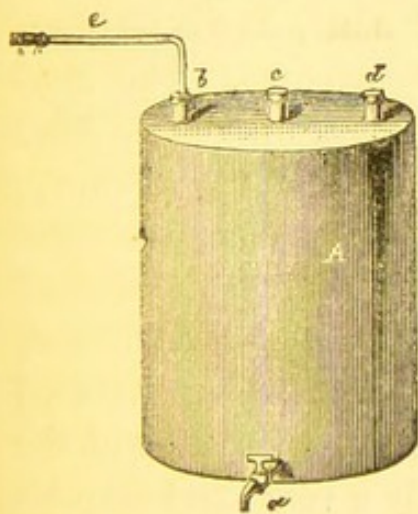


from the apparatus *A* to a long, perfectly dry test tube, FIG. 4, which is heated by a spirit-lamp or sand-bath, to a high temperature, of course below that at which the substance is decomposed. If not the slightest deposition of water is observed upon the sides of the tube, it is certain that the exsiccation of the substance is completed; should this not be the case, the process must be continued at a somewhat

higher temperature.

Mitscherlich employs a similar apparatus for drying organic substances; it only differs from that just described in that the tube *A*, FIG. 1, is placed in communication with an air-pump, by which air is continually drawn through the apparatus until the substance is dry.

FIG. 5.



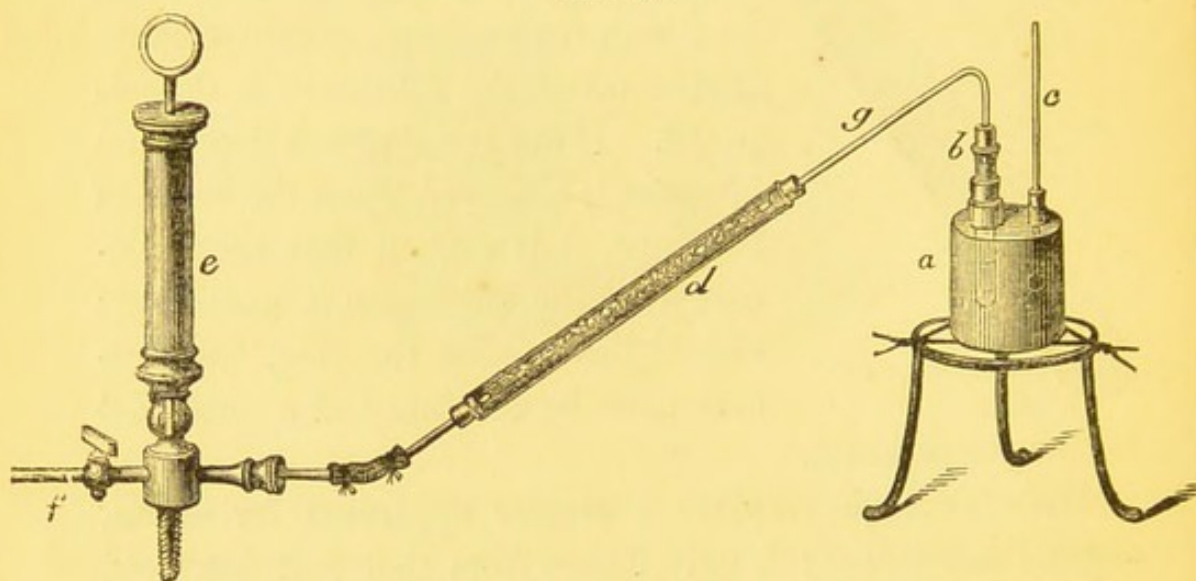
the aspirator is filled up. Lastly, the neck *b* is connected

Instead of the glass bottle, we may conveniently employ an aspirator made of tin-plate, as represented by FIG. 5; it is capable of containing about 40 lbs of water. The opening *d*, which is closed with a cork, or provided with a funnel, is that by which the water is introduced. The centre opening is likewise closed with a cork, and permits the egress of air when

in a suitable manner with the drying tube *A*. The efflux of water is regulated by the stop-cock *a*.

Substances which retain water with great pertinacity are dried *in vacuo*, at a gradually increasing temperature. FIG. 6 exhibits the arrangement for this purpose: *e* is a

FIG. 6.



small air-pump, *d* a chloride-of-calcium-tube, which is connected, by the tube *g*, with a strong cylindrical tube *b*, containing the substance to be dried; this tube is placed in an iron or copper vessel containing a concentrated solution of chloride of zinc, which is heated nearly to the temperature at which the substance is decomposed. The thermometer *c* permits the regulation of the temperature. After the removal of the moist air by means of the air-pump, fresh air is allowed, from time to time, to enter the apparatus, by opening the stop-cock *f*, and being deprived of all moisture in its passage through the chloride-of-calcium-tube, effects the complete removal of the hygroscopic or combined water from the substance; the complete exsiccation of the latter, in this apparatus, requires only a very short time—a few minutes at most.

FIG. 7.



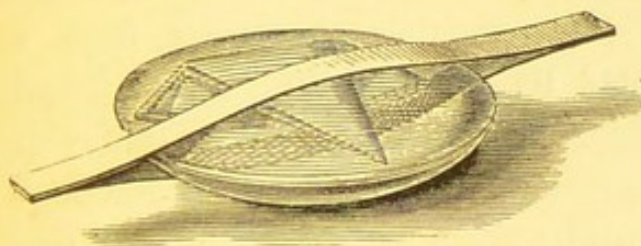
FIG. 8.



When the substance is dry, a certain quantity must be weighed out for analysis. This is best effected in a small, open, cylindrical, narrow tube, which is represented with its proper dimensions in FIG. 7. This tube may be laid horizontally upon the balance-pan, or may be placed in a small conical tube of tin-plate, the wider opening of which rests upon the pan; a foot to this stand is also very convenient, FIG. 8. The tube is weighed, a certain quantity of the substance introduced, and the weighing repeated; the increase of weight gives the amount of substance taken.

Or the tube containing the substance may be counter-balanced by weights in the other pan, the substance then emptied out, and the tube, with any portions which may adhere, replaced in the scale; the weight which must then be added, to restore the equilibrium, expresses the weight of the substance.

FIG. 9.



The weighing may also be conveniently effected between two watch-glasses, placed one above the other, and secured with a

brass clasp, as in FIG. 9.

It is necessary, however, always to avoid weighing in an open watch-glass, or in any wide open vessel. During the short time for which the tube remains in the balance, its form prevents any notable absorption of moisture, and even very hygroscopic substances suffer no increase of weight, during half an hour, under this simple arrangement.

We have now a known weight of substance; in order to determine the carbon and hydrogen contained in it, the carbon must be converted into carbonic acid, the hydrogen into water, and the weight of these products accurately ascertained.

In general, the substance, when dry and in powder, is mixed with oxide of copper; the mixture is heated in a glass tube, surrounded with red-hot charcoal. The combustion-tube is from 15 to 18 inches in length, and from $\frac{1}{3}$ to $\frac{1}{2}$ inch in diameter; one end of it is drawn out to a point, which forms an obtuse angle with the tube, and is hermetically sealed.

Cold oxide of copper absorbs water from the air with avidity; if it were necessary, therefore, to mix the organic substance with oxide of copper at the ordinary temperature, both these would have attracted moisture, which would add to the weight of the water formed by the combustion; hence it is necessary that it be most carefully and completely removed before the operation is commenced.

This is effected in the simplest manner by the arrangement, just described, for removing the water from a substance, at an elevated temperature, under diminished atmospheric pressure. Figs. 10 and 11 exhibit this arrangement. *A* is the air-pump, *B* the chloride-of-calcium-tube, *C* the combustion-tube, filled with the mixture; this is placed in a wooden trough *D*, and surrounded with sand heated to 120° . Before exhausting the air, the combustion-tube should be rapped several times, along its whole length, upon a table, so as to leave a clear space above the surface of the mixture; if we omit to give the air room to escape during the exhaustion, as soon as the air-pump is set in motion, a quantity of the mixture is carried into the chloride-

of-calcium-tube. The air is now exhausted from the tube, and dry air allowed to enter by opening the stop-cock *a*; when this has been repeated ten or twelve times, and it

FIG. 10.

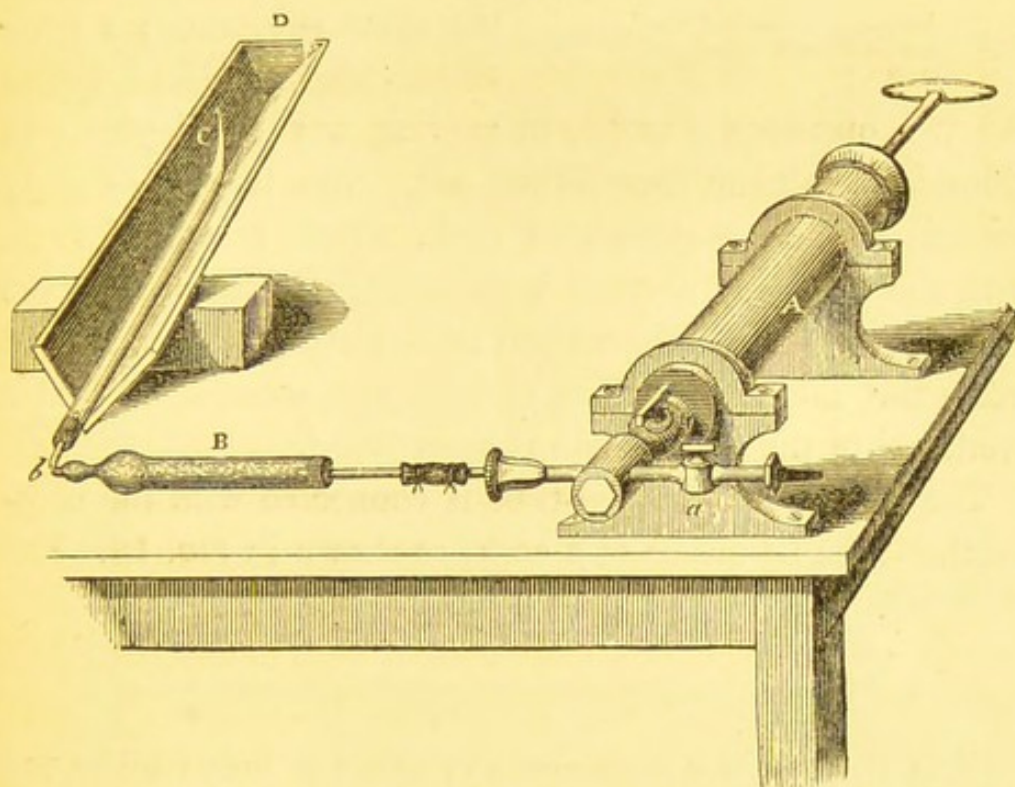
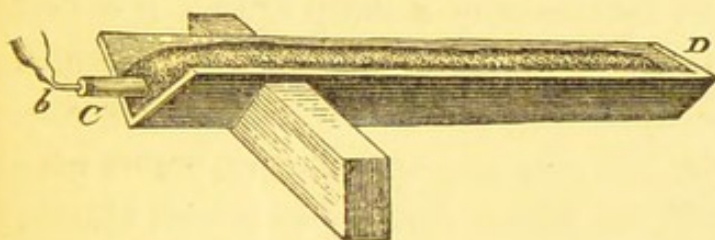


FIG. 11.



is found that no trace of moisture is deposited at *b* in the chloride-of-calcium-tube, even when that

spot is surrounded with cotton-wool moistened with ether, it may be concluded that the mixture is dry.

The operation of mixing the substance with pure oxide of copper, is performed in a clean, warm, porcelain mortar; the more carefully the substance is divided and mixed with oxide of copper, the more easily, rapidly, and completely, is its combustion effected.

The water formed during the combustion is received in the tube shown at FIG. 12, the bulb of which is filled with coarse fragments of fused chloride of calcium, and the long

FIG. 12.



tube, with coarse powder of the same substance; a little cotton-wool is placed before the two openings *a* and *b*, to prevent any small pieces of chloride of calcium from falling out. The tube *b* is tightly passed through a perforated cork, which is cut off flush with the tube, and covered with sealing-wax to prevent the adhesion of dust. The weight of the tube is known, and from the increase of this weight, the amount of water produced in the combustion is ascertained.

The chloride-of-calcium-tube is connected with the combustion-tube by means of a cork, as shown in FIG. 13. The

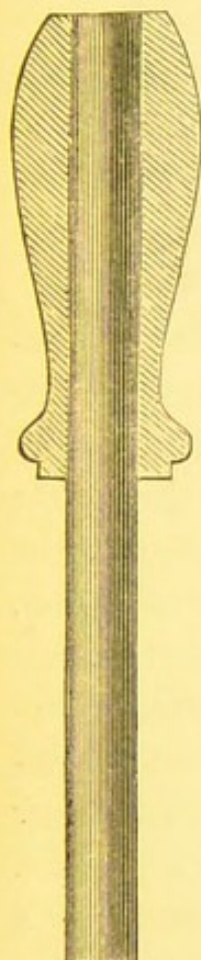
FIG. 13.



cork is perforated with a fine file, and the hole filed to the required size; the cork must be reduced so as to fit the opening of the tube, by means of a sharp knife; it is best to give it a cylindrical or somewhat conical form, which adapts itself to the aperture of the tube. The cork may also be perforated by the very appropriate cork-borers contrived by Mohr. These borers consist, as is well known, of sharpened cylinders of tin or brass, which are furnished, either with a wooden handle, or with a strong metal neck, perforated for the reception of an iron rod to serve as a lever. A set of such cork-borers is shown in FIGS. 14, 15, 16 and 17; FIG. 15 represents one in use; FIG. 16, a set of cork-borers nested; FIG. 17, the case in which they are kept; and lastly, FIG. 18 is a perforated brass-plate, the

holes in which correspond to the different cork-borers, so as to facilitate the selection of the borer required by a particular tube. The perforation of a cork by means

FIG. 14.



FIGS. 15, 16, 17.

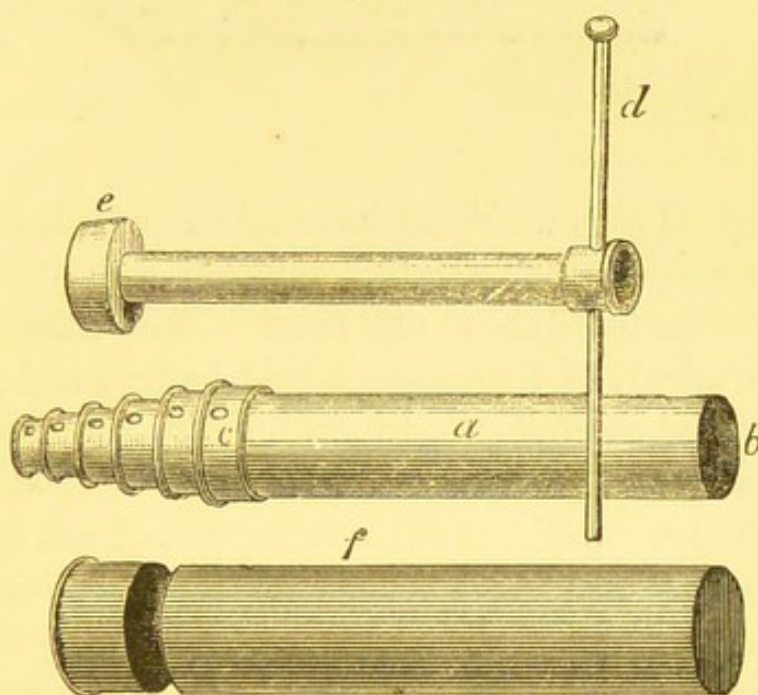
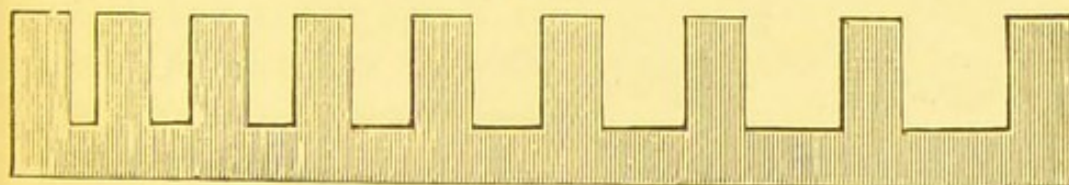


FIG. 18.

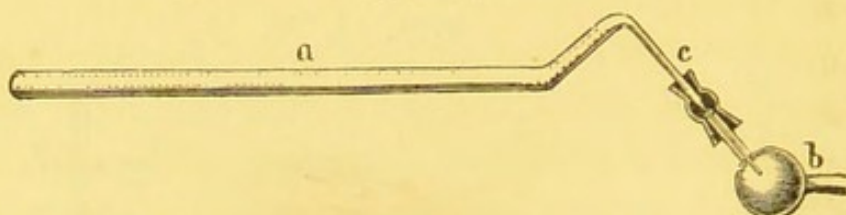


of a red-hot wire must be avoided, since small holes and flaws are thereby produced, which render the cork useless.

Some chemists, adopting the suggestion of Berzelius, give to the chloride-of-calcium-tube the form represented

in FIG. 19. The combustion-tube *a* is drawn out to a point *c*, which is engaged in the chloride-of-calcium-tube *b*, the two being connected by a small caoutchouc tube, tightly ligatured on each side. After the combustion, the point is

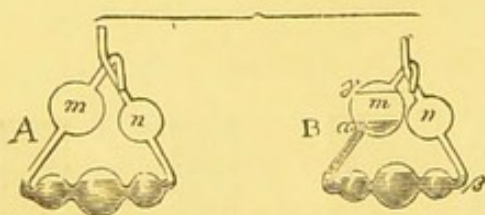
FIG. 19.



cut off at *c*, the caoutchouc tube removed, and the chloride-of-calcium-tube weighed, together with the point *c* of the combustion-tube; this point is then removed, ignited and weighed; if its present weight be then added to the weight of the chloride-of-calcium-tube before the combustion, and this sum be deducted from the weight after combustion, the true weight of the water produced will be ascertained.

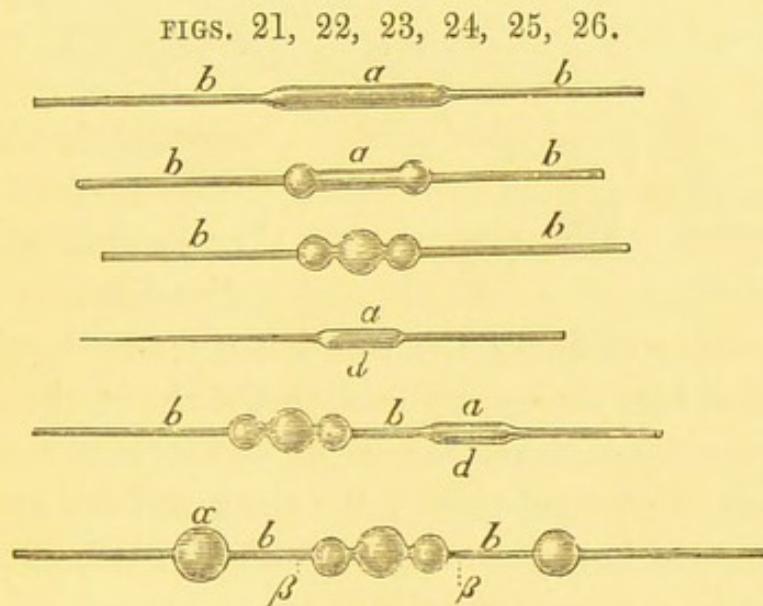
The carbonic acid produced in the combustion is received in the apparatus, FIG. 20, which is filled with solution of potassa in such a manner that a small bubble of air

FIG. 20.



may remain in each bulb. This apparatus consists of a glass tube in which five bulbs are blown, and is made in the following manner: A pretty strong glass tube, *a*, FIG. 21, 3 inches in length, and $\frac{1}{8}$ inch in diameter, is taken, and on to this are joined two barometer tubes, *bb*, $\frac{1}{8}$ inch in diameter; the opening of one of these tubes having been sealed, or stopped with wax, one end of the thick glass tube *a* is softened in the flame, and a bulb blown upon it; the opposite end is then treated in the same way,

as shown in FIG. 22; this being done, the centre portion is very strongly heated, and blown into a somewhat larger bulb, when the whole presents the appearance of FIG. 23. Another narrow piece of barometer tube, similar to the others, is now soldered on to a second piece of the wide tube, about an inch long; one of the openings is then drawn out to a point, FIG. 24, and cut off; this is joined with the tube *b*, FIG. 25, which is first cut off to within about 2 inches of the bulb. When the apparatus is so far completed, the tube *a* is expanded into a bulb, FIG. 26. The opposite end of the apparatus is finished in the same manner.



One of the bulbs may be somewhat smaller than the other, but one, at all events, must be large enough to hold more fluid than the centre bulb. The tubes are now heated at $\beta\beta$, close to the bulbs, FIG. 26, in a spirit-lamp flame, and bent at an angle of 45° , FIG. 27, *A*. These tubes are bent a second time at *a*, above the bulbs *m* and *n*, FIG. 27. We must observe here, that it is convenient to bend the tube *o*, which carries the larger bulb *m*, in such a manner,

FIG. 27.

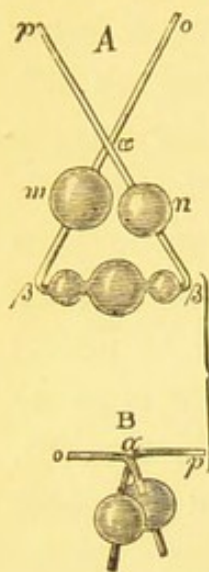
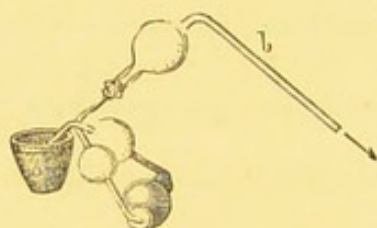


FIG. 28.



FIG. 29.



that its horizontal limb, which is connected with the chloride-of-calcium-tube, may be on the left of the operator. The tubes *o* and *p* should be heated at *a*, FIG. 27 *B*, and bent simultaneously, so that they clasp each other. If the operator has been guided strictly by FIGS. 27, *A* and *B*, he cannot fail to give the most convenient form to the apparatus. The sharp edges of the tubes *o* and *p* should be rendered smooth by fusion.

In order to fill this apparatus with solution of potassa, a small suction-tube, FIG. 28, is employed; one end of the apparatus is connected with this tube by means of a cork, whilst the other dips into an appropriate vessel containing the solution of potassa, which is then sucked into the apparatus with the aid of the mouth.

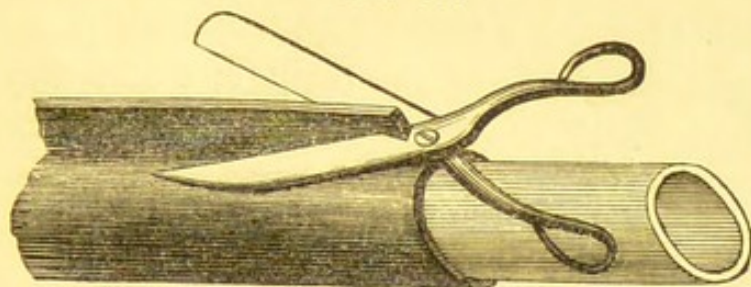
This having been done, the inside of the tube *o* is dried with a roll of blotting-paper; the clean and dry apparatus is then weighed, and connected with the chloride-of-calcium-tube by a tube of caoutchouc.

The bulbs, filled with potassa, weigh from 40 to 50 grms. (600 to 750 grns.) If the solution have a sp. gr. between 1.25 and 1.27, it does not foam, and its capacity of absorption is then greatest. Solution of soda foams like soap-water, and should therefore not be employed.

The caoutchouc tubes are made out of thin sheets of that material; a piece, of an inch and a half in length, is folded together at the edges so as to form a tube having

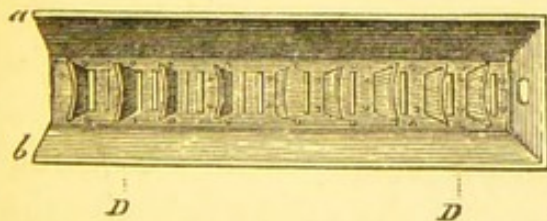
the same diameter as the tubes which are to be connected by it. The superfluous caoutchouc is then cut off from the edges, at one stroke, with a very clean pair of scissors, to within about $\frac{1}{10}$ inch of the tube, throughout its whole length, and the clean, freshly-cut edges thus left, are united by pressing together with the thumb-nails; lastly, the finished tube is to be stretched several times. If the

FIG. 30.



freshly-cut surfaces be touched with the fingers, they will not adhere at that spot. It is well to moisten slightly the inside of the caoutchouc before folding it, in order that the sides of the tube may not adhere. By making another tube of caoutchouc over the first one, a double connector is obtained, which is safer than the single tube. The connectors are tied with strong twisted silken cords, the ends of which are knotted, to prevent them from slipping. There are now extensively manufactured vulcanized caoutchouc tubes of appropriate diameters, which are even more convenient than those made in the laboratory.

FIG. 31.



The furnace in which the combustion of the substance is effected, is represented in FIG. 31; it is of sheet-iron, between 22 and 24 inches long, and 3 inches in height; the bottom is 3 inches in breadth, and is provided at inter-

vals of $\frac{1}{2}$ inch with slits, like a grating; the width of the furnace increases towards the upper part, and may be $4\frac{1}{2}$ inches at *a b*. The furnace stands upon bricks, in such a manner that the two first apertures are left open, while the others are closed by the bricks. If good combustion-tubes be at our disposal, the bricks may be dispensed with, and the furnace supported upon a tripod. The bottom of the furnace is furnished, at intervals, throughout its whole length, with

FIG. 32.



strong supports made of sheet-iron, as shown in FIG. 32; they are all of the same height, and correspond to the aperture in the anterior wall

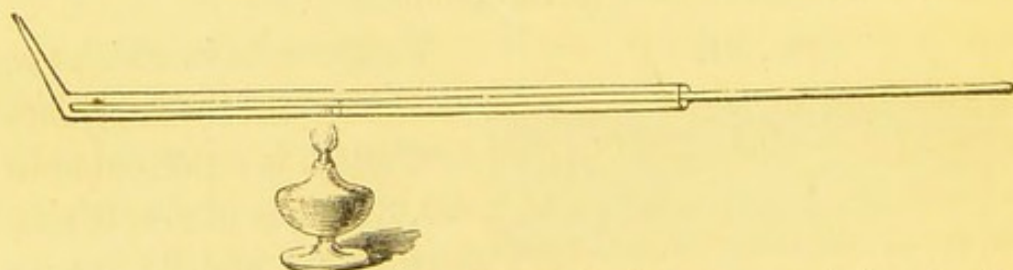
A of the furnace; upon these the combustion-tube rests.

