INSTRUCTIONS

FOR THE

CHEMICAL ANALYSIS

OF

ORGANIC BODIES.

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TRANSLATED FROM THE GERMAN,

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Illustrated by Numerous Engravings.

[Griffin's Scientific Miscellany No I.

GLASGOW:
PRINTED FOR RICHARD GRIFFIN & COMPANY,
AND THOMAS TEGG, LONDON.

MDCCCXXXIX.

TRANSLATOR'S PREFACE.

THE ultimate analysis of organic compounds, although a most important branch of analytical chemistry, and one, the assiduous cultivation of which has already yielded most important results, and promises to yield still more, has hitherto occupied a very small share of the attention of British chemists. It is not easy to account for this apathy; for the amazing progress of organic chemistry in France and Germany, must surely have attracted attention in this country. Yet, for a good many years previous to 1836, no organic analyses were published by any British experimenter. Since that time, indeed, the researches of Dr. Kane and Mr. Johnston have appeared; but a large majority of the chemists of this country are still practically strangers to organic analysis. The time, I trust, is at hand, when we shall at last take our share in the cultivation of organic chemistry. To hasten that time is the object of the present Translation.

Professor Liebig is universally acknowledged as the leader in the rapid march of organic chemistry. It is chiefly to the use of his method, as described in this work, that the sudden development of this department of science must be ascribed; but he is not only the great improver of the method, he is also the author of very numerous memoirs, in all of which he has displayed uncommon sagacity, united with the most rigid accuracy; and any one of which might serve as a model of chemical research. While, therefore, it would be unjust to deny an almost equal share of merit to those philosophers, both in France and Germany, who have so ably cultivated the same field, we cannot hesitate in regarding Professor Liebig as the first authority on the subject of organic analysis.

The present Translation was undertaken at the request of the Author; and, but for unforseen circumstances, would have been published earlier. I venture to hope, that a practical acquaintance with all the processes described, may be considered as qualifying me in some degree for the task I have undertaken.

A few notes have been inserted, so as to present the reader with a view of the actual state of the method of analysis, some slight improvements having been made since the publication of the original.

I would conclude, by expressing a hope that this work may induce some who have not yet practised organic analysis, to turn their attention to the subject, from doing which they may perhaps have been deterred by its supposed difficulty. I have the satisfaction of knowing, that several chemists in this country are now occupied with researches in organic chemistry. All that is required is a beginning. The field of investigation is so boundless, and the harvest of discovery to be reaped in it so abundant and so attractive, that those who have once entered on it will not readily abandon it.

WILLIAM GREGORY.

ANDERSONIAN UNIVERSITY,
March 5th, 1839.

INSTRUCTIONS

FOR

ORGANIC ANALYSIS.

THE Analysis of organic substances has for its object, to determine the nature and quantity of the elements which compose them; and is one of the most important departments of analytical chemistry. The method employed by the earlier chemists to obtain a knowledge of the chemical composition of organic bodies had not the smallest resemblance to the organic analysis of the present day. They subjected these bodies to destructive distillation, and judged of the difference in their composition by the products thus obtained.

It is only within the last thirty years that this department of chemistry has been cultivated on scientific principles; and all the lately proposed methods differ from one another only in the way in which those principles are carried out.

The simplest method of ascertaining the component parts of an organic compound, would seem to be, to endeavour to obtain its elements in a separate form; but it is obvious that, if we can obtain, instead of the elements in the free state, compounds, of known composition, of those elements with others, we can determine their quantity with equal accuracy.

Most vegetable substances contain carbon, hydrogen, and oxygen; a small number contain, besides these elements, nitrogen. Of these four simple substances, nitrogen alone can be obtained in a state of purity from organic compounds; but if all the carbon be converted into carbonic acid, and all the hydrogen into water, we can then calculate, with the utmost precision, the quantity of carbon and hydrogen from that of the carbonic acid and water. Even if the elements of organic substances could be separated from them in a state of purity, we should be forced to give the preference, in analysis, to the indirect method now employed, on account of its superior accuracy.