If a strong fire be required, then, in order to increase the draught, the furnace may be a little inclined to one side, and maintained in that position by wedges of brick thrust under it in two places.

DETAILS OF THE PROCESS.

It is necessary to rinse the combustion-tube with water, and to dry it afterwards with blotting-paper, rolled round a glass rod; when the point has been drawn out and closed, the tube is made very hot, and a long narrow tube is introduced, so as to reach to the closed end, FIG. 33.

FIG. 33.



If air be now sucked out through the narrow tube, by the mouth, all the remaining moisture will be removed. The

dry tube should be rinsed out with some hot oxide of copper, which is then set aside. In order to obtain some idea of the quantity to be mixed with the substance, the tube is three-fourths filled with pure oxide of copper, which is taken out of the crucible in which it has been freshly ignited; care must be taken to avoid the admixture of any foreign substance with the oxide, since it is destined to be mixed with the substance to be burnt.

Solid substances are usually mixed in a hot, deep, porcelain mortar, with smooth, but unglazed sides; the mortar is first rinsed with pure oxide of copper, which is set aside; the substance is then projected into the mortar, and the little tube, in which it was weighed, carefully rinsed with oxide of copper; if the tube, with the substance, had only been counterpoised, it is set aside, after the substance is introduced into the mortar, and weighed again when the process of mixing is completed. The substance is first triturated with a little oxide of copper, mixed as intimately as possible with this, and afterwards, by degrees, with the whole of the oxide which has been introduced into the combustion-tube.

The mixing must be effected with the very least exertion, to admit of which, both the substance and the oxide of copper must be very finely powdered, the former previously to being weighed, the latter, before the second ignition. When the oxide of copper contains hard lumps, an intimate mixture cannot be effected; it then frequently happens that the pestle, striking against these, causes small portions of the mixture to be projected from the mortar. If the latter be placed upon a sheet of smooth white paper, it will be easily seen whether any of the mixture has been spilt.

The mixture is transferred from the mortar to the com-

bustion-tube, into which about half an inch of pure oxide of copper is first introduced ; the mortar is rinsed out with pure oxide of copper, which is also introduced into the tube, and the latter is then filled to within an inch of the mouth with pure oxide of copper. In FIG. 34, the portions

FIG. 34.



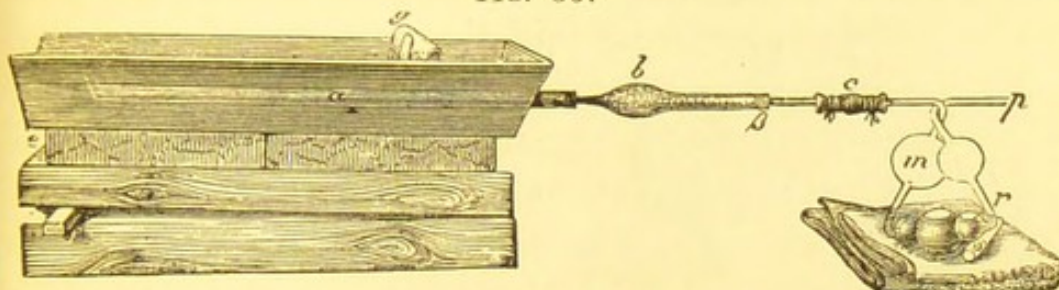
of the tube occupied respectively by the pure oxide, mixture, rinsing, and pure oxide again, are indicated by the dotted lines.

The cork which connects the combustion-tube with the chloride-of-calcium-tube, is gently struck with a light hammer, which renders it highly elastic ; when the perforation is finished, the cork should be dried for some hours in a water-bath, or better, in an air-bath at 120° ; when dried at a higher temperature, cork loses its elasticity, and becomes brittle ; it should not fit too easily into the mouth of the combustion-tube, and its compressibility allows the employment of a certain degree of force, without risk of breaking the apparatus.

The combustion-tube and chloride-of-calcium-tube must either be placed in a perfectly horizontal position, or inclined somewhat towards the potash-apparatus, in order that the water which collects in the narrow part of the chloride-of-calcium-tube may readily flow into the bulb ; for this purpose, the hinder part of the furnace may be raised somewhat higher than the front. FIG. 35 shows all the parts of the apparatus connected and arranged for the combustion. *a* is the combustion-tube ; *b* the chloride-of-calcium-tube ; *c* the caoutchouc connector, *m* the larger

bulb of the potash-apparatus, which is connected with the chloride-of-calcium-tube; *e* is a brick; *f* a piece of iron,

FIG. 35.



designed to give the requisite inclination of the furnace towards the potash-apparatus.

Before the combustion-tube is connected with the chloride-of-calcium-tube, it is smartly rapped, several times, along its whole length, upon a level table; particular attention must be paid to this point, so that an empty space may be left above the oxide of copper, for the escape of the gaseous products; otherwise it frequently happens, either that the oxide of copper is projected, or that the hinder end of the tube becomes stopped. Numerous experiments have shown that this arrangement does not render the combustion less perfect, however much carbon the substance may contain.

The anterior portion of the combustion-tube contains pure oxide of copper, which must be heated to bright redness before the charcoal is placed around that part which contains the mixture.

Before commencing the combustion, however, it is necessary, above all things, to ascertain whether all the joints are air-tight.

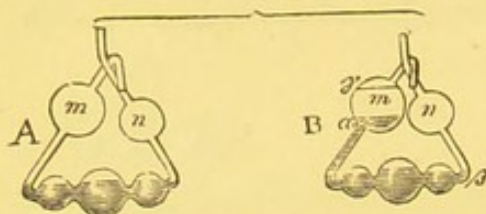
FIG. 36.



For this purpose, a little air is exhausted from the apparatus by the mouth, with the aid of the suction-tube, FIG. 36; as a natural consequence, when the suction

ceases, a certain quantity of potash-solution mounts into the tube, which carries the bulb *m*. The level of the liquid in this tube is therefore about $1\frac{1}{2}$ inches higher than that

FIG. 37.



in the opposite limb, as may be seen in FIG. 37, where *A* and *B* indicate the level of the solution. If the potash-solution does not retain this level for a certain period, but sinks

again into the centre part of the bulb, FIG. 37, it shows that the air re-enters the apparatus, either through the cork or the caoutchouc connector, which must therefore be changed.

The anterior part of the combustion-tube is now surrounded with red-hot charcoal; if the tube be perfectly dry, and contain no flaws, there is no fear of its cracking. If the oxide of copper be not perfectly dry, it will be readily seen by a more or less abundant deposition of moisture in the anterior empty portion of the tube, which projects an inch beyond the furnace; in this case, it may be expected that the determination of the hydrogen will be a little too high.

In order to prevent the falling of the charcoal, and to protect the rest of the tube from the action of the fire, a double screen, FIG. 35, *g* is made use of; this screen is made of strong sheet-iron, and corresponds to the front of the furnace; its form is shown in FIG. 38.

FIG. 38.



At the commencement, the screen is placed behind the anterior part of the combustion-tube, containing the pure oxide of copper; and when this part is heated to redness, the screen may be drawn back half an inch or an inch, and this portion of the tube surrounded with hot charcoal;

the distance through which the screen is withdrawn must depend upon the rapidity of the evolution of gas. In any case, so much ignited charcoal must be placed on at one time, that the tube, which is completely surrounded with it, may be rapidly heated to redness. Even when the evolution of gas is at first more rapid than is considered desirable, the charcoal should not be removed, since that step rarely moderates the evolution, and moreover is liable to render the combustion incomplete; the evolution of gas must be regulated by heating shorter portions of the tube.

In order to avoid the slightest loss of water, the anterior portion of the tube which projects out of the furnace, must, throughout the whole course of the combustion, be maintained at such a temperature, that no trace of water can condense upon it.

The combustion would proceed with the utmost regularity if we could deprive the glass of the combustion-tube of all power of conducting heat; this, however, is not the case; and we cannot be too careful to heat only very small portions of the tube at one time; the bubbles of gas must pass uninterruptedly, but without succeeding each other too rapidly. When there are not enough supports for the combustion-tube, it sometimes bends at one part; but no fear need be entertained lest it should be blown out, since the pressure of the liquid which the gas has to overcome is too slight to affect the softened tube.

The position of the potash-apparatus during the combustion is shown in FIG. 39. A wedge of cork *r* is placed under *s*, so that this part is somewhat higher than the other; the bulbs should be placed upon a pad or folded cloth. At the end of the operation, when the whole of the tube is surrounded with red-hot charcoal, the temperature

is raised throughout the whole length of the furnace, from

FIG. 39.

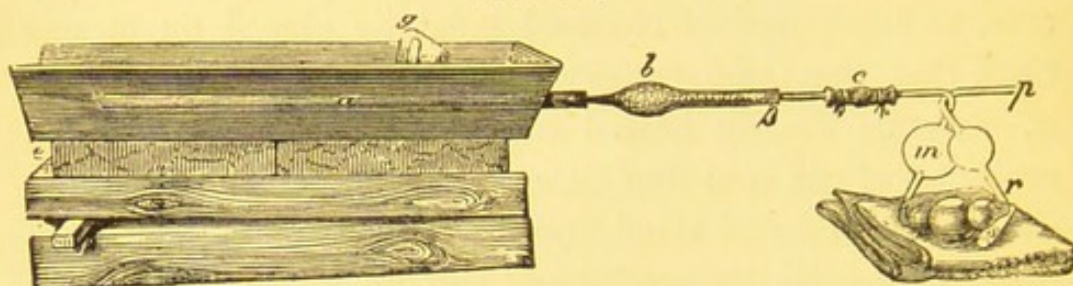
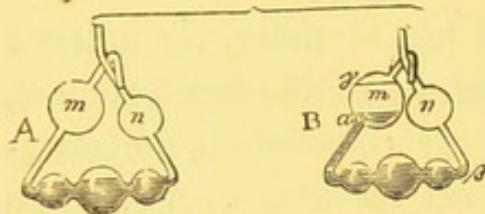


FIG. 40.



below, by giving the air access to the grating, and from above, by means of a fan. As soon as the evolution of gas slackens, the wedge of cork is removed, and the potash-apparatus placed in the position shown by FIG. 40, *A*.

At this juncture we may see whether the combustion has been complete or imperfect; if the evolution of gas ceases suddenly, then are we sure that the combustion was complete; if, on the other hand, it proceeds, at intervals, for a long time, the mixing was not performed with sufficient care, and we may reckon with certainty upon a loss in the carbon.

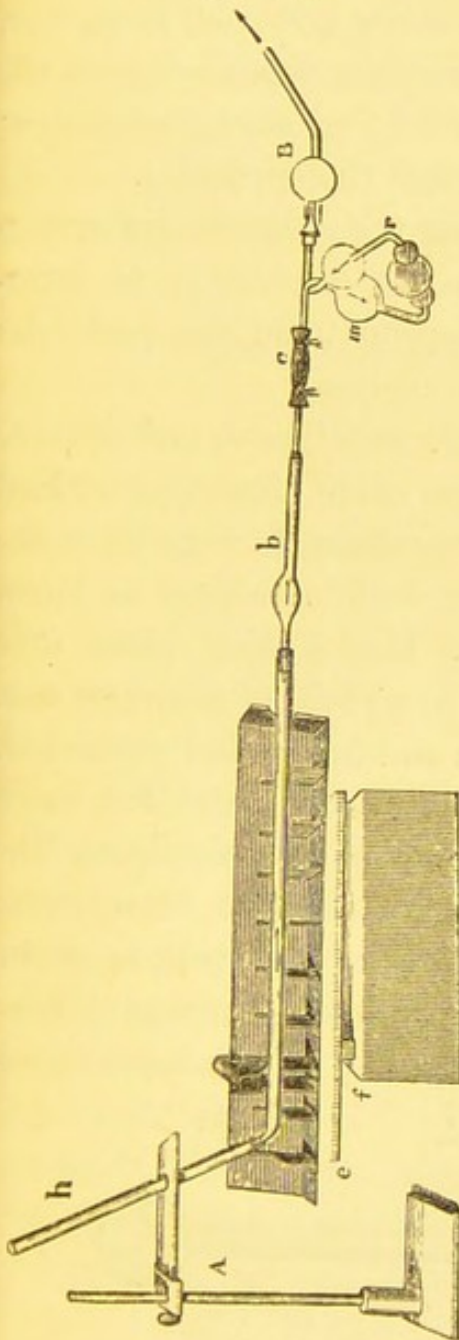
When no more gas is evolved, the solution of potassa mounts into the tube bearing the bulb *m*; the size of this bulb removes all danger of regurgitation of the liquid into the chloride-of-calcium-tube, leaving sufficient time for the remaining operations; for when this bulb is half full of fluid, the latter ceases to mount, since, the lower portion of the apparatus being horizontal, it is now half empty, and bubbles of air pass into the bulb *m*, FIG. 40, *B*. γ indicates the height to which the potash-solution may rise; when it reaches this point, the air at once enters.

FIG. 41.



The charcoal which surrounds the hinder portion of the tube and the bent point, is now removed, and the point is cut off. This is best effected by means of a pair of pincers, FIG. 41, with which the extremity of the point is nipped off.

FIG. 42.



A suitable tube, *h*, 15—20 inches long, is placed over the point, and supported by the stand, FIG. 42, *A*.

The orifice of the potash-apparatus is connected by means of a small perforated cork with the small suction-tube, (FIG. 29,) and a certain portion of air is drawn, by the mouth, through the potash-apparatus, which should now be replaced in the position which it had during the combustion. All the carbonic acid and aqueous vapour which had remained behind in the apparatus, are thus absorbed by the potassa and chloride of calcium. FIG. 42 shows the disposition of the apparatus at this moment. The potash-apparatus is raised a little at *r* in the left hand of the operator, while the suction-tube *B* is held in the right hand.

In a complete combustion, the air which is thus drawn

through the apparatus should not possess the slightest taste: if the combustion be incomplete, however, it will taste more or less empyreumatic; in the latter case, however, we cannot conclude with certainty that the analysis has been unsuccessful, since it often happens that two analyses agree perfectly with each other, although in one case the empyreuma was perceived, and not in the other.

If, in the combustion of substances very rich in carbon, a little of this element should have been deposited upon the reduced copper, this is afterwards burnt at the expense of the oxygen of the air drawn through the apparatus.

In the process just described for the estimation of carbon and hydrogen, it is advantageous in many cases to introduce a few alterations, which depend upon the particular characters of the substance to be analysed.

In the case of very hygroscopic substances, and of those which cannot be mixed with warm oxide of copper without danger of decomposition, it is necessary to proceed in the following manner: The oxide of copper is introduced, almost red-hot, into a wide glass tube terminating at one end in a globe of moderate size, FIG. 43; when the open end has cooled somewhat, it is closed air-tight with a cork, and the oxide of copper allowed to cool completely. The clean and dry combustion-tube is then introduced into the tube containing the oxide, as shown in FIG. 44, and a layer of 3 or 4 inches allowed to fall into it. The quantity of substance neces-

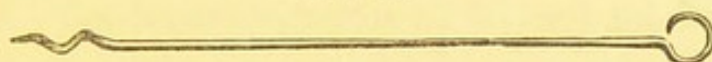


FIG. 44.



sary for the analysis is next projected, out of the tube in which it was weighed, into the combustion-tube, which is then closed with a cork; the little tube being again carefully weighed, we ascertain the amount of substance taken for the analysis. About 5 inches of oxide of copper are now introduced into the combustion-tube, in the same manner as before, care being taken to rinse down any particles of the substance which might have adhered to the sides. The next point is to obtain an intimate mixture of the substance with the oxide of copper, and this is effected by means of a bright iron wire twisted once round at the extremity, FIG. 45, which is continually turned whilst

FIG. 45.



it is drawn to and fro in the tube; in this way the mixing is generally completed in six minutes. Although by this process, which was first employed by Mitscherlich, and at a later period by Erdmann, Marchand, and Bunsen, the mixture cannot be effected so completely as in a mortar, the method nevertheless succeeds in most cases, especially if a stream of oxygen be passed through the tube at the close of the operation.

There are several substances in which it is impossible to estimate the carbon correctly by combustion with oxide of copper. Examples of these are the different varieties of coal, graphite, indigo, ulmin, and all similar substances. In the case of coal, for instance, the evolution of gas does not cease at the end of the combustion; it becomes gradually slower, but even after an hour, with a strong fire, the potassa does not go back.

The cause of this is undoubtedly to be found in the

irregular nature of the combustion. On the first application of heat, combustible gases are evolved, which reduce the oxide of copper in the immediate vicinity of each particle of substance, and there remains behind too large a quantity of carbon to be burnt by cementation.

In all these cases, the ordinary process of combustion must be modified; such substances must be burnt, either with chromate of lead, or with oxide of copper and oxygen gas.

COMBUSTION WITH CHROMATE OF LEAD.

Chromate of lead presents many advantages over oxide of copper for combustion. It is not hygroscopic, and may therefore be mixed with the substance, in a slightly warm mortar, without fear of its attracting moisture. Moreover, since it fuses at a red-heat, it comes into closer contact with the substance to be burnt, than the infusible oxide of copper; lastly, at a strong red-heat, it gradually evolves oxygen gas, which consumes any particles of carbon which may have separated. Addition of $\frac{1}{10}$ of its weight of bichromate of potassa furnishes a still more efficient agent of combustion.

In employing chromate of lead instead of oxide of copper, we proceed according to the method first described. Before every analysis, the chromate of lead is heated in a porcelain capsule, over the spirit-lamp, until its brownish-yellow colour has changed to a dark yellowish-red; it is then allowed to cool somewhat, and mixed, in a warm mortar, with the organic substance. The mixture is now introduced into the combustion-tube, in which a layer of an inch of chromate of lead has been previously placed; the mortar is rinsed out with chromate of lead, which is also transferred to the combustion-tube, and the latter is lastly filled

to within an inch, with chromate of lead. It is also well, after introducing the mixture and rinsings, to fill up the combustion-tube with strongly ignited lumps of oxide of copper, which present a larger surface to the gases evolved in the combustion, than the chromate of lead, especially when the latter is in a state of fusion.

The combustion with chromate of lead is conducted in the ordinary manner. The anterior portion of the tube is heated to redness, but so as not to fuse the chromate of lead. The mixture of chromate of lead with the organic substance, however, should be heated till the former fuses, and ultimately, till it evolves oxygen gas, which is seen to pass in small bubbles (unabsorbed) through the potash-solution. The high temperature necessary for this purpose can be supported only by very good tubes of Bohemian glass. With glass of inferior quality, it is advisable to surround that part of the combustion-tube which is to be very strongly heated, with a thin sheet of copper, secured by an iron wire twisted round the tube.

COMBUSTION WITH OXIDE OF COPPER AND OXYGEN GAS.

Organic substances, which cannot be reduced to a fine powder, or which are exceedingly rich in carbon, are most conveniently burnt in such a manner that, after coarsely mixing the substance with oxide of copper, the volatile portions may be transformed into carbonic acid and water, and the residual carbon subsequently converted into carbonic acid by passing a stream of oxygen gas over it. This may be effected in different ways, since the oxygen may either be evolved in the tube itself, or may be passed through the tube from a gas-holder. The latter process requires a very complicated apparatus, which has been

described, with different alterations, by Hess, Dumas and Stass, Erdmann and Marchand, and Wöhler.

a) *Combustion with Oxide of Copper and Chlorate or Perchlorate of Potassa.*

When it appears necessary to complete the combustion in oxygen gas, this may be evolved, most simply, in the tube itself, either from chlorate of potassa, or, according to Bunsen's proposal, from the perchlorate. For this purpose, we introduce into the end of the combustion-tube, a layer of $1\frac{1}{2}$ inch of a mixture of 1 part of chlorate of potassa and 8 parts of oxide of copper, which is first gently heated over the spirit-lamp, and introduced while yet warm. This is followed by $\frac{1}{2}$ inch of pure oxide of copper, and the tube is then filled as usual with the mixture of oxide of copper with the substance to be burnt, and lastly with pure oxide of copper. When perchlorate of potassa is employed, it is introduced in a fused state, and while yet warm, into the end of the tube, and is kept separate from the oxide of copper and the mixture, by a freshly ignited plug of asbestos.

The combustion is completed in the usual manner; at its termination, heat is gradually applied, by means of red-hot charcoal, to that portion of the tube which contains the chlorate or perchlorate of potassa. The evolved oxygen sweeps the carbonic acid before it, consumes the residual carbon, and re-oxidises the reduced copper, while the excess of this gas passes unabsorbed, in small bubbles, through the potash-apparatus. If so much oxygen is evolved that a great number of bubbles pass undiminished through the potassa, it will be unnecessary to break off the point, and to draw air through the tube. If, however, this has not been the case,

a part of the carbonic acid is still left in the chloride-of-calcium-tube and in the combustion-tube, so that the point of the latter must be broken off, and air drawn through the apparatus in the usual manner. Since, in the first case, the chloride-of-calcium-tube and potash-apparatus are filled with oxygen, this must be displaced by sucking a little air through them before weighing. In all cases where oxygen gas is employed, it is advisable to connect with the potash-apparatus, a small tube, 2 inches long, filled with hydrate of potassa, which retains any water carried away from the potash-solution by the gas passed through it. This little tube is drawn out to a point at one extremity, the other being connected, by means of a cork covered with sealing-wax, with the potash-apparatus, so that both may be weighed together. It is seldom necessary to change the hydrate of potassa in this tube.

b) *Combustion with Oxide of Copper and Oxygen Gas, according to the process of Hess,* modified by Erdmann and Marchand.†*

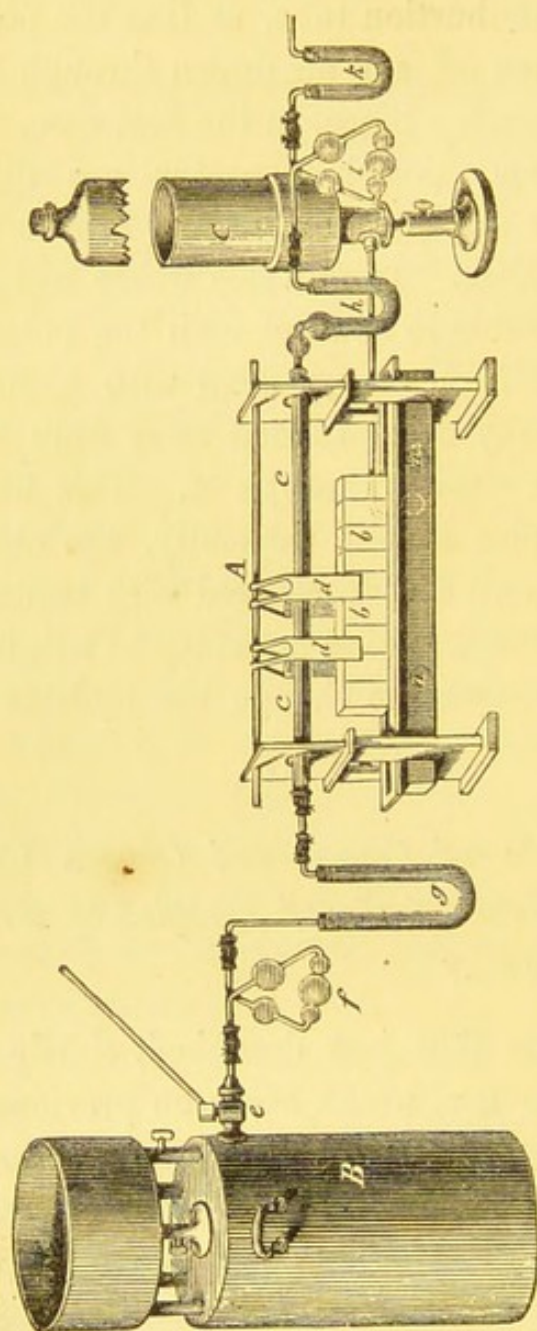
This process differs from that just described, chiefly in the employment of oxygen gas, which has been previously collected in a gas-holder, and in the use of a spirit-flame instead of a charcoal fire for heating the combustion-tube.

The annexed figure (46) exhibits the apparatus employed by Hess. The combustion-tube *cc* lays in a narrow trough of sheet-iron, upon a bed of calcined magnesia; to the anterior extremity of the tube is attached, by means of a

* Description of the lamp-apparatus by Hess. Pogg. Ann. XLVI, 179.

† Journ. f. Pract. Chem., XXVII, 129.

FIG. 46.



oxygen to be regulated at will. The combustion-tube is heated by means of the lamp-apparatus *A*. The trough *aa*, resting upon a frame-work at each end, is half filled with spirit which is replaced, in measure as it is consumed, from the adjoining vessel *c*, furnished with a tube which

cork, the chloride-of-calcium-tube *l*, which is connected with the potash-apparatus *i*, and lastly with a tube *k*, filled with hydrate of potassa. The oxygen enters into the hinder end of the combustion-tube from the gas-holder *B*, after passing through a bulb-apparatus filled with concentrated sulphuric acid, and afterwards through a U-tube, containing fragments of hydrate of potassa, whereby it is freed from aqueous vapour and carbonic acid; the narrow tube conveying the oxygen is connected with the combustion-tube by means of a cork. The stop-cock *e*, furnished with a long lever, allows the flow of

opens beneath the level of the spirit in the trough. Within this trough, stand several wick-holders *bb* of tin-plate, which carry flat wicks, having nearly the same breadth as the trough. Above these, a cross-piece supports an equal number of screens *dd*, which retain the heat and answer the purpose of chimneys.

In filling and preparing the tube, Erdmann and Marchand introduce into the anterior portion a thick plug of fine copper turnings; the tube is then two-thirds filled with oxide of copper, and connected with the potash-tube *g*. They now pass through the combustion-tube, from another gas-holder, a stream of atmospheric air, which is deprived of water and carbonic acid, by passing through the bulb-apparatus *f*, and the potash-tube *g*; the tube is then heated to redness. When the greater part of the moisture has been thus removed, a chloride-of-calcium-tube is attached in front by means of a cork, and the combustion-tube heated to full redness in the stream of dry air, after which the lamp is gradually extinguished, and the tube allowed to cool in the slow current of air.

In this process we must have recourse to the method of mixing the substance to be analysed, with the oxide of copper, in the tube itself. The quantity of substance to be employed for the combustion is projected into the tube from a small, rather long tube, closed at one end; the substance is then mixed (generally somewhat coarsely) with the oxide, by means of an iron or brass wire twisted, corkscrew fashion, at one end. When the wire is withdrawn, the hinder part of the combustion-tube is filled with oxide of copper, which should have been previously ignited in a crucible, and allowed to cool in a closed tube. The com-

bustion-tube is then rapped upon the table in order to clear a passage. Care must be taken that the tube is not filled to within 4 or 5 inches of its hinder extremity, as this must always be kept cold.

The mode of conducting the combustion requires some attention. After the weighed chloride-of-calcium-tube and potash-apparatus, together with the potash-tube, have been connected with the combustion-tube in the usual manner, the anterior portion of the tube is ignited by one of the wicks, while another is lighted at the hinder end of the tube, so as to heat to redness the oxide which it contains. By gradually removing one wick, and kindling a fresh one, we advance towards the mixture of the organic substance with oxide of copper; and by then allowing a slow, gradually increasing stream of oxygen to flow through the tube, the aqueous vapour and carbonic acid are prevented from passing back into the drying tube. The stream of gas, however, should not be so strong as to force oxygen gas through the potash-apparatus. When the tube is ignited throughout its whole length, and no more gas is evolved, the stream of oxygen is increased so that it may begin to pass in bubbles through the potash-apparatus. The stop-cock is now closed, the lamps extinguished, the oxygen gas-holder replaced by another containing atmospheric air, from which a slow stream is passed through the apparatus until it is cold. The increase of weight of the chloride-of-calcium-tube gives the amount of water formed, and the sum of the weights gained by the potash-apparatus and the potash-tube expresses the quantity of the carbonic acid.

After the termination of the first combustion, the tube is ready for a second without farther preparation.

It is obvious that for this combustion in oxygen, we may replace the lamp-apparatus (which consumes about 1 litre (1.76 pint) of spirit in each operation) very well by an ordinary combustion-furnace with a charcoal-fire.

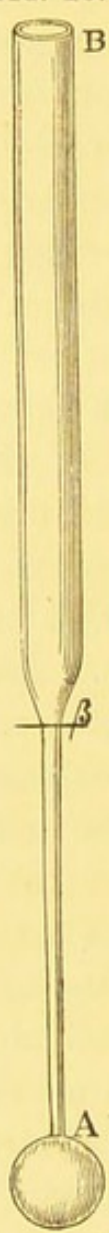
The method employed by Wöhler, for combustions with oxide of copper and oxygen gas, differs somewhat from that just described. The combustion-tube is drawn out to a strong straight point, and a layer of several inches of strongly ignited oxide of copper, cooled in a closed tube, is introduced. This is separated from the rest of the tube by a plug of ignited asbestos, and the weighed organic substance is then introduced in a little platinum tray, which is followed by another plug of asbestos, so that the tray is nowhere in contact with oxide of copper. Lastly, the empty portion of the tube is filled with strongly ignited and cooled oxide of copper; the chloride-of-calcium-tube and the potash-apparatus, together with the potash-tube, are then attached. The hinder end of the tube is connected, by a tube of caoutchouc, with an oxygen gas-holder, in the manner shown at FIG. 46, so that the gas may be freed from moisture and carbonic acid by passing through concentrated sulphuric acid and hydrate of potassa. The combustion is conducted, as usual, in a combustion-furnace, with a charcoal fire. When the anterior portion of the tube is heated to redness, heat is applied to the spot occupied by the platinum tray, oxygen gas being slowly passed through the apparatus. At the end of the combustion, the stream of oxygen is increased, and the operation is concluded by passing a stream of air, dry and free from carbonic acid, in order to displace the oxygen.

If the organic substance, which was burnt, contained any

FIG. 47.



FIG. 48.



non-volatile inorganic matters, these remain behind, in an oxidised state, in the little platinum tray, and may be estimated in the same operation.

COMBUSTION OF VOLATILE LIQUIDS.

The analysis of this class of substances is the easiest and simplest, giving also the most accurate results, so that beginners will do well to occupy themselves, at first, entirely with the combustion of such substances.

The liquids are weighed in sealed glass bulbs, which are made in the following manner: A piece of barometer tube, 12 inches long, and $\frac{1}{4}$ inch in diameter, is drawn out before the lamp to a long point *c*, FIG. 47, which is then used as a handle in order to draw off a small piece of tube with a long stem. The long point *c* is drawn off at *d*, and the piece of tube *A* softened in the flame and blown out to a bulb, FIG. 48, by forcing in air at *B*. The tube is then cut off at β ; any required number of bulbs may be made in this way out of one length of glass tube. The moisture from the mouth does not enter the bulbs, on account of the length of the glass tube *B*.

It is obvious that the piece of tube *A* need not be expanded if it be already sufficiently large. The neck of the bulb should be 1 to $1\frac{1}{2}$ inch

long: its sharp edge must be rounded in the flame, lest any splinters should be detached from it in filling the bulb.

In order to introduce the liquid, the bulb is warmed, and its open point dipped into the liquid, a certain quantity of which enters as the bulb cools; it is then again heated, when the vapour expels the greater part of the air, and, on immersing the point a second time in the liquid, this fills the globule to about three-fourths. The point is then sealed in the blowpipe flame.

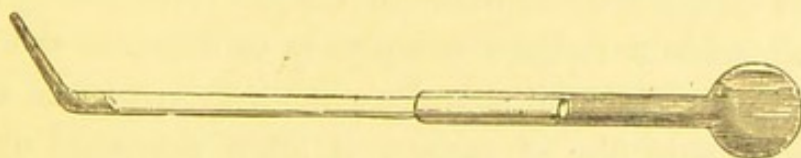
FIG. 49. The weight of the liquid is ascertained by deducting the weight of the empty bulb from that of the bulb when filled with liquid.



Before weighing the liquid, the analyst should have heated the oxide of copper to bright redness, and transferred it, still red-hot, from the crucible into the glass tube, FIG. 49, which is then stopped with a dry cork, and allowed to cool completely. It is less convenient to allow the crucible to cool beneath a bell-jar over concentrated sulphuric acid.

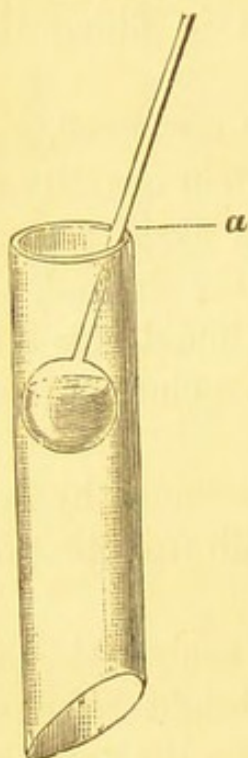
The tube, FIG. 49, should be sufficiently wide to allow the combustion-tube to be introduced into it with facility. A layer of about 1 or $1\frac{1}{2}$ inch of the perfectly dry oxide of copper is first allowed to fall into the tube, as shown in FIG. 50; the glass bulb is then to be imbedded in the

FIG. 50.



oxide of copper, in such a manner that the latter may not

FIG. 51.



attract any moisture during the operation. In order to effect this, a deep file-mark is made in the middle of the stem (at *a*, FIG. 51) and the bulb being introduced into the orifice of the combustion tube, the point is broken off, and both bulb and point are allowed to fall into the tube.

Two bulbs are sufficient, containing from 400 to 500 milligrammes (6.2 to 7.7 grains) of liquid; the bulbs are separated from each other by a layer of 2 or 3 inches of oxide of copper. If the combustion-tube is 18 inches long, there will be a layer of 11 or 12 inches of oxide of copper in front of the second bulb. FIG. 52 shows the bulbs surrounded with oxide of copper.

FIG. 52.



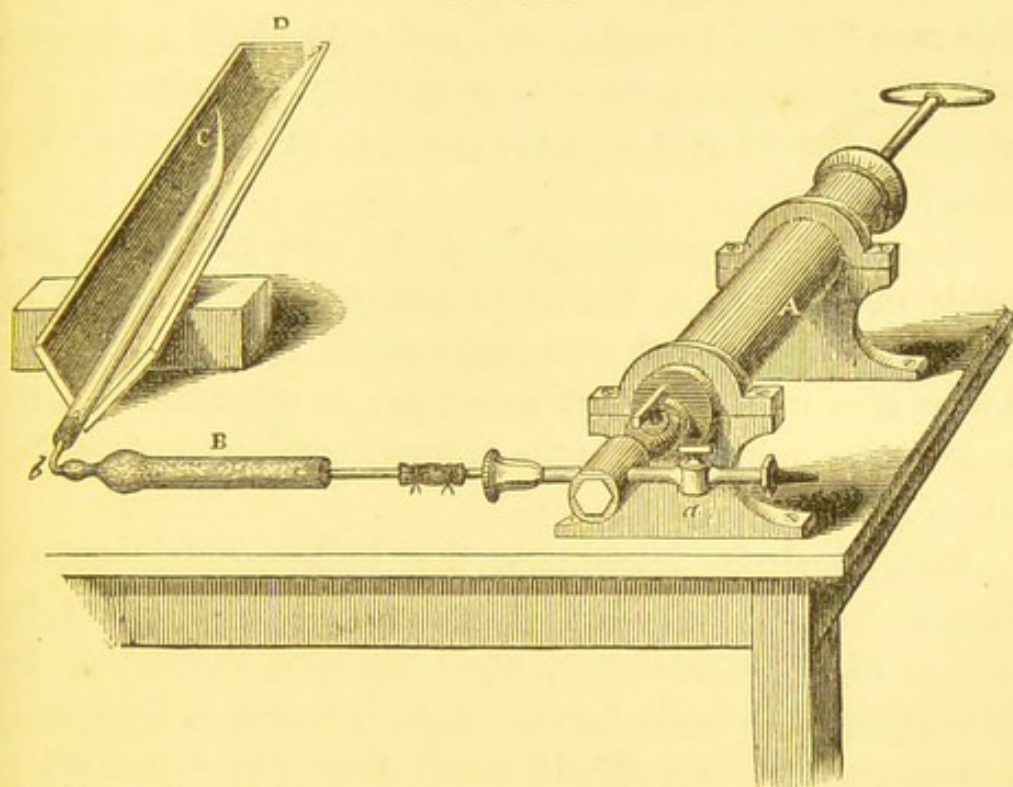
Liquids which have a high boiling-point, and are very rich in carbon, should be distributed among three bulbs, containing altogether not more than from 500 to 600 milligrammes (7.7 to 9.3 grains); they are separated from each other by a layer of oxide.

This precaution must not be omitted in the case of ethereal oils, since the oxide of copper immediately around the bulb seldom suffices completely to consume the vapour which issues from it; and, when the oxide is entirely reduced, a thin film of carbon is often deposited upon the metallic copper. Although this carbon is oxidised and

converted into carbonic acid when air is passed through the tube after the combustion, it is nevertheless better not to rely upon this mode of retrieving the error.

In the case of liquids which are not very volatile, the bulbs may be emptied before the combustion. For this purpose, the combustion-tube, when filled, is connected with the air-pump, as in FIG. 53, and the air rarified by a

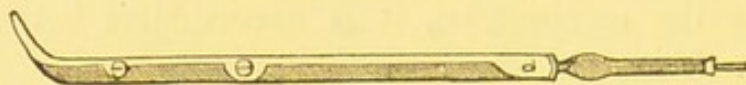
FIG. 53.



single stroke of the piston, when the bubbles of air within the bulbs are expanded, all the oil being forced out, and absorbed by the surrounding oxide of copper.

In the combustion of very volatile liquids, a second screen is placed over the spot where the first globule is situated, FIG. 54, in order to protect it from the heat whilst the anterior portion of oxide of copper is heated to redness; it is always better not to heat this portion all at once, but to surround it gradually with red-hot coals, commencing in front.

FIG. 54.



A red-hot coal should be allowed to remain, from the commencement, under the point of the combustion-tube, in order to prevent the liquid from condensing there, whence it can be expelled again only by a strong heat; in this case it boils tumultuously, and with slight explosions, when it easily happens that a quantity of unburnt substance is carried over with the gases, in the form of a white cloud.

As soon as the anterior part of the tube, containing pure oxide of copper, is heated to redness, the screen is removed, and a red-hot coal approached, from time to time, to the spot where the first bulb lays; in other respects, the process is conducted as in the ordinary combustion described above.

Mitscherlich introduces the bulbs containing the liquid, unopened, into the combustion-tube, and, in the course of the combustion, heats the spot where they are placed until the bulbs burst. It is, however, indispensably necessary, that this should result from the expansion of the liquid, and not from the tension of the vapour, since in the latter case it is impossible to avoid a sudden extrication of vapour which may even burst the combustion-tube. Hence the globules which are to be introduced, sealed, into the combustion-tube, should be drawn out to a very fine long point; they must be almost entirely filled with the liquid, and sealed with a pointed blowpipe-flame.

For the combustion of liquids in a stream of oxygen, according to the process of Erdmann and Marchand,

sealed bulbs must always be employed. With substances which are easily volatile, such as ether, it is impossible to avoid explosions; so that this method is not applicable for the analysis of substances of this class.

When it appears necessary, therefore (in the case of liquids very rich in carbon), to complete the combustion in a stream of oxygen, a layer of chlorate or perchlorate of potassa is introduced into the end of the tube, as described at p. 32; the combustion having been terminated in the usual



manner, the oxygen is evolved in the tube itself, by applying heat to the chlorate or perchlorate of potassa.



Fat oils are weighed in the small glass tube, FIG. 55, which is placed, during the weighing, in the foot, FIG. 56, made of tin-plate.

A layer of two inches of oxide of copper having been introduced into the combustion-tube, the little tube containing the oil is dropped in, its mouth still unclosed. The operator now inclines the combustion-tube, so that the oil may flow out, and should endeavour to distribute it over the sides of the combustion-tube, throughout the half of its length; the tube is then filled, as described at p. 40, with pure oxide of copper.

Substances which are easily fusible can be treated exactly in the same manner.

Those substances which are fusible, but cannot be mixed in a mortar, such as wax, &c., are introduced, in weighed fragments, into the clean combustion-tube which is then closed with a cork, and gently heated till the substance fuses, when it is to be spread over the inside of the tube

for three-fourths of its length from the closed end; when cool, the tube is filled with oxide of copper.

Organic substances of this description may also be weighed in a vessel shaped like a small boat, FIG. 57, which

FIG. 57.



may be easily made by softening a piece of glass tube $\frac{1}{4}$ inch in diameter, drawing it upwards in two places, and afterwards splitting it with a red-hot point of charcoal. In the combustion of bodies belonging to this class, we must make choice of tubes having a greater length and diameter than those employed for ordinary combustions.

MODIFICATIONS OF THE PROCESS FOR ORGANIC ANALYSIS IN PARTICULAR CASES.

The method described above enables us to determine the carbon and hydrogen in all organic substances which contain *only* carbon, hydrogen, and oxygen. Organic substances, however, frequently contain other elements, which are either essential constituents of the organic compound, like the nitrogen and sulphur contained in many animal matters, or are only united with them to form an easily decomposable combination, like the metallic oxides in the salts of organic acids. The general process for the determination of the carbon and hydrogen in such substances is the same as that already described; but there are certain modifications necessary (dependent upon the nature of the other elements present), which we are now about to notice in detail.

DETERMINATION OF CARBON AND HYDROGEN IN
NITROGENISED ORGANIC SUBSTANCES.

The presence of nitrogen in a substance is indicated, in the determination of the carbon, by the passage of unabsorbed bubbles of gas through the potash-apparatus during the whole course of the combustion. Most nitrogenised substances, when burnt with oxide of copper, evolve their nitrogen in the uncombined state, mixed with the carbonic acid and water produced in the combustion; other substances, however, especially such as contain nitric acid, or, above all, a large quantity of oxygen, give rise to the production of binoxide of nitrogen, which is partly absorbed by the potassa, and thus causes an error in the determination of carbon. In such a case, the taste of the binoxide of nitrogen will be distinctly perceived in the air drawn through the apparatus after the combustion.

It is well, therefore, to ascertain the presence or absence of nitrogen in the substance, previously to the combustion, and this may be effected by different methods.

Most substances containing nitrogen, when heated with hydrate of potassa or soda-lime, evolve ammonia, which may be easily recognised by its odour or by the well-known reagents. A small portion of the substance is fused in a test tube with from four to ten times its weight of hydrate of potassa, when, if a distinct odour of ammonia be obtained, the presence of nitrogen may be inferred. Small quantities of nitrogen (2 to 3 per cent) in organic substances cannot be detected with certainty by this method; but so small an amount as this would have no influence upon the determination of carbon.

According to Lassaigne, the smallest quantity of nitrogen may be detected in an organic substance by the following method: A portion of the substance is fused in a test tube with a small fragment of potassium; on cooling, water is added, and the solution heated to boiling with partly oxidised sulphate of iron; the solution is now acidified with dilute hydrochloric acid, when a blue precipitate (Prussian blue) indicates the presence of nitrogen. When a very small quantity of this element is present, only a tinge of bluish-green is imparted to the solution.

In those substances which contain nitric acid or other oxides of nitrogen, that element cannot be detected with certainty by heating with hydrate of potassa. Such substances, for the most part, evolve red vapours when heated alone; if such matters be mixed with a little potassa, they deflagrate when heated.

When the presence of nitrogen in the substance to be analysed has been ascertained by one or other of these methods, we must endeavour, in the combustion, to avoid the error arising from the binoxide of nitrogen, both by preventing, as far as possible, the formation of that compound, and by decomposing any which may be formed. Numerous observations have proved, that the more slowly the combustion proceeds, the less binoxide of nitrogen is formed. Far more of this compound is produced in the combustion with chromate of lead or in a stream of oxygen, than with oxide of copper. The two former methods must therefore be avoided in the analysis of nitrogenised substances, and the combustion conducted, as slowly as possible, with oxide of copper.

Bin oxide of nitrogen is completely decomposed by red-hot copper, oxide of copper being formed, and nitrogen set

free; the binoxide of nitrogen produced in the combustion may therefore be decomposed by passing over ignited copper. For this purpose, in the combustion of nitrogenised substances, a longer combustion-tube is selected, and filled, as usual, with the substance and oxide of copper, to within 5 inches of the anterior end, into which is introduced a layer of copper-turnings, or a roll of thin sheet-copper.

It is important that the copper-turnings or the copper sheet should present a clean metallic surface, to ensure which, they are heated in the air until they become coated with black oxide, which is then reduced by heating the metal in a stream of hydrogen. It is well, after heating the copper-turnings in the air, to give them a cylindrical form by pressing them into a tube, so that they may afterwards be more easily introduced into the combustion-tube. Since the finely divided metallic copper condenses much water upon its surface, it should be transferred immediately from the hot air- or water-bath to the combustion-tube.

In the combustion, the metallic copper in the anterior part of the tube must first be heated to redness, and the application of heat subsequently proceeded with in the usual manner. During the whole period of the combustion, the metallic copper must be maintained at a *bright red* heat, since, in this case only, will it decompose the binoxide of nitrogen. If much binoxide of nitrogen be produced (as, for example, in combustions with chromate of lead), it is scarcely possible, even with a long layer of copper-turnings, to decompose the whole of it.

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC
SUBSTANCES CONTAINING SULPHUR.

Organic substances which contain sulphur, such as the xanthates, taurin, &c., when burnt with oxide of copper, evolve sulphurous acid, which is absorbed by the solution of potassa, and increases its weight.

The presence of sulphur in an organic substance may always be ascertained by fusing it with hydrate of potassa and a little nitre. This gives rise, in all cases where sulphur is present, to the formation of sulphate of potassa, which gives a white precipitate with chloride of barium after supersaturation with hydrochloric acid.

The error arising from the formation of sulphurous acid may be easily avoided by introducing a small tube, filled with binoxide of lead, between the chloride-of-calcium-tube and the potash-apparatus. The binoxide retains the sulphurous acid in the form of sulphate of protoxide of lead.

A concentrated aqueous solution of chloride of calcium, such as is formed in the tube containing that salt, does not absorb sulphurous acid, especially if it be allowed to remain until all the water has become solid—that is, until the hydrated chloride of calcium has crystallised.

The tube containing the binoxide of lead should not be introduced between the combustion-tube and that containing chloride of calcium.

In the combustion with chromate of lead, generally speaking, no sulphurous acid is produced; and it is only in the case of substances very rich in sulphur that a tube with binoxide of lead is necessary.

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC
SUBSTANCES CONTAINING CHLORINE.

When organic substances containing chlorine are burnt with oxide of copper, the determination of hydrogen is often inaccurate, since the chloride of copper which is formed volatilises, and is deposited in the chloride-of-calcium-tube.

The chlorine may be contained in organic substances, either in the form of hydrochloric acid, as an oxygen-compound of chlorine, or as an essential constituent of the organic substance; in which last case, the chlorine can be detected only after destroying the organic matter. In order, therefore, always to detect chlorine with certainty in organic compounds, they are fused with pure hydrate of potassa, and the chlorine subsequently detected by means of a solution of silver.

In order to avoid the error above alluded to in the hydrogen-determination, chlorinated organic substances are burnt with chromate of lead; chloride of lead is then formed, which is not in the least volatile.

The combustion of chlorinated substances in oxygen gas is liable to error from another cause. The chloride of copper formed in the combustion-tube is decomposed by the oxygen, with evolution of chlorine, which increases the weight both of the chloride-of-calcium-tube and of the potash-apparatus. To obviate this, Städeler* proposes to introduce into the anterior portion of the tube, a quantity of metallic copper (as in the combustion of nitrogenised substances), which is maintained at a red heat during

* Annal. d. Chem. u. Pharm. LXIX, 335.

the combustion. The liberated chlorine then combines with the copper, and the stream of oxygen must be arrested as soon as the anterior portion of the metal begins to oxidise.

DETERMINATION OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES WHICH CONTAIN FIXED INORGANIC MATTERS.

If an organic substance, when ignited in air, leaves a residue which evolves carbonic acid on treatment with hydrochloric acid, the analysis of this substance, by combustion with oxide of copper, would be inaccurate, because the whole of the carbonic acid would not pass into the potash-apparatus. This is especially the case in the compounds of organic acids with the alkalies or alkaline earths. It has been shown that, in these cases, a neutral carbonate is not left in the residue, but that the quantity of carbonic acid retained by the base depends upon accidental circumstances. In order, on these occasions, to obtain the whole of the carbonic acid, in the combustion with oxide of copper, a quantity of ignited phosphate of copper, or some teroxide of antimony, is added to the mixture of the organic substance with oxide of copper; in other respects, the process is conducted in the usual manner.

It is better, however, to burn the salts of organic acids with alkalies or alkaline earths, with the aid of chromate of lead, when the chromic acid expels the carbonic acid from the alkaline carbonate which is produced; and the whole of the carbon contained in the organic substance is obtained, as carbonic acid, in the potash-apparatus.

In the preparation of the oxide of copper and chromate of lead employed in organic analysis, as also in the choice of the combustion-tubes, some care is necessary.

OXIDE OF COPPER.

This oxide may be prepared by decomposing sulphate of copper with carbonate of soda; the solutions are mixed while hot, and the bluish precipitate allowed to stand for eight to fourteen days in a warm place; it will then have lost its gelatinous character, and have become green, granular and crystalline, so that it may be easily washed; after being dried and strongly ignited, it is fit for use, but must be carefully tested for sulphuric acid and soda; it cannot be employed if it contains even the smallest quantities of these impurities.

The pure oxide thus obtained has a dark brown colour, is exceedingly porous and light, and very hygroscopic; organic substances, when mixed with it, are burnt with the greatest facility, but the mixture sometimes burns throughout the tube when only a portion of it is ignited, so that the analysis is lost.

It is better to employ the oxide of copper obtained from the nitrate, since its preparation is simpler and less costly, and there can be no doubt of its purity.

In order to prepare it, sheet-copper is heated to redness and plunged into cold water, when all the dirt and impurities scale off together with the oxide; the clean metal is then dissolved in pure nitric acid, the solution evaporated to dryness in a porcelain dish, and the dry residue ignited in a well-covered Hessian crucible; during the ignition, the oxide should be frequently stirred with a

hot glass rod, in order that none of the nitrate may remain undecomposed.

A platinum crucible must not be employed, since it is gradually roughened, and corroded to a considerable extent, in this operation.

The ignited oxide is finely powdered in a mortar, and preserved in a well-closed bottle; it is coal-black, dense, and heavy; its power of absorbing moisture depends upon the temperature to which it has been exposed.

When very strongly ignited, the oxide shrinks very much, becomes very hard, and almost entirely loses its hygroscopic properties; if it be then broken into small fragments, and separated from the fine powder, it may be employed with advantage in the analysis of liquids and of difficultly combustible fatty or fusible substances; the tube may be entirely filled with it without shaking it down, since the interspaces left in the porous oxide will suffice for the passage of the gases.

Instead of these fragments, Dumas employs the oxide obtained by heating copper-turnings in air; this retains the form of the turnings, and answers the same purpose as the small lumps of oxide.

The oxide of copper which has been employed for combustions, may be rendered again fit for use by moistening it with pure nitric acid, and igniting a second time.

If the metallic copper which has been used for the preparation of the oxide, should contain any zinc, the oxide must not be employed in the determination of nitrogen, since nitrate of zinc is not completely decomposed when heated to redness, except when organic matters are present.

When the oxide has been used for the combustion of compounds of organic substances with alkaline bases, it

must be digested with cold dilute nitric acid, afterwards boiled with water, and well washed.

Should a chlorine-compound have been burnt with the oxide, the latter must be entirely dissolved in nitric acid, and the chlorine precipitated by nitrate of silver; the excess of oxide of silver is reduced in the subsequent ignition of the nitrate of copper, and does not interfere in the uses of the oxide.

CHROMATE OF LEAD.

This compound may be obtained in a perfectly pure state, by precipitating a soluble lead-salt with bichromate of potassa, and washing the precipitate thoroughly; the chromate, however, in the state in which it is obtained by drying this precipitate, is not fit for use in analysis; it must be strongly ignited until it fuses, and afterwards reduced to a very fine powder. On ignition, its fine yellow colour changes to a dirty brown-red, which it retains even after cooling.

Chromate of lead may be employed, for almost every kind of combustion, quite as well as pure oxide of copper; the combustion takes place easily, and even at a lower temperature than with the latter substance; it is always complete, for the gases obtained at the end of the operation are invariably quite tasteless.