The method, then, which we employ to procure an exact knowledge of the composition of an organic compound, consists in the conversion of a known weight of the substance into carbonic acid and water; and the success of the analysis only depends on the apparatus employed, in so far as that apparatus must allow us to collect these products without loss, and to determine their weight. When the compound contains nitrogen, this element is collected in the separate state; and the oxygen is always ascertained indirectly.

Gay-Lussac, and Thénard, the first chemists who executed organic analyses, used chlorate of potash for the combustion of organic bodies. The substance to be analysed was mixed with it, the mixture formed into pellets, and introduced in small quantities into a red hot tube of glass, placed vertically. The gaseous matter disengaged by the combustion was, by means of a lateral tube, collected in a jar over mercury.

The whole gas was accurately measured, and, the corrections for barometer and thermometer being made, caustic potash was introduced into the jar. After all the carbonic acid was absorbed, there remained either pure oxygen gas, or a mixture of oxygen and nitrogen. The relative quantity of the latter was ascertained by the eudiometer. The knowledge of the weight of the substance, and that of the chlorate of potash; of the quantity of carbonic acid formed, and of the oxygen remaining, supplied all the data necessary for calculating the composition of the body analysed. That portion of the oxygen of the chlorate of potash which had disappeared, had of course formed water with the hydrogen of the substance.

The only objection to the apparatus of Gay-Lussac and Thénard was, that it made the accuracy of the results to depend too much on the dexterity of the operator. The analysis of substances containing nitrogen, moreover, by means of chlorate of potash, was not very exact, in consequence of the formation of nitrous acid; and it was obviously impossible to employ that salt in the analysis of liquid or volatile substances.

Berzelius endeavoured, and successfully, to render this method more convenient in the execution, and to diminish the number of calculations required. He placed the tube of combustion in the horizontal position, and collected the water formed. He also employed the chlorate of potash, mixed with a large quantity of common salt, by which means the combustion was rendered slower, and at the same time the advantage was gained of introducing the whole of the substance to be burned, into the tube, before commencing the combustion.

These forms of apparatus, which were applicable only to a very limited class of bodies, were greatly and most essentially improved by the use of oxide of copper, instead of chlorate of potash; which was first proposed by Gay-Lussac, and employed by him in the analysis of uric acid. At present, the superiority of oxide of copper is so generally admitted, that chlorate of potash is no longer employed. Besides oxide of copper, chromate of lead has of late been used in the analysis of many substances containing a large proportion of carbon.

De Saussure and Prout have both described forms of apparatus for the analysis of organic bodies, which differ from the original one of

Gay-Lussac and Thénard, only in their form, and in the substitution of oxygen gas, and oxide of copper, instead of chlorate of potash.

The apparatus of Prout is so arranged that the substance to be analysed is burned, either alone, or mixed with some other body, in a known volume of oxygen gas, and the volume of the gas, after the combustion, is compared with its original bulk. This method is founded on the well known fact, that, when carbon is burned in oxygen gas, the carbonic acid gas produced, occupies exactly the same space as the oxygen consumed, and consequently does not alter its volume: as also, that when hydrogen unites with oxygen, for each volume of hydrogen, half a volume of oxygen disappears by the condensation of the water which is formed.

Consequently, if the substance to be burned consists of carbon, hydrogen, and oxygen, there are only three cases possible. Either the volume of the oxygen is unaltered; and, in this case, the substance contains oxygen and hydrogen in the proportions necessary to form water; or the volume of the oxygen is diminished, or it is increased. In the latter cases, the body either contains more hydrogen, and consequently less oxygen than is sufficient to form water; or there is less hydrogen, and consequently more oxygen than is required for that purpose. The diminution or increase in the volume of the oxygen can be exactly measured, and, the quantity of the carbonic acid produced being ascertained, it is easy to express the composition of the substance in numbers.

But this apparatus cannot be applied to the analysis of substances containing nitrogen, nor to that of many other bodies. Lately, Brunner has constructed an apparatus on a similar principle. All these forms of apparatus, however, have been employed by their inventors alone; and as they have no advantage over the one now commonly employed, it is unnecessary to describe them minutely in this place.