In equal weights, there is more oxygen in oxide of copper than in the chromate of lead, but in equal volumes, upwards of half as much more oxygen is contained in the latter, since its sp. gr. is more than twice that of the oxide of copper.

It will be seen at once, that the chromate of lead is to

be preferred, in many cases, to the oxide of copper, when an accurate determination of hydrogen is required; for the chromate is not in the least hygroscopic, and any traces of moisture which the substance may have absorbed during the mixing, can be much more easily removed from the mixture than when oxide of copper is employed.

COMBUSTION-TUBES.

Great care should be bestowed upon the choice of the glass from which these tubes are made; the best is the Bohemian potash-glass which contains no lead; the tubes made of this glass do not crack even when rapidly surrounded with red-hot charcoal; the glass is exceedingly difficult to fuse, and, even when softened, is very tough; the German green bottle-glass, on the other hand, easily cracks in the fire, and, though difficultly fusible, becomes very liquid when once fused, so that the softened portions of the tube are blown into holes by a comparatively feeble pressure.

The French white and green bottle-glass must be rejected; the latter may be completely fused in a tube of Bohemian glass, without altering the form of the latter.

Having described in the foregoing pages the precautions and manipulations necessary for the execution of an unimpeachable analysis, we have now to consider what degree of accuracy can be attained in the estimation of the carbon and hydrogen.

CARBON.

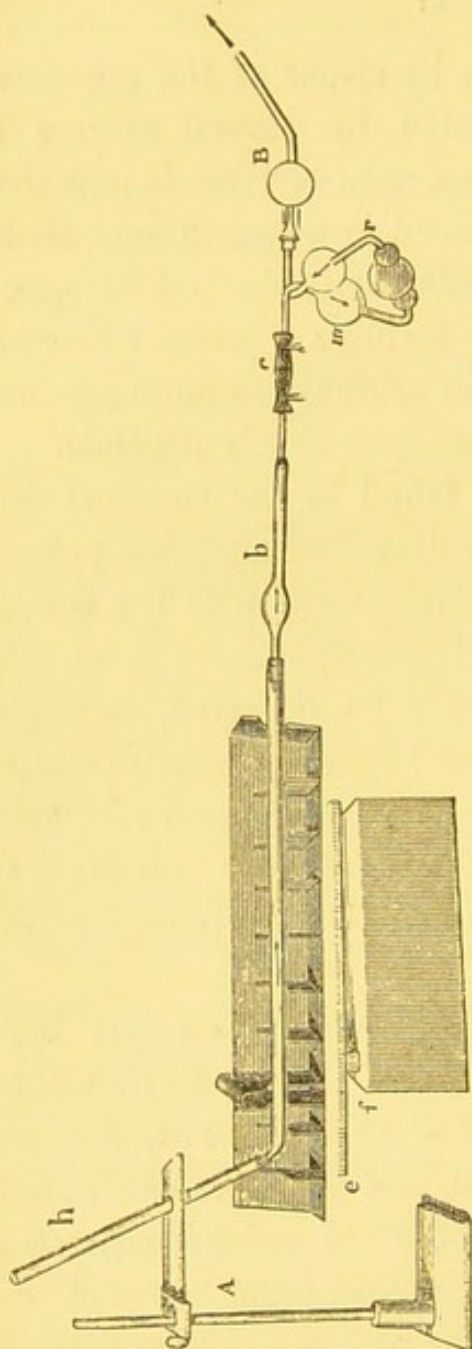
The determination of carbon by means of the apparatus above described, may be vitiated by several sources of error. The first and most important of these is imperfect combustion, which may be avoided in a second analysis by increasing the length of the combustion-tube and the quantity of oxide of copper, which involves a greater division of the substance, and renders its combustion more gradual, upon which the success of the analysis chiefly depends.

A second source of error is found in the circumstance, already adverted to, that the air drawn through the potash-solution after the combustion, carries away with it a certain quantity of water, by which the weight of the potash-apparatus is diminished. It will be observed, however, that the loss of water thus suffered by the potash-apparatus, is in part compensated for by the carbonic acid contained in the air, so that the loss of weight varies according to the amount of carbonic acid which the air contains at the time of making the experiment.

Upon this subject, satisfactory information has been elicited by direct experiment. When the combustion-tube and its open point (without the tube *h*), FIG. 58, are surrounded with red-hot charcoal, and air is drawn through the apparatus to the amount of 2000 cubic centimetres (about 122 cubic inches), the potash-bulbs do not diminish in weight, but gain, on the contrary, $18\frac{1}{2}$ milligrams. (0.286 grain.)

In order to determine the quantity of water carried away from the potash-apparatus, the latter was connected with a similar one filled with concentrated sulphuric acid; it is obvious that the water taken up in the form of vapour, by

FIG. 58.



the air, in its passage through the potash-solution, was absorbed by the sulphuric acid, and estimated from the increase of weight of the latter.

The weight of the apparatus filled with concentrated sulphuric acid, and connected with the potash-bulbs, had been increased by 14 milligrams. (0.216 grn.) Consequently, the potash-solution had absorbed $32\frac{1}{2}$ milligrams. (0.502 grn.) of carbonic acid from the air, and had lost 14 milligrams. (0.216 grn.) of water, so that, instead of a loss of carbon taking place, this experiment furnished an excess.

When, at the termination of the combustion, the tube *h*, FIG. 58, 12—15 inches long, was placed over the open point, surrounded with red-hot charcoal, and 2000 cub. cent. (about 122 cub. in.) of air drawn through the apparatus in the usual manner, the bulbs containing sulphuric acid gained 13.6 milligrams. (0.210 grn.), while the potash-apparatus had lost 5 milligrams. (0.077 grn.)

It is evident, then, that the error in the determination of

carbon, arising from the loss of water, is fully compensated for by the carbonic acid absorbed from the air.

In passing 200 cub. cent. (12.205 cub. in.) of air through the potash-bulbs, the loss amounted to $\frac{1}{2}$ milligram. (0.008 grn.); this would correspond to only 0.000136 grms. (0.002 grn.) of carbon, which would be distributed over 400 to 800 milligrams. (6 to 12 grns.) of substance.

Those who, at the end of the combustion, connect the point of the combustion-tube with a tube containing hydrate of potassa, to absorb the carbonic acid from the air which is passed through it, must add to the weight of the potash-apparatus, on an average, 1.3 milligram. (0.02 grn.) for every 200 cub. cent. (12.205 cub. in.) of air passed through the apparatus.

The experiments above cited, however, show that this correction is not worth the trouble, and it is always better to follow the prescribed course.

If the quantity of carbonic acid absorbed be very great, and the bubbles follow each other very rapidly, the potash-solution becomes hot, and the loss, arising from the escape of water from it, increases.

In weighing the apparatus, it must be remembered that less water is condensed upon its surface when warm, than is the case before the combustion; this difference amounts to 3 or 4 milligrams. (0.046 or 0.062 grn.), and even sometimes, when the air is very moist, rises as high as 6 milligrams. (0.093 grn.)

The comparison of the analyses of several substances will give the most accurate idea of the precision with which the carbon may be determined in this apparatus.

It is known with sufficient certainty, that the equivalent of lactate of zinc is 121.5; 100 parts of this salt, when

burnt, gave 108.0 and 108.3 parts of carbonic acid. According to theory, 100 parts of lactate of zinc should give 108.6 parts of carbonic acid. The loss, therefore, amounts to 0.003—0.006 of carbonic acid, or, taking the mean of the two results, to 0.001 carbon. There is no description of analysis in which greater accuracy can be attained.

HYDROGEN.

The only error, with regard to the estimation of hydrogen, with which the method above described is attended, arises from the water contained in the air drawn through the apparatus in order to sweep out the carbonic acid.

Numerous observations have shown that the quantity of water absorbed by the chloride-of-calcium-tube from every 200 cub. cent. (12.2 cub. in.) of air, never exceeds 5 or 6 milligrms. (0.077 or 0.093 grn.), which would correspond to 0.55 or 0.66 milligrms. (0.0085 or 0.0102 grn.) of hydrogen; this excess is distributed over from 300 to 500 milligrms. (4.5 to 7.5 grns.) of substance, and is the same whether the latter contain much or little hydrogen. In proportion as the substance analysed is rich in hydrogen, and as its atomic weight is small, in the same proportion will this error be less than 1 equiv. of hydrogen; in this case, there can be no uncertainty respecting the number of atoms of hydrogen. An example will render this apparent:

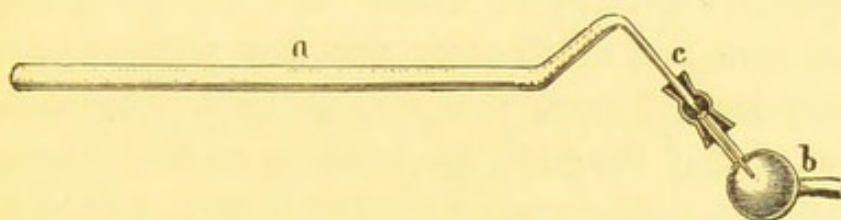
100 parts of acetone furnish, as a mean, 94.23 of water; theoretically, 93.10 parts of water should be obtained, so that the analysis gives 1.1 water, or 0.13 per cent of hydrogen, in excess. The atomic weight of acetone is 29, and if this quantity had been burnt, 0.038 of hydrogen in excess would have been obtained; now since the equivalent of hydrogen is 1, it is obvious that the above error amounts

to much less than 1 equiv., and may therefore be disregarded, especially since the cause of the error is known, as well as the limits within which it is confined.

When, therefore, the method described above is followed, we may, in all cases, expect an excess of hydrogen amounting only to 0.1 or 0.2 per cent; the estimation of hydrogen, then, may be regarded as accurate only when this excess is not greater than 0.2 per cent.

Berzelius and his followers prefer the method of connecting the combustion-tube with the chloride-of-calcium-tube, which is represented in FIG. 59, to the employment of

FIG. 59.



a dry cork; but considerable difficulty is thus introduced into the operation, without any particular advantage; for the long point is very thin and fragile, so that the least agitation of the apparatus is liable to break it off, and all the time and trouble bestowed upon the experiment are then lost.

When the point of the combustion-tube does not penetrate far into the bulb of the chloride-of-calcium-tube, it frequently happens that a drop of water is drawn into the space between the sides of the two tubes, so that, on removing the caoutchouc tube, it is found to be moist, and the hydrogen-determination must of course be sacrificed.

The cutting off the point, the removal of the caoutchouc tube without withdrawing the point from the chloride-of-calcium-tube, the ignition of the point, &c., are all prac-

licable operations, but they are of such a nature that they frequently give rise to accidents.

The ostensible reason for which Berzelius and the supporters of his proposition require so needless an expenditure of trouble and dexterity on the part of the operator, is the alleged hygroscopic nature of the cork which, they assert, when heated during the combustion, gives up the water which it had previously absorbed from the air.

There is no question that we should be obliged to concede the preference to this method of connecting the two tubes, if the stigma of inaccuracy which has been cast upon the other plan had any sound reason in its favour; but special experiments, which were conducted with the greatest care, and which every one may repeat who desires to satisfy himself upon this subject, have placed it beyond a doubt, that if the cork be dried in an air-bath at 120° , and be then introduced, with dry fingers, into the combustion-tube, it does not furnish any moisture when heated, even if dry air be allowed to pass slowly through the apparatus; the weight of the chloride-of-calcium-tube, before and after the experiment, does not differ even by 1 milligram. (0.015 grn.)

Every day experience shows that the determinations of hydrogen conducted on the plan of Berzelius, are not in the least degree more accurate; it may even be asserted that, in most cases, they furnish less precise results.

The reason, upon which we wish to lay great stress, of our opposition to the method followed by Berzelius, is that in the hands of most persons, it would deprive the process of that precision and certainty which it possesses when conducted according to the plan described above, and by diminishing the simplicity of the manipulations, would

render them attainable by only a limited number of individuals.

The determination of hydrogen is inaccurate, when a compound containing chlorine is burnt with oxide of copper; for the chloride of copper which is formed, volatilises in the stream of carbonic acid and aqueous vapour, and is deposited in the chloride-of-calcium-tube, the weight of which it increases. The more slowly the combustion is allowed to proceed, the smaller is the error arising from this source, but it can never be entirely neglected. The weight of the chloride-of-calcium-tube is usually increased by 10 to 15 milligrms. (0.154 to 6.231 grn.) from this cause.

Above all things, it is necessary, in the analysis of substances of this description, to pay particular attention to the regulation of the stream of air at the end of the combustion; for if the bubbles of air drawn through the potash-apparatus succeed each other somewhat rapidly, the chloride of copper is seen to pass, in white vapours, even through the potash-solution, and the nauseous metallic taste of the copper-salt is perceived in the mouth.

By the employment of chromate of lead, this error may be entirely avoided.

In order to prevent the breaking of the chloride-of-calcium-tubes, they must be emptied immediately after use, otherwise, the concentrated solution of the chloride of calcium, in the water produced by the combustion, will crystallise, and crack the bulb of the tube.

DETERMINATION OF NITROGEN.

In the analysis of nitrogenised substances, the carbon and hydrogen are determined according to the method

described above, and the estimation of the nitrogen is the object of a distinct operation in which the carbon and hydrogen are disregarded.

As a rule, it is to be observed, in the estimation of nitrogen, that *the more intimately and carefully the mixture with oxide of copper is effected, and the more slowly the combustion proceeds, the less likelihood is there of the formation of binoxide of nitrogen.* In order to give some notion of the rate at which the process should be conducted, we may remark that the combustion of a nitrogenised substance requires twice as long a period as that of a substance free from nitrogen.

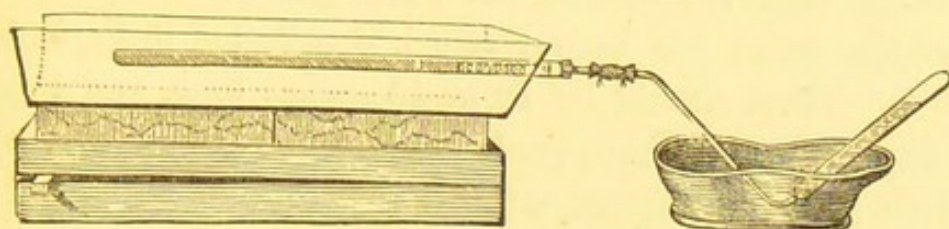
The estimation of the nitrogen is effected by different processes, which are more or less simple according to the quantity of this element which is present in the compound.

Every determination of nitrogen must be preceded by the qualitative analysis of the gaseous mixture evolved in the combustion of the substance; the knowledge of the relative proportions by volume of nitrogen and carbonic acid, enables us in most cases to calculate the amount of nitrogen contained in the substance, and the employment of a special process becomes then unnecessary. The apparatus required for this purpose is of the simplest description, the whole operation, including all the preparations, occupies about two hours, and the result obtained either determines the choice of another process, or renders any other operation unnecessary.

The substance may be weighed or not, indifferently; in every case, forty or fifty times as much oxide of copper must be mixed with it, as is required for its complete combustion. The mixture should occupy half the length of the combustion-tube, FIG. 60; one of the remaining fourths

of the combustion-tube is filled with oxide of copper, the other portion being occupied by a layer of copper-turn-

FIG. 60.



ings; the tube is placed in the furnace, and connected with a delivery-tube, which may be rendered flexible by means of a caoutchouc tube; its aperture dips just beneath the surface of the mercury-trough.

A screen having been placed between the mixture and the pure oxide of copper, the latter, together with the copper-turnings, are heated to bright redness; the apertures in the grate beneath these portions of the tube are left open in order that they may be exposed to the strongest heat; if the combustion-tube be not of Bohemian glass, its anterior part should be surrounded with a sheet of copper, secured by copper wire; if this be omitted, the softened tube will be blown into a hole by the pressure exerted upon the gas by the column of mercury.

As soon as the oxide of copper and the copper-turnings are heated to redness, a second screen is placed in such a manner that one inch of the closed end of the tube may project beyond it; this portion is now surrounded with red-hot charcoal. The combustion of the substance in this part of the tube then commences, and the gases which are evolved sweep the atmospheric air out of the apparatus, which, after a short time, is completely filled with the products of the combustion. The operation is then con-

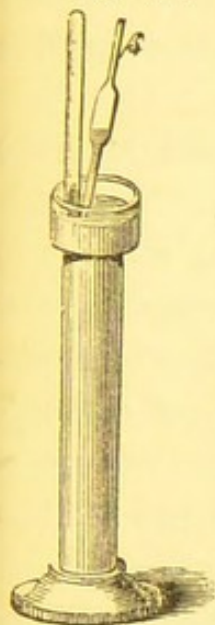
tinued, as usual, proceeding from the front backwards. The first screen is drawn back half an inch towards the closed end, the portion thus exposed being surrounded with glowing charcoal, and so on. The gas which is evolved after this point has been reached, is collected in graduated tubes. These should be 12 or 15 inches long, and $\frac{1}{2}$ inch in diameter, and their graduations must be uniform and correct; it is indifferent whether the tubes be graduated to cubic inches, or cubic centimetres, or whether the divisions be entirely arbitrary.

When three-fourths of the first tube are filled with gas, it is raised out of the mercury, and the latter allowed to run out, when its place is occupied by atmospheric air, which, mixing with the gas after some seconds, allows us to ascertain if it be free from binoxide of nitrogen, for if it contain only $\frac{1}{10000}$ of its volume of this gas, the well-known red cloud will be produced, which appears yellow when a very small quantity is present, and may be most distinctly perceived on looking through the whole length of the tube, which is held, for this purpose, in a horizontal position.

Binoxide of nitrogen is sometimes formed at the commencement of the combustion, and not towards the middle, since the surface of the oxide of copper is reduced at *a*, and assists the deoxidising action of the copper-turnings. The analyst should not omit to apply the above test to the gas at the commencement, in the middle, and towards the end of the combustion. If the formation of binoxide of nitrogen is observed throughout the whole of the operation, either the mixture of the substance with the oxide of copper was not sufficiently complete, or the combustion has proceeded too rapidly, or lastly, the length of the layer of copper-turnings must be increased.

It is not worth the trouble to complete such an operation, since it does not teach anything, but originates false ideas respecting the composition of the substance, and

FIG. 61. leaves room for a doubt in regard to the correctness of a better analysis by which it may be followed.



Six or eight tubes have now been filled with gas, the total quantity of which amounts to between 300 and 600 cub. cent. (18 and 36 cub. in.) We have now to determine the relative proportions, by volume, of nitrogen and carbonic acid. The tubes are introduced, one after the other, into the cylinder, FIG. 61, the diameter of which is greater above than below; this cylinder is filled with mercury, the level of which is equalised, both

within and without the tube, and the volume of the gas is then read off.

FIG. 62. By means of the pipette, FIG. 62, which is filled with solution of potassa, and closed, at the lower part, with mercury, a small layer of the alkaline ley is introduced into the graduated tube; this is usually effected by applying, with the mouth, a feeble pressure, not stronger than is necessary to cause the solution of potassa to ascend into the tube.



When the curved point of the pipette is about $1\frac{1}{2}$ inch long, and projects above the mercury inside the graduated tube, it is only necessary to lift this a little out of the mercury, in order that the pressure of the external air may cause the potassa to mount into the tube.

By carefully moving the graduated tube up and down,

all the carbonic acid contained in the gas is rapidly absorbed, and nothing but nitrogen remains. In this operation, the lower part of the graduated tube is easily struck against the side, and broken; this may be entirely avoided by pressing the edge of the opening firmly against the side of the cylinder.

The level of the mercury is again equalised and the volume of the gas noted.

Suppose the original volume of the gaseous mixture to have amounted, in the six tubes, to 620 measures, and that, altogether, 124 measures have been left after treatment with potassa; 496 measures, therefore, of carbonic acid have disappeared; in this case, then, the volume of the nitrogen is to that of the carbonic acid, as $124 : 496 = 1 : 4$.

The amount of nitrogen contained in a substance may be calculated in different ways from the proportions by volume, *provided that we know the quantity of carbonic acid furnished by a given weight of the substance*. One method consists in reducing the carbonic acid into volumes, and dividing these by the number expressing its proportion by volume; the quotient expresses the corresponding amount of nitrogen, also in volumes. For example, 0.100 gm. (1.543 grn.) of caffeine, yields, when burnt, 0.181 gm. (2.794 grns.) of carbonic acid. The gaseous mixture obtained by the combustion of this substance, contains nitrogen and carbonic acid in the proportion, by volume, of 1 : 4. Now, 1000 cub. cent. (61.03 cub. in.) of carbonic acid weigh 1.987 gm. (30.667 grns.); hence 0.181 gm. (2.794 grns.) correspond to 91.09 cub. cent. (5.56 cub. in.); if we divide this number by 4, we obtain 22.77 cub. cent. (1.39 cub. in.) These 22.77 cub. cent. (1.39 cub. in.) are

calculated as nitrogen; we know that 1000 cub. cent. (61.03 cub. in.) of the latter gas weigh 1.26 gm. (19.447 grns.); so that 100 parts of caffeine contain 28.86 nitrogen and 49.48 carbon.

This extensive calculation may be avoided if we reflect that 1 volume of carbonic acid corresponds to 1 equiv. of carbon, and 1 volume of nitrogen, to 1 equiv. of this element. Hence, the quantity of carbon, and the relation by volume between the gases obtained in the combustion, being known, we can calculate the quantity of nitrogen from the atomic weights.

According to the determination of carbon, caffeine contains 49.48 per cent; this substance furnished nitrogen and carbonic acid in the ratio of 1 : 4; it contains therefore 1 equiv. of nitrogen for every 4 equivs. of carbon.

For 4×6 (= 4 equivs.) carbon, 14 (= 1 equiv.) nitrogen are present, and consequently, for 49.48 per cent of carbon, $x = \frac{14 \times 49.48}{4 \times 6} = 28.86$ per cent. of nitrogen are present, as will be evident from the proportion $4 \times 6 : 49.48 = 14 : x$.

The qualitative determination which has just been described, is quite trustworthy and accurate for all nitrogenised substances in which the proportion of the nitrogen to the carbon is not less than 1 : 8.

Bunsen has altered the indirect method of determining nitrogen, in such a manner, that it gives far more accurate results, though at a sacrifice of simplicity and rapidity of execution. In this process, the combustion of the nitrogenised substance is effected with oxide of copper in a space hermetically sealed, and filled with an atmosphere of hydrogen; the gaseous mixture of carbonic acid and

nitrogen is afterwards analysed in a carefully graduated eudiometer.

FIG. 63.

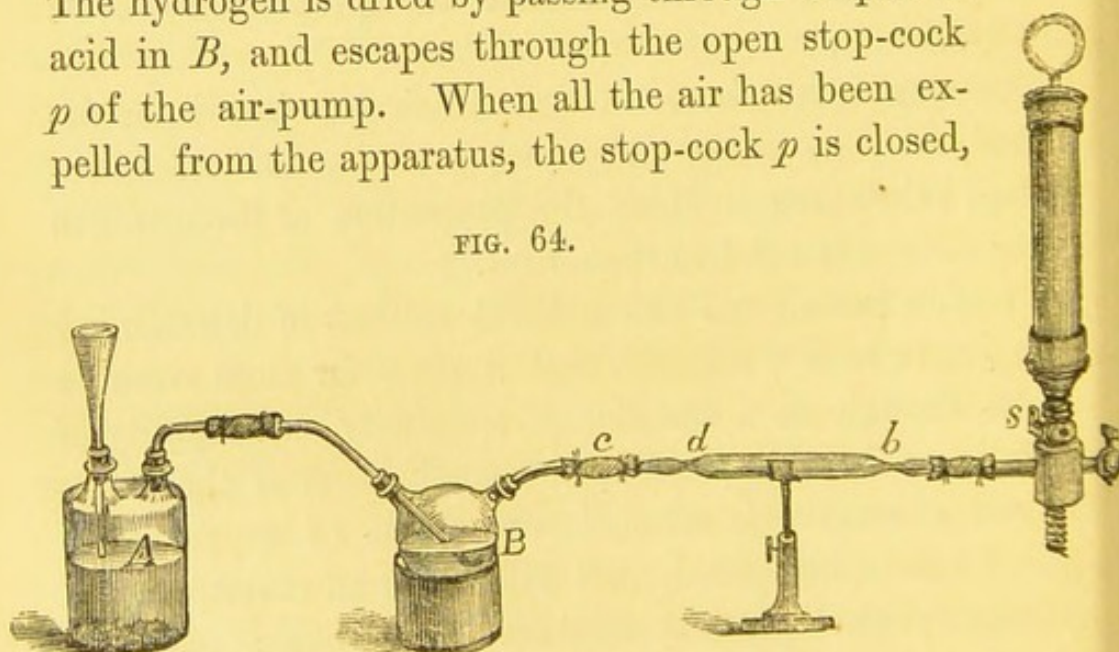


A clean stout tube of strong Bohemian glass, about $\frac{1}{4}$ foot long, and $\frac{3}{4}$ inch in the bore, is drawn out at one end to a conical point, as shown in FIG. 63, *A*, and very much narrowed at *a*, FIG. 63, *B*, by continued fusion.

An intimate mixture of 5 grms. (77.17 grns.) of oxide of copper and 0.03—0.05 gm. (0.463—0.772 grn.) of the substance to be analysed, is introduced into this tube, together with some copper-turnings; the anterior end of the tube is then drawn out before the glass-blower's lamp, at about 6 or 7 inches from the part already narrowed, and this portion of the tube is then narrowed in the same way as the former one.

The tube is now to be filled with hydrogen gas, for which purpose one end of it is connected with a hydrogen evolution bottle, *A*, FIG. 64, the other with an air-pump. The hydrogen is dried by passing through sulphuric acid in *B*, and escapes through the open stop-cock *p* of the air-pump. When all the air has been expelled from the apparatus, the stop-cock *p* is closed,

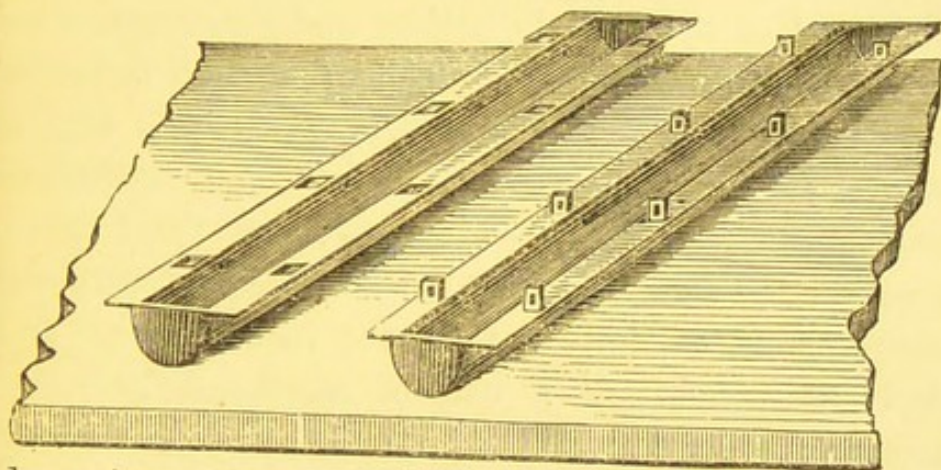
FIG. 64.



the bottle *A* opened, the caoutchouc tube *c* tightly ligatured, a partial vacuum produced by one stroke of the air-pump, and the stop-cock *s* rapidly closed. The tube is now sealed with the blow-pipe-flame at the narrowed portions *d* and *b*, in which there is no fear of any blowing out, because of the diminished pressure within the tube.

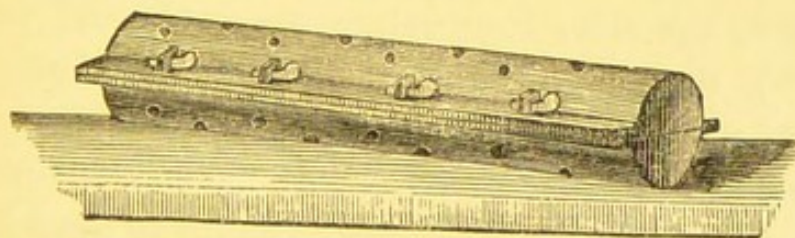
Before heating the tube to redness, it is necessary to imbed it in plaster of Paris in order to prevent it from blowing out, which would otherwise be inevitable. The mould represented in FIG. 65 is made of strong iron-plate,

FIG. 65.



and consists of two portions which fit accurately together, forming a hollow cylinder of 1 foot in length and 2 inches in diameter. FIG. 66 represents the closed mould, the two

FIG. 66.



halves being tightly forced together by wedges of iron; each half is perforated in several places.

Both halves of this mould are filled with a paste of

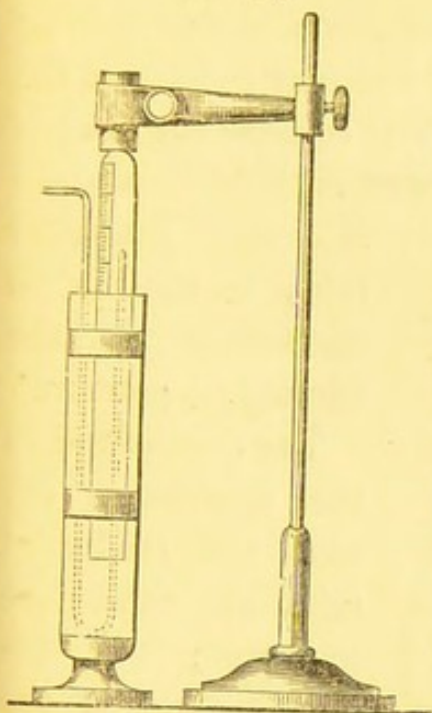
plaster of Paris, with which a little cow-hair has been worked up; the combustion-tube is pressed into the middle of one half, and as soon as the plaster begins to set, the two halves are fitted together. When the plaster has hardened, the mould is placed in a suitable furnace, and heated to dull redness for an hour; it is then allowed to cool slowly, and the tube carefully removed. Its surface should be dull and blistered from the effect of the high temperature. Sometimes the tube is found to have blown out, which arises from the employment of too high a temperature or too large a quantity of substance.

The point of the tube is broken under mercury in such a manner that the gas may be collected in an eudiometer filled with mercury. The mixture of carbonic acid and nitrogen is then saturated with moisture, by introducing a drop of water into the eudiometer, and the volume of gas accurately measured, the temperature and barometric pressure being carefully noted; the carbonic acid is removed by introducing a ball of moistened hydrate of potassa fused on to an iron wire, and the residual nitrogen gas is afterwards dried by introducing a second ball of fused hydrate of potassa (the first one having been previously removed); the volume of gas is then again noted. If the observed volumes of carbonic acid and nitrogen be reduced to the same temperature (*e. g.* 0°) and pressure (*e. g.* 1^m), they express the proportion of the equivalents of carbon and nitrogen contained in the substance.

In order to control this qualitative method, the nitrogen may be determined quantitatively by means of the following apparatus.

It consists of a cylinder, FIG. 67, standing upon a foot, into which three rings of cork, FIG. 68, are fixed, the one

FIG. 67.



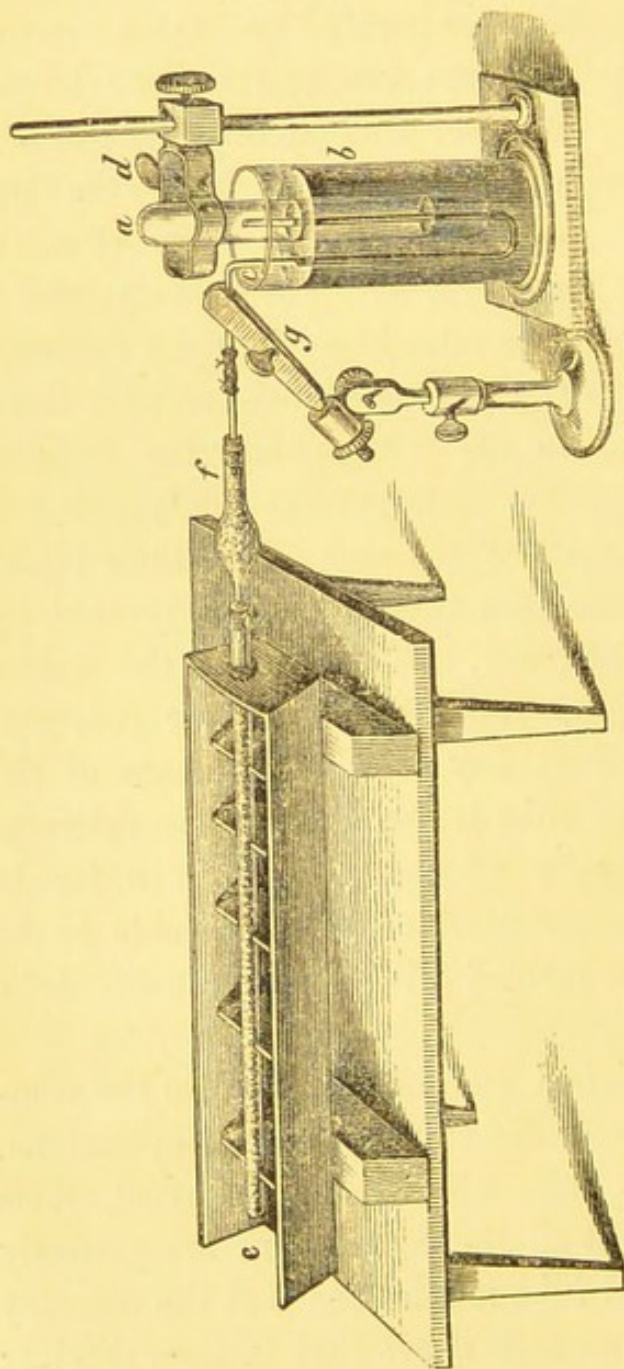
at the bottom of the cylinder, and the others in the middle and at the top ; these serve to protect the little graduated bell in its movements. The tube through which the gas is passed, has two perpendicular parallel limbs, the ascending one having the same length as the graduated bell, and the other passing through the two apertures in the rings of cork, FIG. 68, X. The delivery-tube is now introduced into the cylinder, the graduated bell pressed down to the bottom, and the cylinder

FIG. 68. filled with mercury. Both the graduated bell and the delivery-tube are secured in their places by the holder, so that they cannot be pressed up again by the mercury. The arm of the holder may be moved up and down upon the rod, and may be secured at any height by means of the screw. A short piece of tube is attached to the delivery-tube by means of a tube of caoutchouc, in order to render the apparatus more flexible and less liable to be broken. This tube is connected with the combustion-tube by an air-tight cork.

The substance is weighed and introduced into the combustion-tube in the manner described in former operations. Before surrounding the tube with red-hot charcoal, it is necessary to ascertain that all the connections are perfectly air-tight. The graduated tube is raised so that the mercury inside may stand about an inch above that in the cylinder ;

the level of the mercury is then noted, and if it remain unchanged for a quarter of an hour, we may conclude that no air has entered at any of the joints, and may commence the combustion. We must, however, first equalise the level of the mercury, and determine the volume of the air contained

FIG. 69.



in the graduated tube, as well as its temperature, and the barometric pressure.

The gas evolved in the combustion enters the graduated tube, and expels the mercury; if the wooden arm of the holder, however, be allowed to slip gradually up the rod, the mercury may always be maintained at the same level.

Instead of the arrangement described, we may use the holder represented in FIG. 69, which shows the whole apparatus. Here the delivery-tube is secured in the mercury by a second holder, as shown at *g*, FIG. 69.

When the combustion is completed, which is known by there being no farther increase of the volume of gas in the graduated tube, the charcoal is removed, and the apparatus allowed to cool. The level of the mercury, which is now altered, is equalised, the temperature and barometric pressure observed, and the volume of gas carefully noted. In order to obtain the actual volume of gas evolved, we must deduct, from the total volume, that of the air contained in the graduated tube before the combustion, and must reduce the remainder to 0° and 28 inches barometer, provided that the pressure and temperature have not changed during the experiment, for should a change have taken place, the different volumes must be reduced separately.

We have now ascertained what is the sum of the volumes of nitrogen and carbonic acid furnished by a given weight of the substance, and we know moreover, from the determination of carbon, the quantity of carbonic acid; from this we calculate the volume of carbonic acid furnished by the weight of substance taken for the last experiment, and deduct this from the volume of gas obtained; the remainder is nitrogen gas, the volume of which we reduce to weight. The relation between the volume of the nitrogen and that of the carbonic acid must be a very simple one, and the same as that obtained in the qualitative analysis; should there be any considerable difference, in this respect, between the two analyses, one of them is erroneous, and must be repeated.

For example, 0.100 grm. (1.543 grn.) of caffeine, when burnt in this apparatus, furnish 114.06 cub. cent. (6.96 cub. in.) of gas, at 0° and 28 inches B. The same quantity, when burnt in the usual manner, gives 0.181 grm.

(2.794 grns.) of carbonic acid, which corresponds, at 0° and 28 inches B., to 91.09 cub. cent. (5.559 cub. in.); hence 0.100 grm. of caffeine give $114.06 - 91.09 = 22.85$ cub. cent. of nitrogen, or 28.86 per cent.

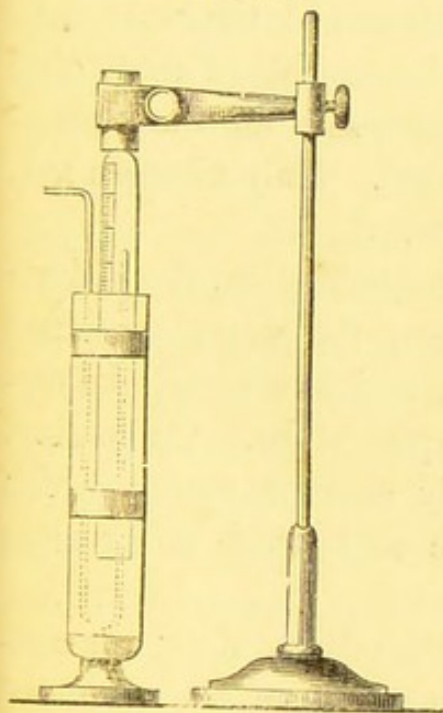
The quantity of substance which can be analysed with this apparatus depends upon the capacity of the graduated tube; for every milligramme (0.015 grn.) of nitrogen and carbon, 2 cub. cent. (0.122 cub. in.) must be allowed in the tube, beside a space of 15—20 cub. cent. (0.915—1.221 cub. in.) for the alterations of volume before and after the combustion. If, for example, the graduated tube be capable of containing only 100 cub. cent. (6.103 cub. in.), we shall be enabled to measure the gas from only 60 milligrms. (0.926 grn.) of caffeine, or from 90 to 100 milligrms. (1.389 to 1.543 grn.) of morphine, supposing that 15 cub. cent. (0.915 cub. in.) of air were contained in the graduated tube before the combustion. These tubes commonly contain 200 or 250 cub. cent. (12.205 or 15.257 cub. in.); but it is evident that in all these cases the quantity of the substance analysed is very small, and that the errors of experiment or of observation have, under all circumstances, a great influence upon the determination of the nitrogen, so that when the quantity of this element contained in any substance is very small, this apparatus ceases to give accurate and trustworthy results.

One of the principal sources of error in this process is the softening of the tube, by the application of too great a heat in the combustion; the form of the tube is thus altered, which of course influences the volume of gas in the graduated tube; this happens especially when the pressure of the mercury in the graduated tube is not regulated with

sufficient care. It is advisable to surround the lower half of the combustion-tube with a thin copper-plate bent into the form of a trough, upon which a layer of fine charcoal-powder is strewn, to prevent its adhering to the glass. This purpose is best answered by a plate of platinum, of the same length as the tube, and not broader than necessary to prevent it from bending.

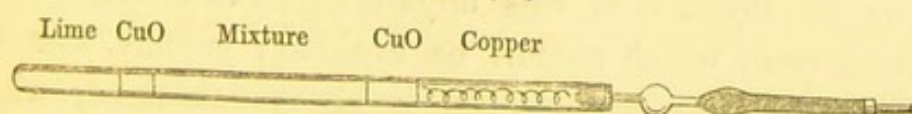
DIRECT DETERMINATION OF NITROGEN.

FIG. 70.



In substances which contain a very small amount of nitrogen, the whole quantity of that gas which is evolved during the combustion is determined in a single operation. For this purpose, the gas-jar, FIG. 70, is again employed, and the operation is conducted as follows: Into the closed end of a combustion-tube 18 inches in length, a layer of from 2 to $2\frac{1}{2}$ inches of dry hydrate of lime is introduced; the weight of the hydrate of lime must amount to at least 4 or 5 grms. (61.736 to 77.170 grms.); upon this, 1 inch of oxide of copper is introduced, then the mixture of the substance with oxide of copper; the other divisions, FIG. 71, represent the oxide of

FIG. 71.



copper which is employed for rinsing out the mixture, afterwards, the pure oxide of copper, and lastly, the copper-turnings.

The combustion-tube is connected with a large tube provided with two bulbs; the bulb *a* is empty, but the other bulb and the wide tube adjoining it are filled with dry hydrate of potassa. After this apparatus has been arranged in the furnace, it is connected, by means of a caoutchouc tube, with the gas-delivery tube, and the gasometer, FIG. 70, and the combustion conducted in the usual manner. If the absorption-tube be 12 inches in length, the bulb 1 inch in diameter, and the wide tube $\frac{1}{4}$ of an inch in diameter, it will be capable of containing thirty times more potassa than is necessary for the absorption of all the carbonic acid produced. Only nitrogen gas, therefore, enters the graduated tube.

When, at the termination of the combustion, the hydrate of lime is heated to dull redness, the water contained therein is converted into vapour, and sweeps all the carbonic acid before it into the absorption-tube. On cooling, the combustion-tube contains only aqueous vapour which condenses; any traces of carbonic acid which still remain are absorbed by the caustic lime.

Before the combustion, a certain volume of air was contained in the graduated jar; this volume has increased after the combustion; the increase of volume expresses the exact amount of the nitrogen evolved; it is measured, reduced to 0° and the ordinary barometric pressure, and converted into the corresponding weight.

The employment of this apparatus is attended with a constant error which cannot be avoided; namely, that too small a quantity of nitrogen is always obtained, which

arises, without doubt, from the circumstance that the oxygen of the air in the tube takes part in the combustion. By a series of analyses of nitrogenised substances of known composition, conducted with every precaution, the limits of this error have been ascertained, and it has been found that if 1 per cent be added to the amount of nitrogen obtained, it expresses accurately the quantity of nitrogen contained in the substance.

When the following apparatus is employed, the quantity of nitrogen obtained is always somewhat too high, the excess amounting, in good analyses, to from 1 to $1\frac{1}{2}$ cub. cent. (0.061 to 0.0915 cub. in.), in the whole volume obtained; when nitric oxide is formed, this error is still greater. The mean of two analyses of a nitrogenised substance, one of which is conducted according to the method just described, and the other by the following process, will give the amount of nitrogen with the greatest accuracy at present to be attained in such determinations. A combustion-tube of 24 inches in length is taken, and a layer of 6 inches of carbonate of copper introduced into the closed end; upon this is placed a layer of 2 inches of pure oxide of copper, then the mixture of the substance with oxide of copper, again a layer of the pure oxide, and lastly, copper-turnings; the different layers are shown in FIG. 72. The combustion-tube is connected, by means of a cork, covered externally with sealing-wax, with the

FIG. 72.

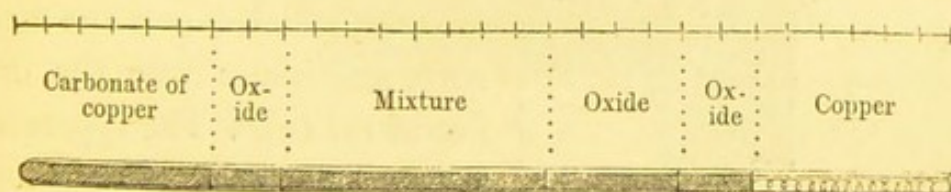


FIG. 73.

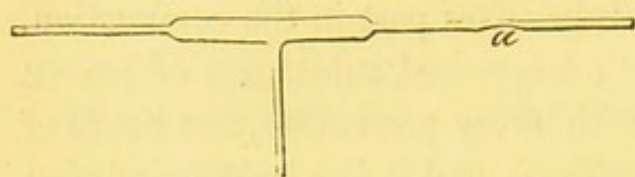
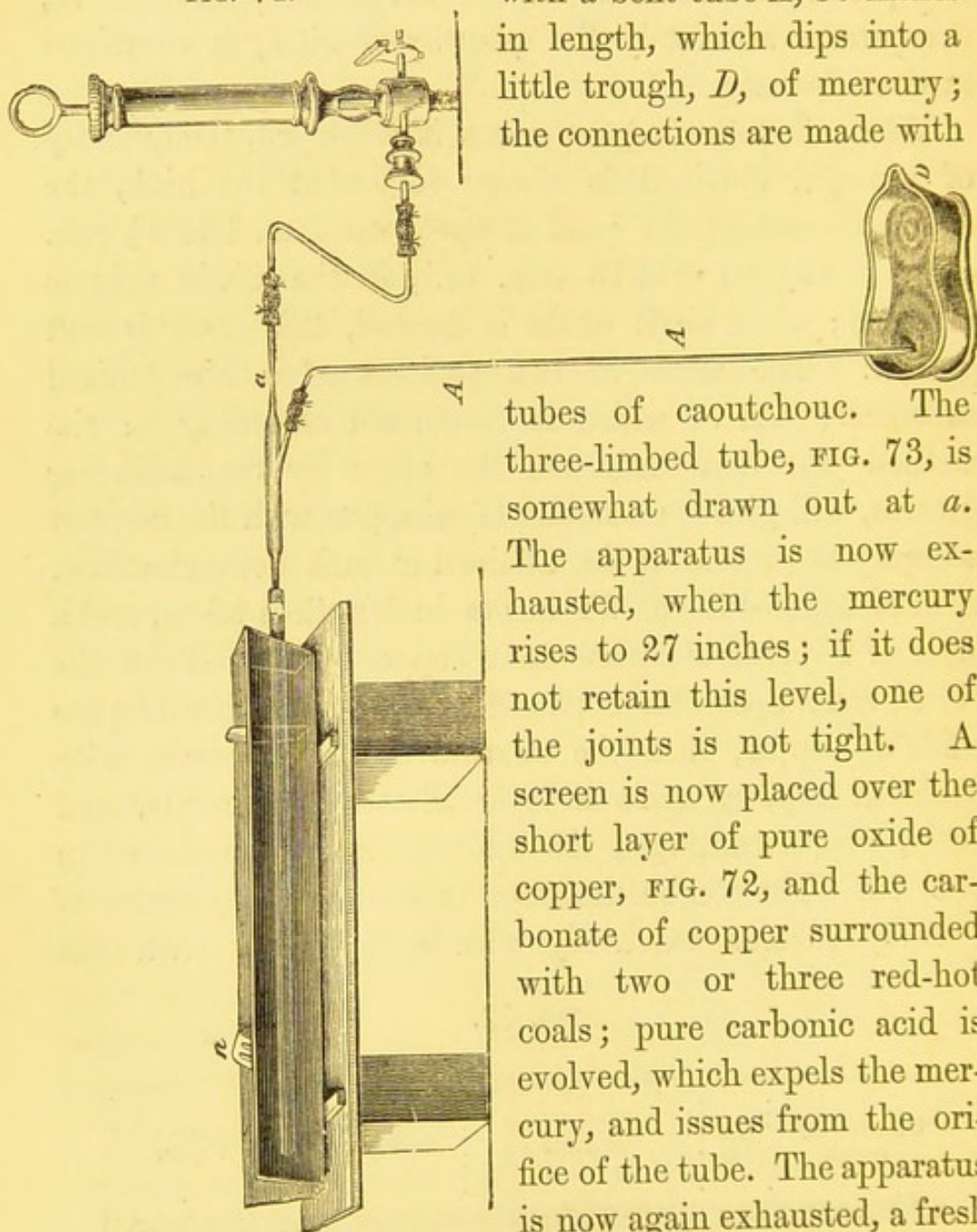


FIG. 74.

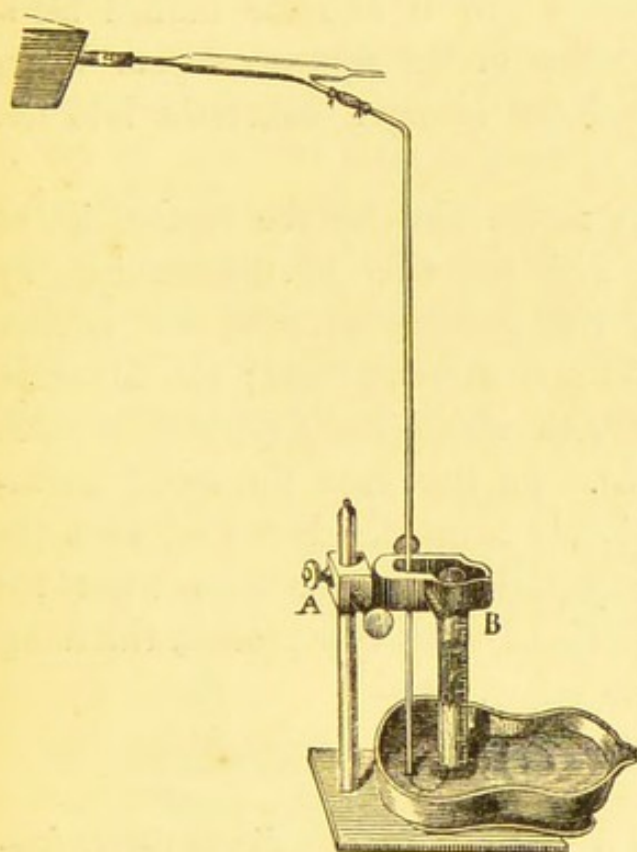


T-shaped tube, FIG. 73, of which one limb is in connection with the air-pump *B*, FIG. 74, and the other with a bent tube *A*, 30 inches in length, which dips into a little trough, *D*, of mercury; the connections are made with

tubes of caoutchouc. The three-limbed tube, FIG. 73, is somewhat drawn out at *a*. The apparatus is now exhausted, when the mercury rises to 27 inches; if it does not retain this level, one of the joints is not tight. A screen is now placed over the short layer of pure oxide of copper, FIG. 72, and the carbonate of copper surrounded with two or three red-hot coals; pure carbonic acid is evolved, which expels the mercury, and issues from the orifice of the tube. The apparatus is now again exhausted, a fresh

quantity of carbonic acid evolved, and so on, four or five times, until the gas-bubbles evolved from the tube *A* are absorbed, with the exception of a trifling bubble of air, when they are collected in a small glass tube filled with solution of potassa. All the atmospheric air is thus expelled from the apparatus. The narrow portion *a* of the three-limbed tube, FIG. 73, is now sealed with a spirit-lamp, and the air-pump, together with the S-shaped connecting tube *C*, removed; a graduated tube, capable of containing about 100 cub. cent. (6.103 cub. in.) half filled with solution of potassa, and half with mercury, is then supported over the extremity of the delivery-tube, by means of the stand *A*, FIG. 75;

FIG. 75.



the combustion is afterwards conducted as usual, when nitrogen and carbonic acid are evolved, the latter being absorbed by the potassa, so that only nitrogen is collected in the tube.

When the combustion of the substance is terminated, the gas which occupies the interior of the apparatus still contains a quantity of nitrogen which must be passed into the graduated

tube *B*, FIG. 75. One half of the carbonate of copper has been employed to sweep the atmospheric air out of

the apparatus, the portion which remains now serves to carry the gaseous mixture into the graduated tube. The hinder part of the combustion-tube is surrounded with red-hot charcoal, and about 300 or 400 cub. cent. (18.308 or 24.411 cub. in.) of gas passed into the graduated tube; the carbonic acid of the carbonate of copper thus carries all the products of combustion into the measuring tube.

When no more absorption is observed to take place in the graduated tube, even on agitating it, the mouth of the tube is closed with a polished glass plate, and it is conveyed to a large vessel of water; the mercury and potassa-solution are thus displaced by water.

After noting the state of the barometer and thermometer, the gas is measured, reduced to 0° and the normal barometric pressure, the tension of the aqueous vapour being taken into account, and the nitrogen converted into the corresponding weight.

The above apparatus serves also for the combustion of substances *in vacuo*, with the view of determining, by qualitative analysis of the gaseous mixture, the relative proportions of nitrogen and carbonic acid; the influence of the atmospheric air with which the apparatus is filled may be thus prevented. In this case the use of carbonate of copper is obviously omitted. However, when the substance contains very little nitrogen, even when the greatest attention is bestowed upon this process, the result cannot be relied on with safety.