GENERAL METHOD OF PROCEEDING.

In the next section we shall describe the instruments and processes which are at present employed by the majority of chemists for organic analysis; and we shall here prefix some general remarks on the operations which occur in such analyses.

It will be observed, that all the parts of the apparatus used for this purpose are extremely simple, and for their employment require no especial dexterity. The essential conditions for performing a good analysis are, the greatest accuracy in weighing, and the strictest conscientiousness in the execution of all the preparatory steps of the process. Let us not flatter ourselves that we can obtain an accurate result, if any thing be neglected that can secure it. All the time and labour we bestow are thrown away, if we omit any one of the precautions which are recommended.

It is obvious that the object in view may be attained by various means, and that the methods described in the following pages are susceptible of improvement: but all the so-called improvements, hitherto proposed, only prove that their authors are ignorant of the most general principles of what a method ought to be.

Every chemist will be able, when he has acquired some experience in organic analysis, to alter the apparatus here described, in particular cases, according to his ideas, and to adapt it to the object he has in view; but it would be going too far to consider this deviation in a special case, as an improvement of the process in general, and to recommend it as such.

There is within the human mind an innate desire for improvement—hence the efforts to improve what we possess, and to discover new means of attaining the desired object. But we frequently commit the error of neglecting to test the utility of the known methods, or even to make ourselves familiar with them. We begin by deviating from the customary path; and if our efforts be crowned with success, the satisfaction we experience in the discovery we have made, leads us to overlook the circuitous nature of the route we have followed, and the difficulties we have had to overcome, which we should not have encountered on the beaten path.

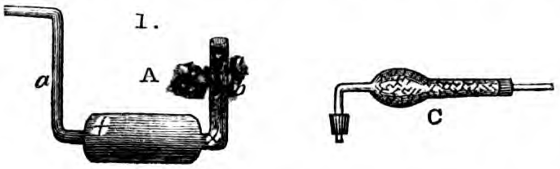
In what follows, we hold to the rule of Berzelius, the most experienced chemist of our own, and probably also of all times; and of two equally good methods, we prefer the simple to the complicated one.

The first problem to be solved, in performing an organic analysis, is, to procure the substance to be analysed in the highest degree of purity. No means should be neglected to satisfy ourselves of the absence of foreign matters. The matter being supposed pure, we must attend to the difficulty of determining the weight of the body to be analysed, as one source of uncertainty in the results of the analysis, and of the variations occurring in different analyses of the same substance. All organic bodies greedily absorb moisture from the air, and thus become heavier. They must, therefore, first be deprived of all hygrometric moisture, and then weighed in such a manner that it is hardly possible for them to attract moisture during the time they are in the scale.

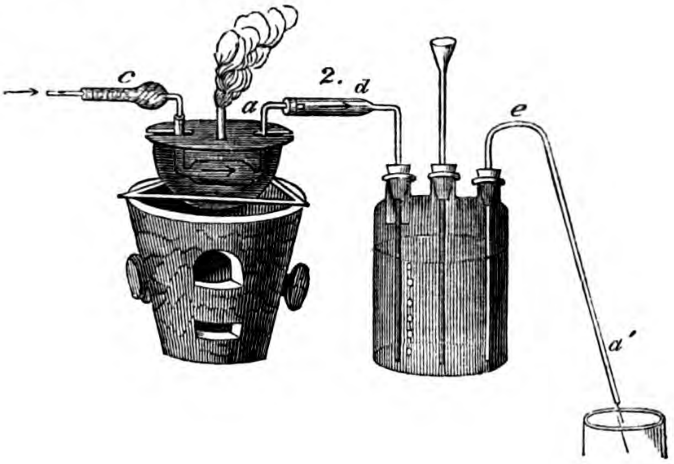
When we consider that an excess of water, to the amount of $\frac{7}{100}$ths or $\frac{8}{100}$ths of a grain is equivalent to a loss of twice as much carbonic acid, we cannot surely bestow too much attention on the accurate determination of the weight of the substance to be analysed.