The original process of Dumas for the direct determination of nitrogen has been so far modified that the somewhat inconvenient use of the air-pump may be avoided.

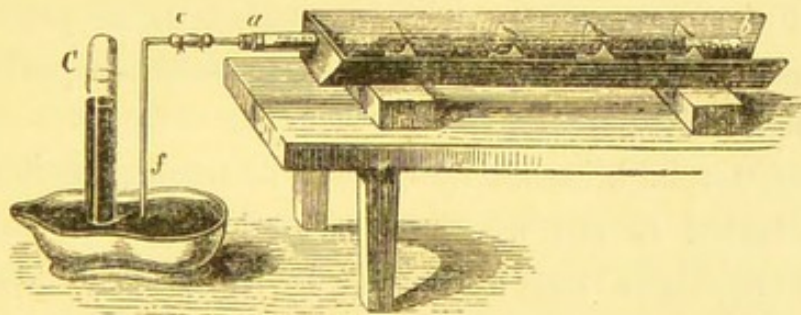
Into the end of a combustion-tube which should be about 30 inches long, FIG. 76, is introduced a layer of 6 inches

FIG. 76.



of bicarbonate of soda, *ab*, then a layer of oxide of copper, *bc*, next, the mixture of the substance with oxide of copper, *cd*, a layer of pure, strongly ignited oxide of copper, *de*, and lastly, copper-turnings, *ef*. Melsens* employs tubes 4 or 5 feet in length, which are filled as follows: 10 cent. (3.937 in.) of bicarbonate of soda, 20 cent. (7.874 in.) of coarse oxide of copper, 30 cent. (11.811 in.) of the mixture of the substance with fine oxide of copper, 30 cent. (11.811 in.) of coarse oxide, and 20 cent. (7.874 in.) of metallic copper. The tube is well rapped upon the table, in order to clear a passage for the gas, and surrounded with sheet-copper so as to leave exposed only the end which contains the bicarbonate of soda; a short gas-delivery tube, *ef*, is now connected with the combustion-tube by means of a good cork. The tube is placed in a combustion-furnace, FIG. 77, and the bicarbonate of soda

FIG. 77.



* Annal. d. Chem. u. Pharm. LX, p. 115.

slowly heated by gradually surrounding it with red-hot charcoal, the other part of the tube being protected by a screen. The carbonic acid evolved by the action of heat upon the bicarbonate of soda, expels all the air from the tube; when the evolution of carbonic acid has lasted for some time, the gas issuing from the tube is tested for atmospheric air by collecting it in a test-tube, over mercury, and introducing solution of potassa. As soon as the potassa absorbs the whole of the gas, the delivery-tube is placed beneath the graduated jar, half filled with solution of potassa, and half with mercury; the charcoal is then removed from the bicarbonate of soda, and the combustion conducted in the usual way; when the operation is concluded, the bicarbonate of soda still remaining is again heated, and a stream of carbonic acid thus produced, which carries all the nitrogen into the graduated jar. For this purpose it is necessary that only half the bicarbonate of soda should have been employed in expelling the air from the apparatus at the commencement. An excellent mode of completing the combustion in analyses of this kind, consists in adding powdered arsenious acid to the oxide of copper which is mixed with the substance. On heating, the arsenious acid evaporates and effects, like a current of oxygen, the combustion of every particle of carbon. The reduced arsenic remains with the copper, while portions of unreduced arsenious acid sublime in the anterior part of the combustion-tube.

If commercial bicarbonate of soda be employed, it should first be tested to see whether, when heated to redness, it evolves any gas not absorbed by potassa. Melsens recommends that, in order to test all the substances employed in these nitrogen-determinations, a trial combustion

should be made, without any substance, when at most only $\frac{1}{2}$ to $1\frac{1}{2}$ cub. cent. (0.031 to 0.092 cub. in.) of gas not absorbed by potassa, should be obtained.

In all nitrogen-determinations, the accuracy of the weights which are employed should be rigorously tested. All are aware that, in other analyses, it is indifferent whether the weights be accurate or not, provided that they agree among themselves; but in these determinations, if the gramme (15.434 grns.) and its subdivisions, which are employed in weighing the substance, be incorrect, we may expect a considerable difference in the result when we reduce the volume of the gas to its correct weight.

METHOD OF VARRENTRAPP AND WILL FOR THE DETERMINATION OF NITROGEN.

Most nitrogenised organic substances, when heated to redness with hydrate of potassa, evolve the whole of their nitrogen in the form of ammonia. In this case, the carbon of the organic substance combines with the oxygen of the water contained in the hydrate of potassa, to form carbonic acid, while the liberated hydrogen uniting with the nitrogen of the organic substance, produces ammonia; if less nitrogen be present than is necessary to combine with the whole of the liberated hydrogen, the excess of the latter is evolved as gas. There exists no organic substance, if we except those containing nitric acid, in which so much nitrogen is present that the hydrogen evolved upon burning their carbon at the expense of the water of the hydrate of potassa, would be insufficient to convert the whole of the nitrogen into ammonia. In many cases, when nitrogenised

organic substances are heated with hydrate of potassa, cyanide of potassium is at first produced, which, however, evolves the whole of its nitrogen in the form of ammonia, at a higher temperature, provided that sufficient hydrate of potassa be present.

The determination of nitrogen by the method of Varentrapp and Will is founded upon the foregoing facts: the liberated ammonia is received in hydrochloric acid, and weighed in combination with bichloride of platinum.

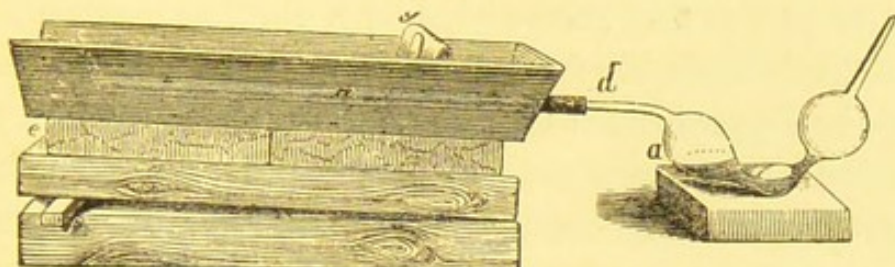
This operation requires very little apparatus and affords highly accurate results.

In order to evolve the ammonia, instead of hydrate of potassa, which would easily destroy the tubes, a mixture of 1 part of hydrate of potassa and 3 parts of caustic lime, or still better, of 1 part of hydrate of soda, and 2 parts of caustic lime is employed. This may be easily obtained by adding to a solution of potassa or soda of known strength the requisite quantity of unslaked lime, drying the mixture in an iron vessel, and subsequently igniting it in a crucible; it must then be finely powdered. This mixture does not fuse at a red heat, may be easily reduced to a fine powder, and attracts moisture slowly from the air. The powdered potash-lime or soda-lime should be preserved in closed bottles with wide mouths. If commercial hydrate of soda be employed for the preparation of soda-lime, it should first be tested for nitric acid, since if this were present, it would render the analysis inaccurate.

The combustion of the organic substance with soda-lime is effected in an ordinary combustion-tube, 16 to 18 inches long, and $\frac{1}{4}$ to $\frac{1}{2}$ inch in diameter. This tube is connected, by means of a cork, with a bulb-apparatus, the form of

which is apparent from FIG. 78, and into which enough dilute hydrochloric acid (sp. gr. 1.13) is introduced to half fill one of the bulbs.

FIG. 78.



Before the organic substance is mixed with the soda-lime, the latter should be warmed, in a porcelain dish, in order to expel any moisture and ammonia which it may have absorbed. The clean combustion-tube is then half-filled with the warm soda-lime, which is allowed to cool in the tube, and subsequently mixed, in a warm mixing mortar, with the accurately-weighed quantity of the finely-powdered organic substance. If the substance be rich in nitrogen 200 milligrms. (3.087 grns.) will suffice, and even in the case of a substance containing little nitrogen, it is seldom necessary to employ more than 400 milligrms. (6.174 grns.) The mixing with soda-lime must be effected without pressure, only by stirring gently; care must be taken that the mortar be perfectly dry, otherwise particles are very liable to adhere to the pestle or to the sides of the mortar. When the mixture has been introduced into the combustion-tube, in the usual manner, the mortar is repeatedly rinsed out with soda-lime, and the tube filled up with the same, to within an inch of the mouth. In order that, during the combustion, the vapours may not expel particles of the light powder, a loose plug of ignited asbestos is thrust into the mouth of the tube; the latter is

now rapped upon the table, to clear a passage for the evolved gases, and connected with the hydrochloric-acid-apparatus by means of a soft, air-tight cork.

The tube is heated in the combustion-furnace; the anterior part is first surrounded with glowing charcoal, and when this is heated to full redness, the screen is drawn backwards by degrees, until the substance is reached, which may be known by the production of clouds of sal-ammoniac in the first bulb. The combustion is now conducted in such a manner that a constant but slow stream of gas may pass through the hydrochloric-acid-apparatus. In general, there are produced, simultaneously with the ammonia, hydrogen and various hydro-carbons, some gaseous, as marsh-gas, others liquid, as benzol, which form an oily layer on the surface of the hydrochloric acid. Even when the evolution of gas is pretty rapid, there is no fear of the escape of ammonia, while, on the other hand, a sudden regurgitation of the acid, in consequence of the cessation of the disengagement of gas, is much more likely to be attended with injury to the experiment. The white fumes which are generally seen to issue from the apparatus do not indicate any loss of ammonia. Throughout the whole of the combustion, the cork must be maintained at such a temperature that no water can condense upon it, since this would retain a certain quantity of ammonia.

At the end of the combustion, a strong red heat is applied to the tube, so that the separated carbon may be completely burnt, and the cyanogen-compounds entirely decomposed; the mass in the tube, which becomes somewhat dark at first, should be perfectly white at the end of the combustion. When no more gas is evolved, the point of the combustion-tube is broken off, and air drawn

through the apparatus, so that all the ammonia still contained in it may be absorbed by the hydrochloric acid.

The execution of the foregoing operation is generally easy, but some substances, such as urea, mellon, &c., when heated with soda-lime, evolve pure ammonia, unmixed with either hydrogen or any other gas, in which case, as soon as the evolution of gas slackens, the hydrochloric acid regurgitates with such violence that it is frequently projected into the combustion-tube. To prevent this, nitrogenised substances of this description are mixed with a little sugar or tartaric acid, which may easily be obtained in a pure state, and evolve sufficient gas to dilute the ammonia.

In liquid substances, the nitrogen may also be determined in this manner, the operation being conducted in the same way as in the combustion of liquids with oxide of copper.

We have now to determine the quantity of ammonia absorbed by the hydrochloric acid. The liquid is poured, through the point of the bulb-apparatus, into a porcelain capsule, and the bulbs are rinsed out repeatedly with water, until the washings exhibit no acid reaction. The solution is mixed with an excess of bichloride of platinum, and evaporated to dryness in a water-bath protected from dust. If liquid hydro-carbons have been formed during the combustion with soda-lime, the aqueous solution should be separated from the oily matter, by passing it through a moistened filter. If the bichloride of platinum be not perfectly pure, an error may arise in two directions; for if it should contain ammonia or potassa, these will add to the weight of the ammonia produced in the combustion, so that an excess of nitrogen will be obtained; but if, on the other hand, the bichloride of platinum should contain any

free nitric acid, the evaporation with hydrochloric acid will cause an evolution of chlorine, which will decompose some of the ammonia, and give rise to a loss. In order to guard against these sources of error, the spongy platinum obtained by igniting the ammonio-chloride should be exhausted with dilute hydrochloric acid, dissolved in *aqua-regia*, and the solution evaporated, with addition of hydrochloric acid, until the odour of chlorine is no longer perceptible.

The dry residue in the porcelain dish is now to be treated with a mixture of two volumes of strong alcohol, and one volume of ether, which dissolves the excess of bichloride of platinum, and leaves the ammonio-chloride. If the solution should not be distinctly yellow, enough bichloride of platinum has not been added; in this case, the solution is again evaporated, the residue treated with a little water, a fresh portion of bichloride of platinum added, and the evaporation to dryness repeated.

The undissolved ammonio-chloride of platinum is collected upon a dried and weighed filter, and washed with the above mixture of ether and alcohol as long as the washings have an acid reaction. The filter with the precipitate is then dried in a water-bath, at 100° , weighed, and the weight of the dried filter deducted. 100 parts by weight of ammonio-chloride of platinum contain 6.26 parts of nitrogen.

The ammonio-chloride of platinum may also be ignited, and the amount of nitrogen calculated from the weight of the residual platinum. For this purpose, the filter containing the salt is placed in a weighed crucible of porcelain or platinum, and slowly heated to redness. The vapour of sal-ammoniac and chlorine which are then evolved would easily carry away some particles of the platinum, especially

if heat were applied too rapidly, but this is prevented by the paper which envelopes the salt. Finally, the crucible is placed obliquely, and heated until the filter is completely consumed; the residual metal is then weighed. 1 equiv. of platinum (99) corresponds to 1 equiv. of nitrogen (14) or 100 parts of platinum to 14.14 of nitrogen.

The amounts of nitrogen calculated from the ammoniochloride and from the metal, should, in accurate determinations, exactly coincide. One of the weighings may therefore be omitted; should it be required, however, to control one by the other, it is best effected as follows: An ignited crucible of platinum or porcelain is weighed, the filter introduced into it, dried, in the crucible, at 100° , and their joint weight determined. When the ammoniochloride of platinum has been collected and washed upon the filter, the latter is again dried at 100° , in the same crucible, and the amount of precipitate inferred from the increase of weight. The crucible, with its contents, may then be ignited, and the quantity of metallic platinum ascertained by deducting the original weight of the crucible, and the ash of the filter.

We have already stated that all organic substances containing nitrogen do not evolve the whole of this element in the form of ammonia when heated with soda-lime. The compounds of nitric acid with organic substances, and especially, also, those substances which contain inferior oxides of nitrogen (the nitro-compounds), although evolving some ammonia when ignited with hydrate of potassa, disengage, as Varrentrapp and Will have proved by many experiments, only a part of their nitrogen in this form, so that the determination of nitrogen by the above method, in substances of this description, is inadmissible.

Other nitrogenised organic substances, when ignited with

soda-lime, evolve no ammonia, but, in its stead, organic bases free from oxygen, which resemble ammonia in their characters. Thus, for example, indigo, when heated with hydrate of potassa, evolves aniline ($C_{12}H_7N$); several non-volatile organic bases, when heated with hydrate of potassa or soda-lime, yield volatile organic bases; this is the case with narcotine, morphine, quinine and cinchonine. Many organic bases free from oxygen, such as aniline, lenioline, ethylamine, &c., may be passed over ignited soda-lime without decomposition, or, at all events, without conversion of the whole of their nitrogen into ammonia.

All these volatile organic bases, however, combine with bichloride of platinum to form a double salt corresponding in composition to the ammonio-chloride, and always containing 1 equiv. of platinum for 1 equiv. of nitrogen. If, then, the analysis of substances which yield such bases, be conducted as usual, according to the method of Varrentrapp and Will, the weight of the residual platinum only being determined, it will be indifferent which organic base resulted from the decomposition, since it is only necessary to calculate 1 equiv. of nitrogen for every equiv. of platinum. Since, however, the platinum-double-salts of some of these volatile organic bases are more soluble in alcohol than the ammonio-chloride, they should be washed with ether to which only a few drops of alcohol are added (Hofmann).

Various alterations of the method of Varrentrapp and Will for the determination of nitrogen have been proposed, but cannot, for the most part, be regarded as improvements. Thus, instead of the bulb-apparatus, FIG. 78, employed for collecting the ammonia, other forms have been brought forward, which, however, do not equal this apparatus in convenience and simplicity. Instead of

hydrochloric acid, other liquids have been used for absorbing the ammonia, such as an alcoholic solution of tartaric acid, but have not yet been proved to furnish accurate results.

The following process described by Pélégot,* however, may be advantageously employed in cases where the object is rather rapidity of execution than the greatest possible accuracy, as, for example, in technical analyses.

The combustion with soda-lime is conducted in the usual manner, but the disengaged ammonia is collected in a measured volume of dilute sulphuric acid of known strength. Pélégot prepares this acid with 1 litre (1.761 pint) of water, and 61.25 grms. (945.33 grns.) of hydrate of sulphuric acid.

A solution of lime in sugar-water is now graduated with this dilute acid, the latter being first reddened with tincture of litmus, and the lime-solution added to it, drop by drop, until the red colour just passes into blue. The lime-solution is poured from a graduated burette, and the quantity required for neutralisation is carefully observed. If the sulphuric acid which has been employed to absorb the ammonia, be treated in the same way, less lime-solution will be required for neutralisation, and we learn from this experiment, how much of the sulphuric acid has been neutralised by the ammonia, the difference representing a quantity of the latter equivalent to the difference in the amounts of lime required to neutralise the two solutions.

We are now in possession of the three following data :

1. The weight of ammonia required to neutralise 1 volume of the sulphuric acid, which is inferred from the specific gravity of the acid (*a*).

* Journ. de Pharm. et de Chim. I. xi, p. 334.

2. The number of measures of lime-solution required to neutralise the same volume of sulphuric acid (*b*).

3. The number of measures of lime-solution required to neutralise the same volume of acid after absorbing the ammonia (*c*).

The following equation, then, will give us the weight of ammonia which has been absorbed by the sulphuric acid :

$$x = \frac{b-c}{b} \times a.$$

DETERMINATION OF CHLORINE IN ORGANIC COMPOUNDS.

The organic bases combine with hydrochloric acid to form salts, from which, as from the chlorides of the metals, the chlorine may be precipitated by a solution of oxide of silver, and weighed as chloride of silver. Frequently, however, chlorine exists in organic compounds in such a state that it cannot be precipitated by a silver-solution, and can only be converted into chloride of silver, and weighed, after destroying the organic matter.

Chlorineted organic compounds of this description are strongly heated with an alkali or an alkaline earth, when the chlorine combines with the metal. The simplest plan is to employ quick-lime (calcined marble), which should first be tested for chlorine; if it be not free from the latter, it must be slaked, the chloride of calcium removed by washing with water, and the residual hydrate of lime reconverted into quick-lime by ignition.

The weighed quantity of the substance to be analysed is intimately mixed, in a mortar, with the powdered quick-lime, the mixture introduced into a combustion-tube of 1 or 1½ foot in length, the mortar rinsed out with quick-lime which is likewise transferred to the tube, and the

latter then filled up with quick-lime. The tube is heated with charcoal in a combustion-furnace, commencing, as in a carbon-determination, at the anterior portion, and gradually surrounding the whole of the tube with glowing coals.

Volatile liquids are introduced into the tube in small glass bulbs, and the process conducted as in the ordinary combustion.

When the combustion is terminated, the tube is allowed to cool, its contents shaken into a beaker containing water, the portions adhering to the tube dissolved in dilute nitric acid, this solution added to the other, and the whole of the lime dissolved in dilute nitric acid with the aid of a gentle heat. The solution is filtered if necessary, and the chlorine precipitated by a solution of silver. The precipitated chloride of silver is filtered off as usual, washed, dried, and weighed.

The bromine or iodine contained in an organic substance may be estimated in a similar manner.

ESTIMATION OF SULPHUR IN ORGANIC COMPOUNDS.

Sulphuric acid is sometimes combined with organic substances in such a manner that its reactions remain unchanged, but, in many other cases, it can only be separated from the organic compound by destroying the latter. Other organic substances contain sulphur as sulpho-cyanogen, or combined with the organic body in such a manner that it cannot be oxidised and converted into sulphuric acid by treating the substance with nitric acid.

In these cases, in order to determine the sulphur contained in an organic substance, the latter is decomposed by fusion with hydrate of potassa, to which a little nitre is added in order to complete the combustion, and to convert the sulphur into sulphuric acid.

A few fragments of hydrate of potassa are fused in a capacious silver capsule, together with a little nitre (about $\frac{1}{8}$ of the amount of the potassa), with addition of two drops of water; the mass is allowed to cool, the weighed quantity of the finely-powdered substance added to it, and the whole heated to fusion over a spirit-lamp. The substance is mixed by stirring with a platinum spatula, and the temperature gradually increased, taking care to avoid spitting; the mass which is generally at first black from the separation of carbon, soon becomes colourless. If this should not be the case, a little powdered nitre may be added, in small portions. The colourless liquid solidifies, on cooling, to a mass which is entirely dissolved by water, with the aid of heat. The solution is poured into a beaker, the silver capsule repeatedly rinsed with water, and the mixed fluids supersaturated with hydrochloric acid. Since a considerable effervescence takes place in this operation, the beaker should be covered with a glass plate. Upon adding chloride of barium, sulphate of baryta is precipitated, which should be allowed to stand for twelve hours in the liquid, at a moderate heat, collected upon a filter, washed, dried, and ignited. From the weight of the sulphate of baryta, we may easily calculate the amount of the sulphur. The analyst must not omit to test the sulphate of baryta for caustic baryta, after weighing. It is well known that sulphate of baryta which has been precipitated from solutions containing nitric acid, obstinately retains a quantity of nitrate of baryta which is converted, by ignition, into caustic baryta. The ignited sulphate of baryta should therefore be treated with dilute hydrochloric acid, and the filtrate tested for baryta by adding sulphuric acid. Should baryta be found, the sulphate must be thoroughly washed with hydrochloric

acid, again ignited, and weighed. The admixture of nitrate of baryta, however, may always be avoided by employing as little nitre as possible, and by washing the sulphate of baryta very carefully with boiling water.

It is obviously necessary that both the caustic potassa and the nitre should be perfectly free from sulphur. When they have been fused together, a portion of the mass should be dissolved in water, and tested with chloride of barium. Caustic potassa may easily be obtained free from sulphur by treating ordinary hydrate of potassa with alcohol, when two layers of solution are formed, the upper one consisting of an alcoholic solution of hydrate of potassa which is evaporated in a silver capsule, and the solid hydrate fused.

In order to determine the amount of sulphur in volatile organic compounds, these are burnt with a mixture of carbonate of soda and nitre in a glass tube. A mixture of dry carbonate of soda and nitre is introduced into the end of a combustion-tube, and upon this the weighed portion of the liquid to be examined, contained in open glass bulbs; solid volatile substances are introduced in a small glass boat; the tube is then filled up with a mixture of carbonate of soda and a little nitre. The anterior portion of the tube having been heated to redness, the glass bulbs are gently heated, so as to cause a gradual volatilisation of the liquid, the hinder portion of the tube being kept sufficiently warm to prevent condensation of the vapour. Finally, the end of the tube is likewise heated to redness, when the evolved oxygen entirely consumes any carbon which may have separated. When the tube has cooled, its contents are dissolved in water, neutralised with hydrochloric acid, and precipitated with chloride of barium, the

same precautions being observed as were recommended in the former case.

METHODS OF CONTROLLING ORGANIC ANALYSES.

Having described, in the foregoing pages, all the precautions necessary to ensure an accurate result, it remains for us to consider certain methods which are occasionally employed to control the determinations of carbon and hydrogen.

In the case of substances possessing low atomic weights, and in which the number of the atoms of each element is very small, no farther control is required, than the accurate determination of the atomic weight. The case is very different, however, with a substance the atomic weight of which is rather high; in such a case, a slight difference in the determination of the atomic weight sometimes corresponds to an error of more than half an equivalent of carbon, and often to more than one equivalent of hydrogen; with substances of this description, the following methods of control should not be neglected:

Control for the Carbon.—When the substance is capable of combining with a nitrogenised body, as, for example, with ammonia or nitric acid, the combustion of the compound thus formed, in which the quantity of the nitrogenised constituent is known, allows us strictly to control the carbon-determination by the proportion between the nitrogen and carbonic acid obtained by combustion, which must stand to each other in the ratio of the equivalents of nitrogen and carbon.

Control for the Hydrogen.—In organic bases, the hydrogen-determination may be controlled by a combustion of the hydrochlorate, for since hydrochloric acid combines

with these bases, without decomposition, the amount of water obtained, calculated upon the weight of the base, must be too great by 1 equivalent—that is, by the quantity formed from the hydrogen of the acid. The same principle may be applied in the case of acids, by burning their ammonia-compounds. With substances like stearic acid, oleic acid, &c., an uncertainty always attaches to the determination of hydrogen; in such a case, the analyst must adopt those numbers which agree most closely with the lowest amount of hydrogen obtained in the combustion. The surest method of acquiring certainty upon this head, consists in decomposing the substance into new products, and analysing the latter. The amount of hydrogen contained in these must exhibit a clear and decided relation to that in the original substance; should such a decomposition not be possible, the uncertainty still remains.

DETERMINATION OF THE NUMBER OF ATOMS OF THE
ELEMENTS IN AN ORGANIC COMPOUND.

The processes hitherto described enable us to ascertain the proportions of the various elements in a known weight of the substance analysed, without throwing any light, however, upon the number of atoms of each element present in the compound. It is true, that their relative numbers may be determined with certainty when we are able to decompose the substance into products of known composition, but this method has been applied hitherto only in a few cases, and the determination of the proportion by weight in which the substance enters into combination with the known atomic weight of another

body, still remains the most important auxiliary in the inquiry after the true composition of a substance, and affords the chief control of the results obtained by analysis.

If the substance be an acid, its atomic weight is determined by analysing one of its salts; the silver-, lead- or baryta-salt is best adapted for this purpose. The silver-salt, when it can be obtained, should be preferred to all others, since it is always anhydrous, and, when ignited, leaves pure metallic silver, from which the atomic weight may be easily calculated. Many silver-salts deflagrate when heated; these must be analysed by converting the silver into chloride. It has been proposed to prevent the deflagration by moistening the dry salt with oil of turpentin, and kindling it; but oxalate, fumarate, and other salts of silver deflagrate in spite of this precaution, which fulfils its object in very few cases.

Berzelius analysed lead-salts in a very convenient and expeditious manner. He placed them in a small porcelain capsule, and heated them strongly at the edge, where they generally take fire, and continue to burn until nothing is left but a mixture of oxide of lead and metallic lead. After weighing, the mixture is treated with acetic acid, then with water, lastly, washed by decantation with alcohol, dried, and again weighed; the loss of weight is due to oxide of lead; the increase of the weight of the capsule represents the amount of metallic lead.

In preparing the compounds with oxide of lead, regard must be had to the tendency of insoluble lead-salts to carry down, in combination with them, salts, otherwise soluble, which may exist in the solution.

When an acid forms a basic, or acid, as well as a neutral

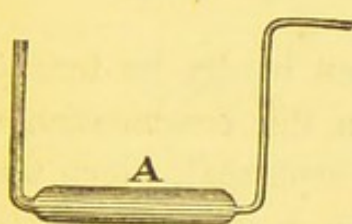
salt, the analyses of these compounds will furnish new data for calculating the atomic weight; all, however, which could be said upon this point, will be obvious to every one who is acquainted with general chemical analysis.

Baryta-compounds are very well suited for the determination of atomic weights; but, in the case of substances with high equivalents, lime-salts are liable to give rise to considerable errors.

The combustion of the acid itself, and of one of its anhydrous salts, decides the amount of water it contains, and that of its water of hydration.

The determination of the water of crystallisation contained in a salt is of importance in organic analysis, and should not be neglected where it is practicable.

FIG. 79.



The capacity of saturation of organic bases is determined with the aid of the apparatus exhibited in FIG. 79. The organic base is introduced into the wider portion of the tube, its weight (in the dry state) then determined, and a stream of dry hydrochloric acid gas passed through it. Combination takes place readily, with evolution of heat; many substances fuse, others remain porous: in all cases, a small excess of hydrochloric acid always remains which does not belong to the compound. In order to remove this, the substance is treated in the same way as if it were to be dried; the apparatus is surrounded with boiling water, and dry air allowed to pass through it until its weight is constant. The increase of weight of the apparatus shows the amount of hydrochloric acid which has combined with the base.

Should it be deemed necessary to ascertain whether any

water has been expelled in the combination of the base with the acid (which would apparently diminish the weight of the latter), a known weight of the hydrochlorate must be dissolved in water, and the hydrochloric acid determined as chloride of silver.

In many cases, the equivalents of the organic bases may be more accurately determined by the analysis of the double compounds formed by their hydrochlorates with bichloride of platinum, or terchloride of gold. These compounds contain, for every equivalent of platinum or gold, 1 equivalent of base, combined with 1 equivalent of hydrochloric acid; and, in the case of platinum, with 2 equivalents, in that of gold, with 3 equivalents, of chlorine. The amount of platinum, or gold, may be easily determined by burning a weighed quantity of the double salt in a porcelain crucible.

Many organic substances, which can hardly be termed acids, combine with oxide of lead; in this combination a certain quantity of water is sometimes separated, which was not evolved from the substance when heated alone; the analysis of the pure substance, and of this compound with oxide of lead, will give us all the information which we require respecting the number of atoms of the various elements.

Other substances combine neither with acids nor bases; they crystallise, however, with a certain quantity of water the estimation of which must be conducted with the greatest care. From the result we may calculate, with equal certainty, the single, half, or double, &c., atomic weight of the substance, which depends, of course, upon the number of atoms of water with which it enters into combination.

Examples. Composition of cholalic acid.

DETERMINATION OF THE EQUIVALENT OF THE ACID.

- I. 0.5235 gm. (8.080 grns.) of the baryta-salt, gave :
 0.1270 „ (1.960 gm.) of sulphate of baryta.
 II. 0.5800 „ (8.952 grns.) of the baryta-salt, gave :
 0.1210 „ (1.868 grns.) of carbonate of baryta.

The equivalent of sulphate of baryta is 116.5; that of cholalate of baryta (x) will therefore be deduced from I., by the proportion

$$0.1270 : 116.5 = 0.5235 : x = 480.2 \quad \text{I.}$$

From the second determination the equivalent of cholalate of baryta is obtained by the following proportion, in which 98.5 represents the equivalent of carbonate of baryta :

$$0.1210 : 98.5 = 0.5800 : x = 472.1 \quad \text{II.}$$

The arithmetical mean of the two equivalents is 476.2.

- III. 0.3361 gm. (5.187 grns.) of the same salt, when burnt with chromate of lead, gave :

0.7425 gm. (11.460 grns.) of carbonic acid, corresponding to 220.9 per cent, or to 60.24 per cent of carbon.

- IV. 0.3410 gm. (5.263 grns.) gave :

0.7505 gm. (11.583 grns.) carbonic acid, or 220.1 per cent, corresponding to 60.02 per cent, of carbon.

100 parts of the baryta-salt give therefore, as a mean :

220.5 parts of carbonic acid, or
 60.13 „ of carbon.

0.3361	grm. (5.187 grns.)	of the baryta-salt	gave, moreover,	0.2500	grm. (3.859 grns.)	of water
0.3410	„ (5.263 grns.)	„	„	0.2530	„ (3.905 grns.)	„
<u>0.6771</u>	<u>10.450</u>			<u>0.5030</u>	<u>7.764</u>	

100 parts of chololate of baryta contain, therefore, 8.25 parts of hydrogen.

If these results be added together, and the difference in 100 parts estimated as oxygen, the following percentage composition of chololate of baryta is obtained :

Carbon	.	.	.	60.13
Hydrogen	.	.	.	8.25
Baryta	.	.	.	16.07
Oxygen	.	.	.	15.55
				<hr/>
				100.00

In order now to deduce the chemical formula—that is, the number of equivalents of the elements contained in one equivalent of the acid—it is necessary to calculate the quantity of each element existing in one equivalent of the salt.

The equivalent found for the baryta-salt, in the example cited above, is 476.2 ; one equivalent of the salt contains, therefore :

$60.13 \times 4.762 = 286.3$	parts (by weight) of	Carbon.
$8.25 \times 4.762 = 39.3$	„	Hydrogen.
$16.07 \times 4.762 = 76.5$	„	Baryta.
$15.55 \times 4.762 = 74.1$	„	Oxygen.
<hr/>		
476.2		

One equivalent of chololate of baryta contains 286.3 parts by weight of carbon ; if this number be divided by the weight of 1 equivalent of carbon, the quotient is the

number of equivalents of that element ; and so on for the rest :

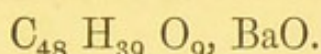
$$286.3 : 6 = 47.7, \text{ say } 48 \text{ equivs. of carbon.}$$

$$39.3 : 1 = 39.3, \text{ ,, } 39 \text{ ,, hydrogen.}$$

$$76.5 : 76.5 = 1 \text{ equiv. of baryta.}$$

$$74.1 : 8 = 9.3, \text{ say } 9 \text{ equivs. of oxygen.}$$

The chemical formula of cholalate of baryta, therefore, is



The comparison of the percentage composition required by the formula, with the numbers obtained by analysis, will show how far the experimental coincides with the calculated result :

		Calculated.	Found, as a mean.
48 equivs. Carbon	= 288	60.57	60.13
39 ,, Hydrogen	= 39	8.20	8.25
9 ,, Oxygen	= 72	15.14	15.55
1 ,, Baryta	= 76.5	16.09	16.07
	<hr/>	<hr/>	<hr/>
	475.5	100.00	100.00

The example here given exhibits the usual method of calculating the number of equivalents of the elements composing an organic substance, from the results of analysis ; the formula arrived at being that which approximates most closely to the numbers found by experiment.

In calculating and controlling the results of the analysis of an organic base, the atomic weight is inferred from the amount of acid with which the base forms a constant combination ; in every other respect the method above described, is followed.

The number of organic substances which do not enter into combination with any other, of known atomic weight, and to which this method of control is therefore inapplica-

ble, is exceedingly small; in such cases, the analyst must be content to find the atomic proportion of the constituents, and to express this in the simplest form.

Mannite was formerly classed among these substances, since no combinations of this body were known.

0.3945 gm. (6.089 grns.) of mannite furnished 0.5720 gm. (8.828 grns.) of carbonic acid, and 0.2745 gm. (4.237 grns.) of water. This gives, for the composition in 100 parts:

Carbon	.	.	.	39.54
Hydrogen	.	.	.	7.73
Oxygen	.	.	.	52.73
				100.00

If these numbers be divided, respectively, by the equivalent weights of carbon, hydrogen, and oxygen, the quotients will be the number of equivalents of these elements contained in 100 parts of the compound. Now, since the equivalent of mannite is not known, only the ratio of its constituent elementary atoms can be determined, and as there are no other methods of ascertaining their absolute number, this ratio can only be given in its simplest form which, in the above example, would be obtained in the following manner:

$$\frac{39.54}{6} = 6.59 \text{ equivs. of Carbon,}$$

$$\frac{7.73}{1} = 7.73 \quad \text{,,} \quad \text{Hydrogen,}$$

$$\frac{52.73}{8} = 6.59 \quad \text{,,} \quad \text{Oxygen.}$$

The number of equivalents of oxygen in organic compounds being usually not very large, the proportion is first

calculated for 1 equivalent of oxygen, and then multiplied successively by 2, 3, 4, 5, &c., until whole numbers are obtained.

In the example before us, there are, for 1 equiv. of oxygen:

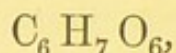
$$\frac{6.59}{6.59} = 1 \quad \text{equiv. of Carbon.}$$

$$\frac{7.73}{6.59} = 1.17 \quad \text{,, Hydrogen.}$$

1 equiv. of oxygen, 1 equiv. of carbon, and 1.17 equiv. of hydrogen, expressed in the simplest whole numbers, become:

6 equivs. of oxygen, 6 equivs. of carbon, and 7 equivs. of hydrogen.

Hence, the empirical formula of mannite would be:

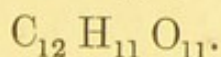


which has been confirmed by the more recent analyses of its combinations.

By the analysis of crystallised cane-sugar, the following percentage composition was obtained:

Carbon	.	41.50	$\frac{41.50}{6} = 6.92$	1.065	11.7
Hydrogen	.	6.45	$\frac{6.45}{1} = 6.45$	0.993	10.9
Oxygen	.	52.05	$\frac{52.05}{8} = 6.50$	1	11

The empirical formula of sugar, therefore, is:



It is customary to calculate the composition of the substance according to the formula thus obtained, and to com-

pare it with the results of the analysis, from which it should not differ more than was stated above to be allowable in good analyses.

	Equiv.	Calculated.		Found.
Carbon .	12	72	42.11	41.50
Hydrogen.	11	11	6.43	6.45
Oxygen .	11	88	51.46	52.05
		<hr/>	<hr/>	<hr/>
		171	100.00	100.00

Very many organic substances, the atomic weights of which cannot be directly determined, are decomposed, when brought in contact, under certain conditions, with other bodies, for instance when treated with acids or alkalies, into new products, the composition of which is either already known or may be easily determined. These modes of decomposition afford very important data for determining the composition of a substance and controlling the analysis. Sugar, in contact with yeast, is decomposed into carbonic acid and alcohol; oxamide into ammonia and oxalic acid. It is evident that if, in the former case, the quantity of carbonic acid, and in the latter, that of the oxalic acid produced, be known, and if it be also certain that sugar yields in this decomposition no farther product except alcohol, and that the sole products of the decomposition of oxamide are oxalic acid and ammonia, the composition of these substances may be thence inferred with the greatest certainty.

Many indifferent nitrogenised bodies are decomposed by the alkalies into ammonia and an acid, the atomic weight of which may be determined. To this class belong asparagin and amygdalin; in these cases the atomic weight may be easily determined from the quantity of the acid or of one of

its salts produced from a known weight of the substance. Thus, for example, 1.357 gm. (20.944 grns.) of amygdalin yields 1.592 gm. (24.571 grns.) of amygdalate of baryta; hence, the atomic weight of amygdalin is obtained by the proportion $1.592 : 434.5 = 1.357 : x = 455.6$.

In the case of a volatile substance, the determination of the specific gravity of its vapour is a valuable method of control for organic analysis. The method which is employed for effecting this, has been published by Dumas, and was first practised and applied to this purpose by that distinguished chemist. The description which Dumas has given of this process embraces all the precautions necessary to ensure an accurate result.*

DETERMINATION OF THE SPECIFIC GRAVITY OF THE VAPOUR
OF A VOLATILE SUBSTANCE WITH A VIEW TO ASCERTAIN
THE NUMBER OF ATOMS OF ITS ELEMENTS.

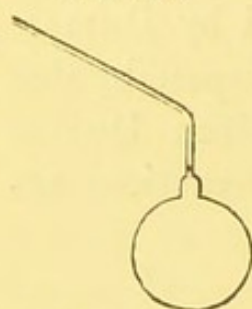
The apparatus employed for ascertaining the specific gravity of a vapour is exceedingly simple, and the whole operation may be executed without a great expenditure of time or skill. The result to be arrived at is the determination of the weight of a known volume of the vapour.

For this purpose, a suitable vessel, filled with dry air of known temperature and pressure, is weighed; the liquid, or volatile body, is then introduced, and heated to a temperature of about 30° or 40° above its boiling-point, until it is entirely converted into vapour, the temperature of which is then ascertained, the vessel hermetically sealed, and again weighed. The weights of the vessel filled with air, and with vapour, are then known, and after reducing

* *Traité de Chimie par Dumas*. Paris, Béchet, jeune, t. v, p. 45.

them to the same temperature and pressure, their respective weights may be calculated, provided we have ascertained previously the capacity of the vessel, and consequently the volume of air or vapour which it is capable of containing. The specific gravity of the vapour is obtained by dividing the weight of a certain volume by that of an equal volume of air, at the same temperature and pressure.

FIG. 80.



The process is conducted as follows: a small, clean, and dry glass flask is taken, FIG. 80, capable of containing from 300 to 500 cub. cent. (18.3 to 30.5 cub. in.); the neck of this flask is connected with the air-pump and the apparatus shown in FIG. 6, the air exhausted, and fresh air allowed to enter, by opening the stop-cock; in this way, the damp air in the flask is replaced by air which has been dried in its passage through the tube filled with chloride of calcium.

The neck of the flask is now drawn out to a long narrow tube, from 6 to 8 inches long, which is bent as shown in the figure; the point should be cut off with a sharp file, and the edge rounded in a spirit-flame. The glass should not blacken or become crystalline when heated, for it would then be difficult, or sometimes impossible, to close the point rapidly in the blowpipe-flame. A bulb or globe with a long point has thus been obtained; this must now be weighed, with its point open, and left for some time in the balance, until no farther alteration in weight takes place, from the condensation of moisture upon the surface of the glass.

The substance is next to be introduced (if a solid, in a fused state); for this purpose the globe is gently heated so as to expel a portion of the air, and allowed to cool with

its open point dipping into the liquid which will then enter and fill the space previously occupied by the expelled air. By cooling the bulb with a few drops of ether, this may be always effected very rapidly. The quantity of liquid which is allowed to enter must be regulated according to the capacity of the globe; 5 grms. (77.17 grns.) may be taken as the minimum, and 10 grms. (154.34 grns.) as the maximum quantity. Should the substance solidify again in the narrow tube, this must, of course, be previously heated.

The globe is now immersed in a bath of water, chloride of calcium, chloride of zinc, &c., which is then heated, in every case, to a temperature 30° or 40° above the boiling-point of the volatile substance. The bath may, of course, be heated to the necessary temperature before immersing the globe, since it need never be feared that the latter will crack. A very accurate thermometer indicates the temperature of the bath.

The globe may be secured in the bath in various ways. FIG. 81 exhibits an arrangement for this purpose. FIG. 82 shows a handle for the globe.

FIG. 81.

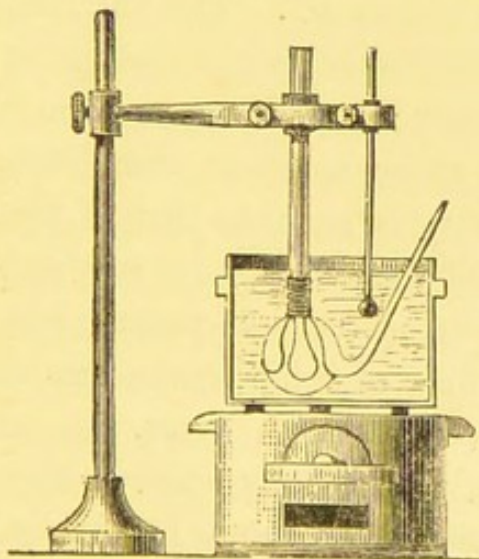


FIG. 82.



As soon as the temperature has risen some degrees above the boiling-point of the substance, a stream of vapour issues from the open point; this stream gradually diminishes, and, after 15 or 20 minutes, a flame applied to the orifice of the point is not in the least deflected. If any drops of the liquid should be seen to condense in that part of the point which is not immersed in the bath, these must be expelled by holding a red-hot coal near that portion of the tube; the point is then rapidly softened in a blowpipe-flame (the globe being still immersed in the bath), when it is easily and effectually closed.

The iron bath is now removed from the fire, the sealed globe withdrawn, and, after being well washed and dried, very accurately weighed.

The vapour of the substance has expelled all the atmospheric air, except a small quantity which must be determined; the volume of the vapour must likewise be ascertained.

In order to determine these, the whole of the point of the globe is immersed in mercury, a scratch is made near to the neck, and the point broken off. The vacuum, caused by the condensation of the vapour when the globe cooled, is then filled by the mercury; in most cases a small bubble of air is left; but the globe is often completely filled. The volume of the mercury is equal to that of the vapour at the high temperature at which the point was sealed. To determine this volume, the mercury is poured into a graduated tube, and the number of cubic centimetres observed. The globe is now filled entirely with water, the volume of which is also determined; it usually exceeds that of the mercury by 1 or 2 cub. cent. (0.06 or 0.12 cub. in.) The

difference between them represents the volume of the residual air.

From the results of this experiment, the specific gravity of the vapour may be calculated. The necessary calculations will be seen by the following example :

DETERMINATION OF THE SPECIFIC GRAVITY OF FURFUROL-VAPOUR.

Boiling-point of furfurool 162° . Weight of the globe, filled with dry air at 20° C. and 759^{mm} (29.88 in.) Bar. 47.770 grms. (737.282 grns.) At the conclusion of the experiment, the capacity of the globe was found, by measuring with water, to be 188 cub. cent. (11.47 cub. in.), which therefore represents the volume of air weighed in the globe ; 188 cub. cent. of air at 20° and 759^{mm} Bar., when reduced to 0° and 760^{mm} (29.92 in.) Bar. (the coefficient of expansion of air for 1° being taken as 0.00367) would become 174.91 cub. cent. (10.67 cub. in.) Since, according to the latest determination of Regnault, 1000 cub. cent. (61.027 cub. in.) of air at 0° and 760^{mm} Bar. weigh 1.2932 gm. (19.959 grns.), the weight of the 174.91 cub. cent. of air contained in the globe would be 0.2262 gm. (3.491 grns.), and if this weight be subtracted from that of the globe filled with air, the weight of the empty globe will be obtained ; $47.770 - 0.2262 = 47.5438$ grms. (733.791 grns.)—The globe, when filled with furfurool-vapour, was sealed at 217° C. and 759^{mm} Bar. ; its weight was then found to be 48.000 grms. (740.832 grns.) On breaking the point, 188 cub. cent. of mercury entered the globe, showing that all the atmospheric air had been expelled by the furfurool-vapour, at the time of sealing. When the weight of the empty globe is subtracted from that of the globe filled with

vapour, there remains $48.000 - 47.5438 = 0.4562$ grm. (7.041 grns.) for the weight of the furfurol-vapour. If the capacity of the globe, at the temperature of sealing the point, be taken as 188 cub. cent., the vapour contained in it at this temperature, on the supposition that it could be cooled without condensation, would become at 0° and 760^{mm} Bar., 104.52 cub. cent. (6.38 cub. in.) This volume of furfurol-vapour weighs 0.4562 grm., and 1000 cub. cent., under the same circumstances, would weigh 4.3649 grms. (67.368 grns.) If this weight be compared with that of an equal volume of atmospheric air at the same temperature and pressure, the number $\frac{4.3649}{1.2932} = 3.375$ is obtained as the specific gravity of furfurol-vapour.

This is the usual method of calculating the specific gravity of a vapour. It appears, at first sight, to require the assumptions that the vapour of the substance under examination (in the above example, furfurol) would admit of being cooled to 0° without condensation, and that the expansion which the vapour suffers when heated is the same as in the case of atmospheric air. The necessity of these assumptions, however, is only apparent, as will be readily seen if it be remembered that the specific gravity of a gas or vapour is nothing else than the relation of its weight to that of an equal volume of atmospheric air under the same conditions. It is quite indifferent whether, for the purpose of making this comparison, the weight and volume of the vapour be sought under those circumstances in which the weight and volume of atmospheric air is known (as was done in the above example), or whether, conversely, the weight and volume of air be sought, under circumstances in which the weight and volume of the

vapour are given. The above experiment showed that 188 cub. cent. of furfurool-vapour at 217° and 759^{mm} Bar. weigh 0.4562 grm. It is easily calculated that 188 cub. cent. of atmospheric air at 217° and 759^{mm} Bar., weigh 0.1352 grm. (2.087 grns.), and the specific gravity of furfurool-vapour would then be $= \frac{0.4562}{0.1352} = 3.375$, as was found

in the former case.

If all the atmospheric air were not expelled from the globe before sealing it, the calculation becomes somewhat more complicated. Let us suppose that on opening the sealed globe under mercury, only 187.5 cub. cent. (11.44 cub. in.) of the metal had entered; then, since the capacity of the globe, determined by measuring with water, was 188 cub. cent., $188 - 187.5 = 0.5$ cub. cent. (0.03 cub. in.) of air had remained in the globe. The weight of this quantity of air must be calculated, and deducted from the total weight of the vapour; its volume, at the temperature of the sealing, is also to be calculated, and deducted from the total volume of vapour indicated by the capacity of the globe. After this correction in the weight and volume of the vapour, the calculation may be proceeded with as in the above example. Should the volume of the residual air be considerable, it must always be taken into consideration, especially in the determination of the specific gravities of vapours much heavier or lighter than atmospheric air.

The process just described for determining the specific gravities of vapours is not capable of absolute accuracy; the volumes measured and weighed are too small, and if large globes be employed, the apparatus loses its simplicity, the manipulations become more difficult, and large balances,

of very accurate workmanship, become indispensable. All this is unnecessary for the attainment of the object in view in this operation; it is sufficient if the specific gravity found by experiment coincide to the first decimal place, with that obtained by calculation. For this reason, it is quite superfluous to take account of the expansion of the glass, or to compare the indications of the mercurial with those of the air thermometer; the influence of these corrections falls far within the limits of the unavoidable errors of experiment. The alterations in the height of the barometer, which are insignificant during the ordinary course of an experiment, may also be neglected. It is likewise unnecessary to take any note of the weight of the residual air, and of its expansion between the temperature at which it was measured, and that at which the globe was sealed (which omissions, to some extent, compensate each other); in this way we arrive at the following very convenient formula for the calculation of the specific gravity of a vapour from the results of an experiment conducted in the manner described above:*

$$f = \frac{P + Vn_t}{(V - v)n_t}$$

in which f represents the required specific gravity of the vapour; P the difference between the weight of the globe filled with air, and that of the globe filled with vapour; V the capacity of the globe in cubic centimeters; v the volume of the residual air; n_t the weight of 1 cub. cent. of atmospheric air, at the temperature at which the globe

* See the paper by J. Müller in the *Annalen der Chemie und Pharmacie*, XXVIII, 162.

filled with air was weighed; n_t , the weight of 1 cub. cent. of atmospheric air, at the temperature at which the globe was sealed. In order to facilitate this calculation, we have given, in the following table, with sufficient accuracy, the weight of 1 cub. cent. of atmospheric air (starting from 0.001293 at 0°, and taking the co-efficient of expansion for 1° as 0.00367), for the temperatures between 0° and 100°:

n		n		n	
0°	0.001293	32°	0.001157	64°	0.001047
1	0.001288	33	0.001154	65	0.001044
2	0.001284	34	0.001150	66	0.001041
3	0.001279	35	0.001146	67	0.001038
4	0.001275	36	0.001142	68	0.001035
5	0.001270	37	0.001138	69	0.001032
6	0.001266	38	0.001134	70	0.001029
7	0.001261	39	0.001131	71	0.001026
8	0.001257	40	0.001128	72	0.001023
9	0.001252	41	0.001124	73	0.001020
10	0.001248	42	0.001121	74	0.001017
11	0.001243	43	0.001118	75	0.001014
12	0.001239	44	0.001114	76	0.001011
13	0.001234	45	0.001111	77	0.001008
14	0.001230	46	0.001108	78	0.001005
15	0.001225	47	0.001105	79	0.001002
16	0.001221	48	0.001102	80	0.001000
17	0.001217	49	0.001098	81	0.000997
18	0.001213	50	0.001095	82	0.000994
19	0.001209	51	0.001091	83	0.000992
20	0.001205	52	0.001088	84	0.000989
21	0.001201	53	0.001084	85	0.000986
22	0.001197	54	0.001081	86	0.000983
23	0.001193	55	0.001077	87	0.000980
24	0.001189	56	0.001074	88	0.000977
25	0.001185	57	0.001070	89	0.000974
26	0.001181	58	0.001067	90	0.000972
27	0.001177	59	0.001063	91	0.000969
28	0.001173	60	0.001060	92	0.000967
29	0.001169	61	0.001057	93	0.000964
30	0.001165	62	0.001053	94	0.000962
31	0.001161	63	0.001050	95	0.000959

<i>n</i>		<i>n</i>		<i>n</i>	
96 ⁰	0.000956	140 ⁰	0.000854	184 ⁰	0.000772
97	0.000953	141	0.000852	185	0.000770
98	0.000951	142	0.000850	186	0.000769
99	0.000948	143	0.000848	187	0.000767
100	0.000946	144	0.000846	188	0.000765
101	0.000943	145	0.000844	189	0.000763
102	0.000941	146	0.000842	190	0.000762
103	0.000938	147	0.000840	191	0.000760
104	0.000936	148	0.000838	192	0.000758
105	0.000933	149	0.000836	193	0.000757
106	0.000931	150	0.000834	194	0.000755
107	0.000928	151	0.000832	195	0.000754
108	0.000926	152	0.000830	196	0.000752
109	0.000923	153	0.000828	197	0.000751
110	0.000921	154	0.000826	198	0.000749
111	0.000919	155	0.000824	199	0.000748
112	0.000916	156	0.000822	200	0.000746
113	0.000914	157	0.000821	201	0.000744
114	0.000911	158	0.000819	202	0.000743
115	0.000909	159	0.000817	203	0.000740
116	0.000907	160	0.000815	204	0.000739
117	0.000905	161	0.000813	205	0.000737
118	0.000903	162	0.000811	206	0.000736
119	0.000900	163	0.000809	207	0.000734
120	0.000898	164	0.000807	208	0.000733
121	0.000896	165	0.000806	209	0.000731
122	0.000894	166	0.000804	210	0.000730
123	0.000891	167	0.000802	211	0.000728
124	0.000889	168	0.000800	212	0.000727
125	0.000887	169	0.000798	213	0.000725
126	0.000884	170	0.000796	214	0.000724
127	0.000882	171	0.000794	215	0.000722
128	0.000880	172	0.000793	216	0.000721
129	0.000878	173	0.000791	217	0.000719
130	0.000876	174	0.000789	218	0.000718
131	0.000874	175	0.000788	219	0.000716
132	0.000871	176	0.000786	220	0.000715
133	0.000869	177	0.000784	221	0.000713
134	0.000867	178	0.000782	222	0.000712
135	0.000865	179	0.000781	223	0.000710
136	0.000863	180	0.000779	224	0.000709
137	0.000860	181	0.000777	225	0.000708
138	0.000858	182	0.000776	226	0.000706
139	0.000856	183	0.000774	227	0.000705

<i>n</i>		<i>n</i>		<i>n</i>	
228°	0·000703	253°	0·000670	277°	0·000641
229	0·000702	254	0·000669	278	0·000640
230	0·000701	255	0·000668	279	0·000639
231	0·000699	256	0·000666	280	0·000638
232	0·000698	257	0·000665	281	0·000636
233	0·000697	258	0·000664	282	0·000635
234	0·000695	259	0·000663	283	0·000634
235	0·000694	260	0·000662	284	0·000633
236	0·000692	261	0·000660	285	0·000631
237	0·000691	262	0·000659	286	0·000630
238	0·000690	263	0·000658	287	0·000629
239	0·000689	264	0·000657	288	0·000628
240	0·000688	265	0·000655	289	0·000627
241	0·000686	266	0·000654	290	0·000626
242	0·000685	267	0·000653	291	0·000625
243	0·000683	268	0·000652	292	0·000624
244	0·000682	269	0·000651	293	0·000623
245	0·000681	270	0·000650	294	0·000622
246	0·000679	271	0·000648	295	0·000621
247	0·000678	272	0·000647	296	0·000620
248	0·000677	273	0·000646	297	0·000619
249	0·000675	274	0·000645	298	0·000618
250	0·000674	275	0·000643	299	0·000617
251	0·000673	276	0·000642	300	0·000616
252	0·000672				

In calculating the above example of furfurol-vapour by this formula: $P=0\cdot230$ ($=48\cdot00-47\cdot77$), $V=188$, $v=0$

$n_t=0\cdot001505$, $n_t'=0\cdot000719$; therefore

$$f = \frac{0\cdot230 + 188 \times 0\cdot001205}{188 \times 0\cdot000719} = \frac{0\cdot4565}{0\cdot1352} = 3\cdot376$$

which scarcely differs from the result calculated above.