This object may be obtained in various ways. The following apparatus gives complete security on this head. It consists of the tube A, *fig.* 1. The wide part below is about half an inch in diameter: the tubes *a* and *b* are barometer tubes, one of $\frac{1}{6}$th, the other of $\frac{1}{4}$th of an inch in diameter. The substance is introduced by the wide tube *b*, which is then connected by means of a cork with the tube C, containing fused

1.



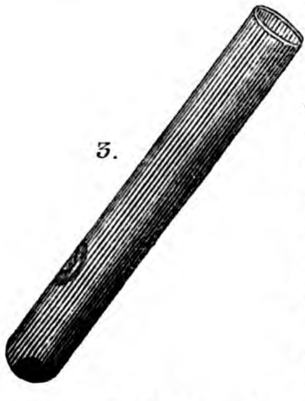
chloride of calcium. The opposite tube *a* is joined with the tube *d*, *fig.* 2: *e* is an ordinary syphon. The tube *d* is about an inch shorter than a', the external limb of the syphon.


2.

By means of this arrangement we can produce a perfectly uniform discharge of water from the three necked bottle; and since the air, which replaces the water must enter the bottle by the tube *d*, we can instantly perceive whether all the joinings are air-tight.

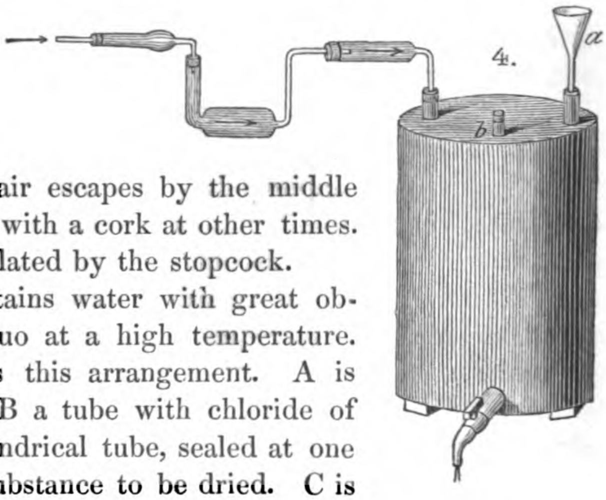
The bottle is filled with water; and, of course, when this water is made to flow out by the syphon, the continual current of dry air thus produced entirely removes all moisture from the substance.

The horizontal part of the drying apparatus is placed in a sand bath, a water bath, a bath of solution of chloride of calcium, &c., according to the temperature to which we wish to expose the substance. If we wish to determine the amount of water, the apparatus A is weighed, first empty, and then with the substance. It is then placed in the water bath, &c., and a stream of dry air is made to pass through it, as long as water condenses in the tube *d*. By weighing occasionally, we ascertain if it loses weight. When the weight becomes constant, a small portion of the substance is shaken out of *b* into a long and perfectly dry test tube, *fig* 3; which is then heated by a spirit lamp or sand bath—of course to a degree insufficient to produce decomposition. If no trace of water bedew the side of the test tube, we may be certain that the substance is perfectly dry: if any moisture appear, the water bath must be replaced by one of a solution of salt, or of chloride of calcium, and the operation repeated at a higher temperature.

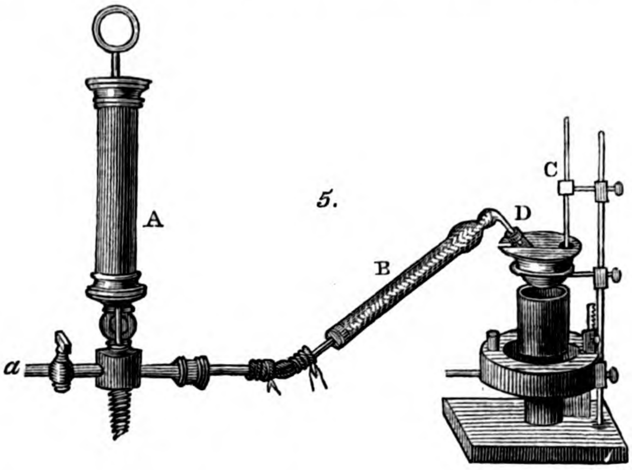

3.