As another example of the application of this formula, let it be supposed that, in a determination of the specific gravity of the vapour of acetic ether, the capacity of the globe $=V=305$ cub. cent., its weight when filled with air at 10° , $=36\cdot000$ grms., the weight of the globe filled with

vapour at 100° , the temperature at the moment of sealing, = 36.488 grms., the volume of the residual air = $v = 10$ cub. cent. Here, $P = 36.488 - 36.000 = 0.488$, n_t , according to the above table = 0.001248, $n_t' = 0.000946$, and hence, the specific gravity of acetic ether vapour,

$$f = \frac{0.488 + 305 \times 0.001248}{(305 - 10) \times 0.000946} = \frac{0.8686}{0.2791} = 3.112$$

APPLICATION OF A KNOWLEDGE OF THE SPECIFIC GRAVITY OF THE VAPOUR TO CONTROL THE ANALYSIS OF A SUBSTANCE.

Knowledge of the vapour-density often serves as a valuable control for the formula deduced from the analysis of a substance, especially in cases where the atomic weight cannot be inferred from the combinations formed with other substances.

It is the result of a well-known law, that gaseous bodies combine with each other only in simple proportions by volume, and that the volume of the resulting gas bears a simple relation to the sum of the volumes of its constituent gases. The weights of equal volumes of the gaseous elements are either actually equivalent weights, or such as stand in a very simple relation to the equivalent weights.

If the analysis of a substance, and the formula deduced from it, be correct, the vapour-density found by experiment must coincide with that calculated from the formula, by a method based upon the proposition above enunciated; and in this case, the determination of the vapour-density serves to confirm both the formula and the analysis from which it was deduced.

If it be assumed that, in the case of oxygen, the equivalent weight is represented by one volume, then there are reasons for making the same assumption for the vapour of carbon (that is, supposing that the specific gravities of oxygen-gas and carbon-vapour are to each other as the equivalent weights of the two elements). Respecting hydrogen, and some other elements, it is known that an equivalent by weight occupies, in the gaseous state, twice the space occupied by an equivalent of oxygen, that is, the equivalent in the former cases represents two volumes. Moreover, the specific gravity may be regarded as the weight of one volume of a gas; the specific gravities of the elements which occur most frequently in organic compounds, have been either directly determined, or deduced from theoretical considerations.

Carbon	.	.	.	0·830
Hydrogen	.	.	.	0·0691
Oxygen	.	.	.	1·106

The analysis of furfural led to the adoption of the formula $C_5H_2O_2$. In order to ascertain how far this agrees with the vapour-density (3·375) found by experiment, the calculation proceeds as follows:

5 eqs. of carbon-vapour represent 5			
vols., which weigh	.	.	$5 \times 0\cdot830 = 4\cdot150$
2 eqs. of hydrogen-gas represent 4			
vols., which weigh	.	.	$4 \times 0\cdot0691 = 0\cdot2764$
2 eqs. of oxygen-gas represent 2			
vols., which weigh	.	.	$2 \times 1\cdot106 = 2\cdot212$

Sum of these weights = 6·6384

If the 5 vols. of carbon-vapour, 4 vols. of hydrogen, and

2 vols. of oxygen were combined to form 1 vol. of furfurol-vapour, or, in other words, if the formula $C_5H_2O_2$, for furfurol, represented a condensation to 1 volume, the weight of this 1 volume, *i. e.* the specific gravity of furfurol-vapour, would be 6.638. But the constituents of a gaseous compound are by no means always condensed into 1 volume; condensation to 2, and, especially, to 4 volumes, frequently occurs. The formula $C_5H_2O_2$ manifestly requires a condensation of vapour to 2 volumes, and, proceeding upon this supposition, a number $\frac{6.638}{2} = 3.319$ is obtained for the theoretical specific gravity, or weight of 1 volume, of furfurol-vapour, which agrees, as closely as can be expected, with that found by experiment (3.375).

This agreement shows, that the atomic ratio of the elements of furfurol, expressed by the formula $C_5H_2O_2$, is really the true one, and consequently, that the analysis is correct, since the specific gravity deduced from this formula, and from the known laws which regulate the combination of gases by volume, coincides with that determined by experiment.

The corroboration thus afforded is confined, however, to the atomic ratio of the elements, as expressed by the formula $C_5H_2O_2$, and does not extend to the atomic weight represented by that formula. For the double formula $C_{10}H_4O_4$ (which expresses the same atomic proportion of the elements) gives also, for the specific gravity of the vapour, 3.319, the calculation being founded, in this case, upon the supposition that a condensation to 4, instead of 2, volumes, takes place, which, in fact, more commonly occurs in organic compounds.

The method just described for calculating the theoretical

specific gravity of a vapour from the formula of the substance, is that usually adopted by chemists. It proceeds, however, upon certain assumptions, for example, that of the specific gravity of carbon-vapour, which have not been fairly established, and involves the consideration that, in the case of some elements, 1 equiv. represents 1 vol. of gas or vapour, whilst, in others, 1 equiv. represents 2 vols., and so forth. These assumptions and considerations are rendered unnecessary by the following method of calculation employed by H. Kopp, which, moreover, has the advantage of being shorter and less laborious than the foregoing.

The weights of the different gaseous or aeriform substances which are expressed by their atomic or equivalent numbers, occupy spaces which are either exactly equal, or which stand in a very simple relation to each other. These relative spaces or volumes are obtained by dividing the atomic or equivalent weight by the specific gravity. As a starting point in this calculation, that volume is taken which is occupied by the atomic weight (8) of oxygen, viz., $\frac{8}{1.106} = 7.23$. which serves as the measure of the volumes occupied by other gases. One atom or equivalent of another substance may occupy a space represented by $2.41 = \frac{1}{3} \times 7.23$ (condensation to $\frac{1}{3}$ vol.; sulphur, for example), or by $14.46 = 2 \times 7.23$ (condensation to 2 vols.; hydrogen, chlorine, water, sulphuretted hydrogen, for examples), or again, by $28.92 = 4 \times 7.23$ (condensation to 4 vols.; ammonia, chloride of ethyl, and most organic substances).

When a correct formula has been found for a substance, and the specific gravity of its vapour has been accurately

determined, the quotient obtained by dividing the atomic weight, deduced from the formula (the atomic weight of H being taken as =1, O=8, and so forth), by the vapour-density, will be either 2.41; 7.23; 14.46; or 28.92, according as the established formula represents a condensation to $\frac{1}{3}$, 1, 2, or 4 volumes.

If the formula and the determination of the vapour-density be correct, one of these numbers will be obtained as the quotient, and this serves to confirm both the determination of the formula and that of the vapour-density. Since, however, the latter operation is seldom susceptible of the degree of accuracy with which the numbers above-cited have been determined, the quotient will only approximate to one of these numbers, and not exactly coincide with it. It is only requisite that the agreement should be so close as to preclude all doubt as to which of the numbers ought to have been obtained, that is, to what condensation the calculated formula corresponds. The theoretical specific gravity is then easily calculated, since it is merely necessary to divide the atomic weight, calculated from the formula, by the corrected number resulting from the foregoing division.

As before stated, the analyses of furfural have led to the adoption of the formula $C_5H_2O_2$, and the density of its vapour has been found, by experiment, to be 3.375. The atomic weight resulting from the formula is 48, and the quotient obtained by dividing this number by the vapour-density found, is $\frac{48}{3.375} = 14.2$. There can be no doubt,

from this, that the above formula requires a condensation to 2 volumes, which is represented, more accurately, by the quotient, 14.46, and calculating back from this latter

number, we obtain, for the theoretical vapour-density, $\frac{48}{14.46} = 3.319$, exactly the number which was obtained by the ordinary method of calculation given above.—The double formula $C_{10}H_4O_4$ corresponds, of course, to a double volume, viz., to 4 volumes.

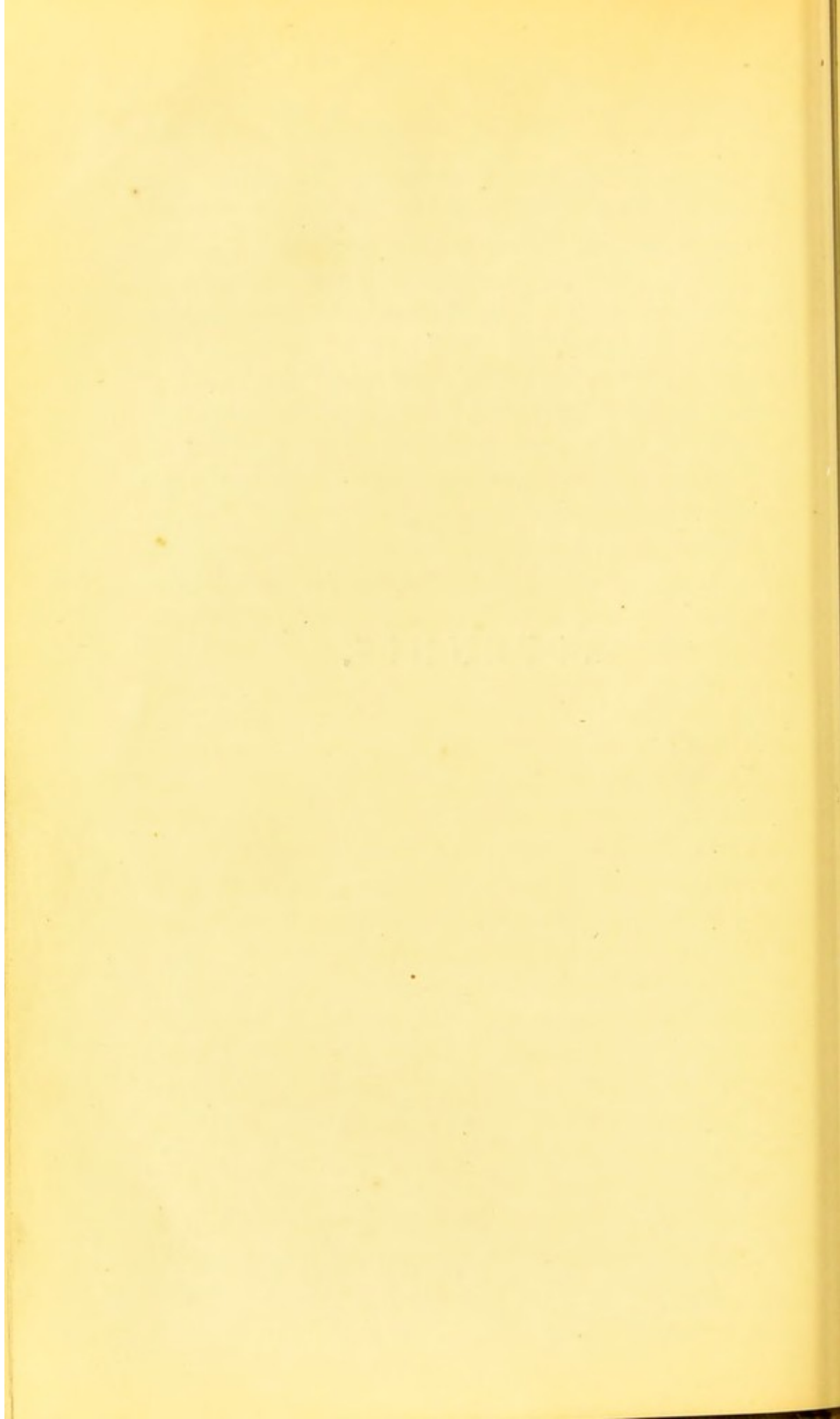
The formula $C_8H_8O_4$, for acetic ether, is well established by analysis, and by the consideration of its mode of formation. This gives 88 as the atomic weight. The specific gravity of its vapour, determined in the experiment quoted above, is 3.112; the quotient $= \frac{88}{3.112} = 28.2$. This points, indisputably, to a condensation to 4 volumes, which would be more accurately expressed by the number 28.92, and with the aid of this latter, the theoretical specific gravity of the vapour is found $= \frac{88}{28.92} = 3.043$.

It is necessary not to lose sight of the circumstance, that with some substances, such as alcohol, the ethers, &c., the specific gravity of the vapour (that is, the relation of the weight of a given volume of the vapour to that of an equal volume of atmospheric air, at the same temperature and pressure), is as great, at a temperature slightly exceeding the boiling-point of the substance, as at higher temperatures; whilst, with other substances, as, for example, with several organic acids, the specific gravity of the vapour is much greater at a temperature slightly above their boiling-points, than at higher temperatures, and first attains a constant value at about 100° above the boiling-point. For instance, Cahours found, for the specific gravity of the vapour of acetic acid, which boils at about 118°;

at 125°	130°	140°	150°	160°	171°	190°	200°	219°	230°	250°	280°	300°	338°
= 3.20	3.12	2.90	2.75	2.48	2.42	2.30	2.22	2.17	2.09	2.08	2.08	2.08	2.08

In such cases, the specific gravity determined at temperatures at which it is constant, can alone be employed for ascertaining the condensation, and for the calculation of the theoretical vapour-density. It is therefore necessary, in those cases where analogy does not lead us to suppose that the specific gravity will be constant, even at temperatures slightly above the boiling-point, either to determine the vapour-density at a temperature considerably above the boiling-point, or to make several determinations at different temperatures, and thus to ascertain that the specific gravity of the vapour is constant at these points.

APPENDIX.



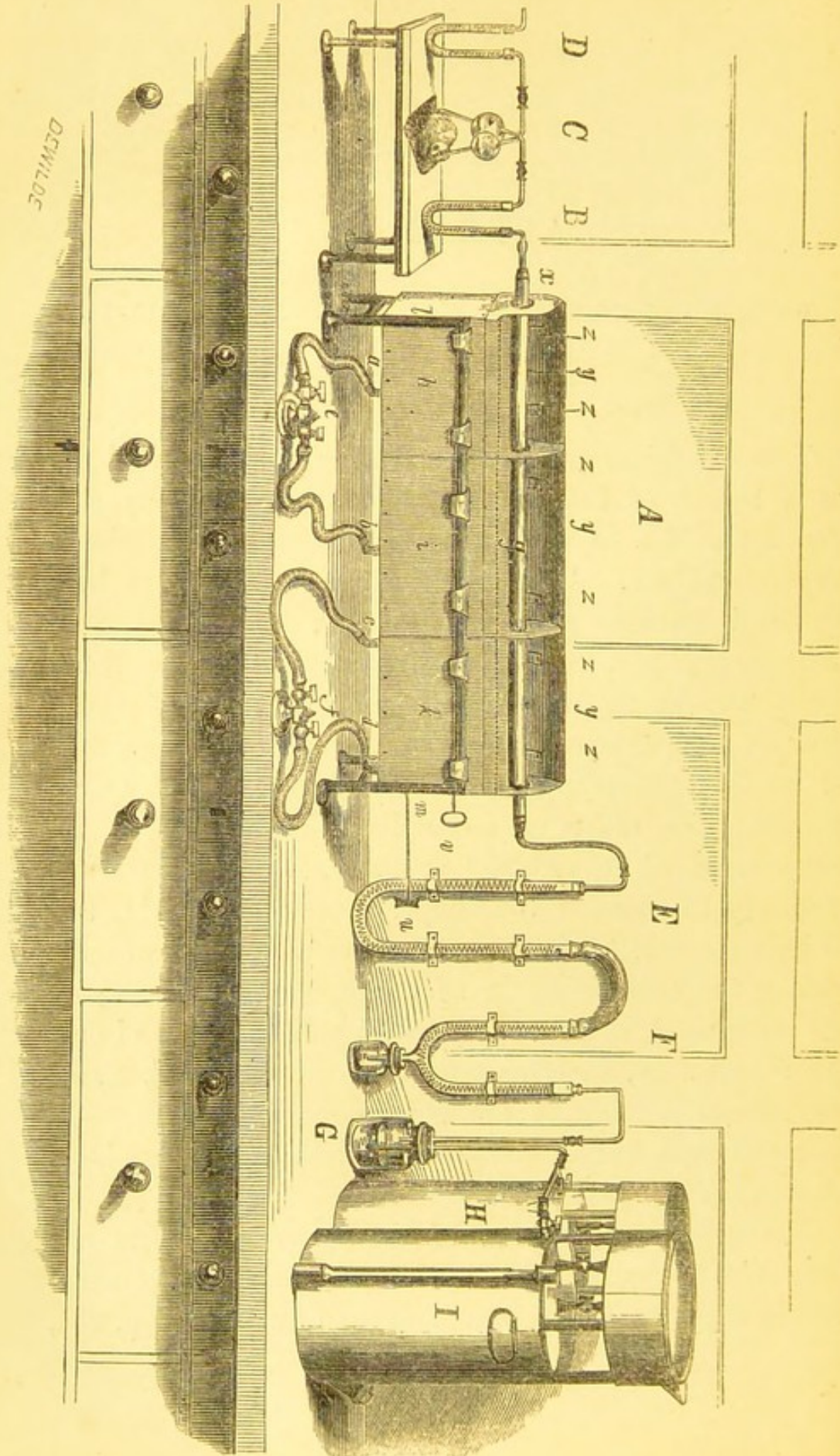
APPENDIX.

ON THE USE OF GAS AS FUEL IN ORGANIC ANALYSIS.

THE extensive and daily increasing application of gas as a source of heat in the laboratory, naturally suggested the idea of using this convenient fuel likewise in organic analysis. A variety of arrangements have been proposed for this purpose, but none has as yet come into general use. The difficulties which present themselves are, in the first place, the production of a sufficiently high temperature; and secondly, the regulation of the heat according to the special requirement of the process. In order to accomplish the analysis at the temperature of an ordinary air-flame, it has been found necessary to abandon the simple process of Liebig, and to have recourse to the more complicated method of completing the combustion in an atmosphere of oxygen; on the other hand, in order to obtain a sufficient control over the temperature, an arrangement has been devised, which may appear intricate at the first glance, but which works with sufficient facility and precision, although it may hereafter probably be simplified.

The general disposition of the apparatus differs but little from the arrangement used in performing the combustion in oxygen-gas by means of spirits of wine (*vide* p. 33),

FIG. 83.



and is sufficiently intelligible by a glance at Fig. 83. *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 combustion-tube communicates by means of a system of desiccators, consisting of a potash-tube *E*, a sulphuric-acid-tube *F*, and a sulphuric-acid-bottle *G*, with the gas-holders *H* and *I*, containing respectively oxygen and atmospheric air. The bottle *G* serves, moreover, as a bubble-gauge for measuring the rapidity of the current.

The furnace consists of three separate compartments of strong iron plate *h i* and *k*, which are supported by a stout iron stand *l m*. The arrangement of these compartments requires a few explanations; their construction is evident from Figs. 84 and 85; *h* and *i* are simply rectangular

FIG. 84.

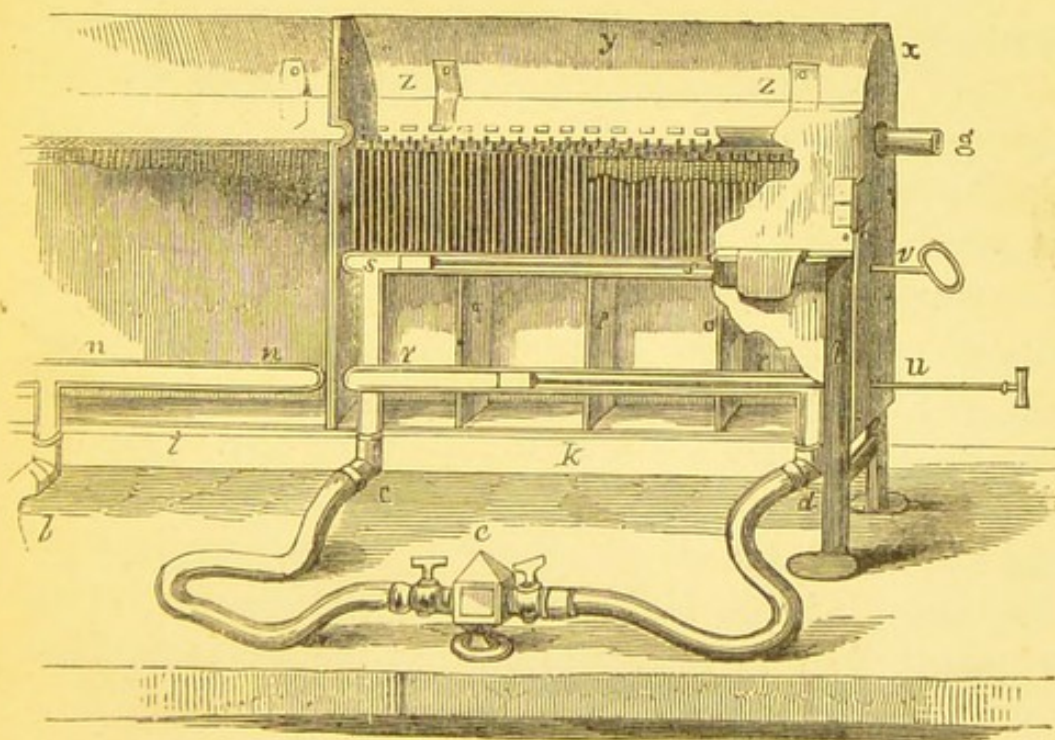
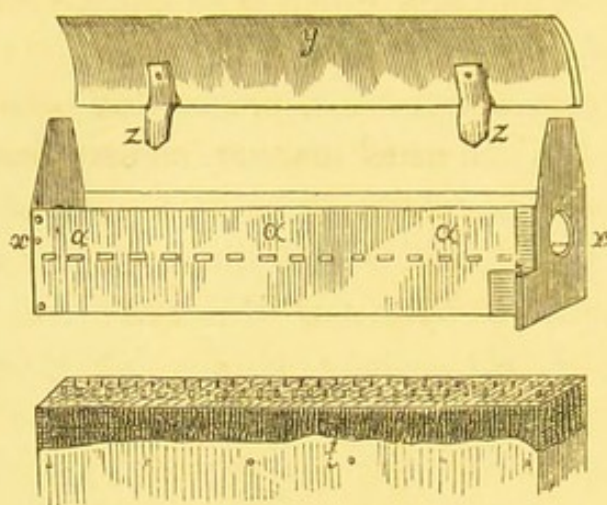


FIG. 85.



iron boxes, open at the bottom and covered at the top, with wire-gauze, which are supplied by horizontal perforated gas-pipes (*n n*, Fig. 84). The last compartment *k* (Fig. 84) 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. The lower pipe *r r* resembles in every respect the gas-pipe *n n* of the other compartments. The upper pipe *s s*, on the other hand, supplies the gas to two rows of vertical fine tubes, somewhat similar to those used in Leslie's gas-burner, the extremities of which project through the wire-gauze cover of the compartment (Fig. 85). 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 case. Fig. 85 shows the manner in which the frame *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*, 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 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, whilst 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 analyzed, introduced at the other extremity, and pushed in about two-thirds of 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 "substance" may now be commenced. For this purpose the gas is admitted, by means of the flexible tube d , to the lower gas-pipe $r r$, and the piston u pushed so far from the inlet as to supply the gas to the chamber $o l$ only, whilst it

is excluded from the other chambers, Fig. 84. In this manner, an air-flame is obtained which keeps the posterior extremity of the combustion-tube at a dull red heat. A small quantity of gas is next admitted to the upper gas-pipe *s s*, by means of the flexible tube *c*, the piston *r* 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 an 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.

At this period the air-current is replaced by a slow stream of oxygen from the gas-holder, 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.

By this time the products of combustion are perfectly swept from the tube, and lodged in their respective receptacles ; moreover, the copper is completely re-oxidized ; the flame is now gradually lowered, and the gas at last entirely turned off ; and if the combustion-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 into 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-turnings are thus heated to redness, and deprive the air-current of the greater part of its oxygen.

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 analyze 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 take 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.

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 made in one piece answers equally well.

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