Mitscherlich employs a similar apparatus for drying organic substances; but instead of the bottle and syphon he connects with the tube *a* a hand air-pump, by means of which he draws air through the apparatus till the substance is dry. But it is extremely fatiguing to continue pumping from four to six hours; and probably no one will adopt this method, except where no three necked bottle is to be had.

Instead of the bottle we may employ, with still greater convenience, a vessel of tin plate, *fig.* 4, which holds about 4 gallons of water. The funnel *a* serves for replenishing the vessel when empty, when the air escapes by the middle opening *b*, which is shut with a cork at other times. The flow of water is regulated by the stopcock.


4.

When the substance retains water with great obstinacy, it is dried in vacuo at a high temperature. The cut, *fig.* 5, exhibits this arrangement. A is a small hand air-pump, B a tube with chloride of calcium, D a strong cylindrical tube, sealed at one end, which contains the substance to be dried. C is a thermometer. The tube D is placed in an iron or copper vessel with a concentrated solution of chloride of zinc, and heated nearly to the temperature at which the substance is decomposed. After the moist air has been removed by the air-pump, air is from time to time admitted into the apparatus by the stopcock *a;* this air, by passing through the chloride of calcium, is each time deprived of all hygrometric moisture, so that in a very short time, at most in a few minutes, we can by this means remove all water, whether hygrometric water or water of crystallization.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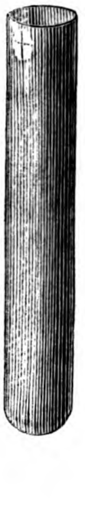


When the substance is dry, a certain quantity of it must be weighed out for analysis. This is best done in a small narrow tube, open at the end. The cut, *fig.* 6, exhibits it of the actual size. This tube may either be placed horizontally on the scale, or set in a conical roll of tin-plate, which rests with its broad end on the pan of the balance. A stand of tin-plate is also very convenient. The tube being weighed, a portion of the substance is introduced and the tube is weighed again. The increase of weight gives the quantity of the substance.

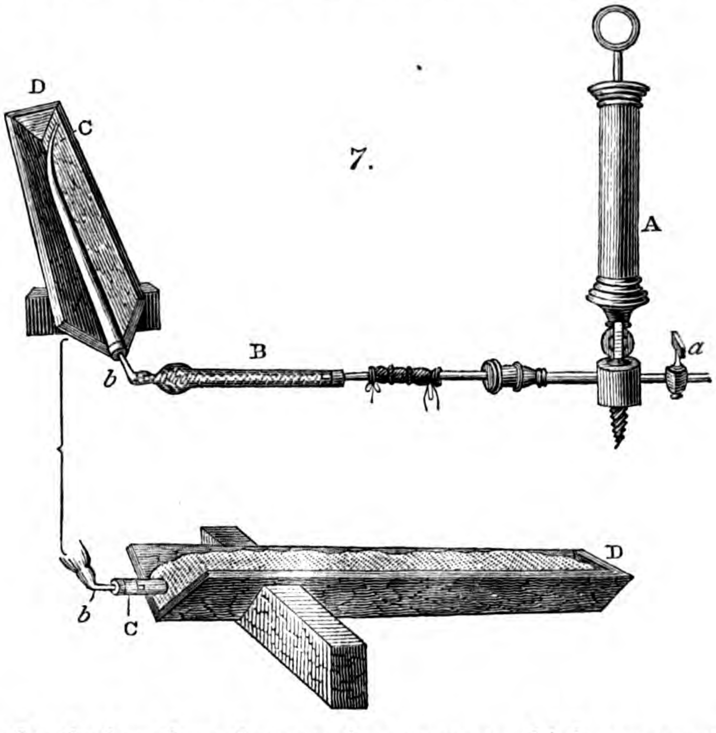
We may also counterpoise the tube with the substance, empty the tube, and return it into the scale with any adhering particles. The weight necessary to restore the counterpoise, gives the quantity taken out of the tube.

As a general rule, we must avoid all weighing in a watch-glass, or any wide vessel. With the narrow tube recommended, no appreciable change of air can take place within it during the short time it lies on the scale; and even when containing highly hygroscopic substances, this simple apparatus does not increase in weight in the course of half an hour.

We have now a known quantity of the substance. To determine the amount of its carbon and hydrogen, we must convert the carbon into carbonic acid, and the hydrogen into water, and we must ascertain the weight of both these products.

In general, the substance, if dry and pulverizable, is mixed with oxide of copper, and the mixture heated in a glass tube by means of a charcoal fire. The tube of combustion is 15 to 18 inches long, and $\frac{1}{3}$ to $\frac{1}{2}$ of an inch in diameter. The closed end is drawn out to a point, which is bent obliquely upwards, and sealed. During the mixture of the substance with the oxide of copper, both bodies attract moisture from the air. This water would increase the weight of that formed in the combustion, and must be most carefully and completely removed before the combustion.

This is most easily effected by an arrangement similar to that above



described, for drying the substance in vacuo at a high temperature. A, *fig.* 7, is the air-pump, B the tube with fused chloride of calcium, C the tube of combustion filled with the mixture, which is placed in a wedge shaped box of wood, D, and surrounded with sand heated to 250° Fahrenheit. Before pumping out the air, the tube with the mixture, C, must be subjected, in the horizontal position, to several smart taps on a table, so that a space is seen to be empty above the mixture all along the tube. If this method of furnishing a free exit to the air when pumped out be neglected, as soon as the pump is worked, a part of the mixture is forced into the tube with chloride of calcium. We now produce a vacuum in the tube, and allow dry air from time to time to enter by the stopcock, and after pumping out the air ten or twelve times, we can perceive no further deposition of moisture at the point *b* of the tube B, even when we surround it with cotton wool, and cool it by dropping ether upon it. The mixture may then be considered dry.

The substance is mixed with pure oxide of copper in a clean and warm mortar of Wedgewood's ware or porcelain. The more carefully we divide the substance and mix it with the oxide of copper, the more easy and complete is the combustion.

Mitscherlich leaves the point of the tube of combustion open, joins either end with a tube containing chloride of calcium, with the other end of which is connected a pair of bellows; heats the oxide of copper, which has been introduced so as to fill half of the tube, to a low red heat, and forces, by means of the bellows, dry air over the hot oxide. The point is then sealed up. He now counterpoises the tube with the oxide of copper, and shakes out of the tube in which it has been dried, a portion of the substance to be analysed, into the counterpoise tube. The increase of weight gives the quantity of the substance.

He now mixes it with the oxide of copper in the following manner:—He bends one end of a long copper wire into the form of a corkscrew, screws this half way into the layer of oxide, and moves it up and down till the mixture appears sufficiently intimate.

This method is less convenient and more troublesome than the one above described. In the first place the weight of the tube with oxide of copper, (from 1800 to 2100 grains,) does not permit us to determine the weight of the substance to be analysed to the $\frac{1}{300}$th of a grain. This is a source of uncertainty. Again, we cannot effect a complete mixture by means of a cork-screw wire. This is easily shown. If we mix some starch as intimately as possible with oxide of copper in this manner, and press the mixture in a mortar with the pestle, we easily recognise the unmixed or cohering particles of starch by a number of round white spots. The interior of these particles would only be charred, not burned. Berzelius recommends this method, when we have not an air-pump; but in that case it would be better not to attempt the analysis of organic bodies at all.

The water formed in the combustion is collected in the tube, *fig* 8, which is filled with chloride of calcium—large fragments being placed in the bulb, and coarse powder in the long tube. Near the two open ends of this tube, at *a* and *b*, is put a little cotton-wool, in order to prevent any chloride of

8.

calcium from falling out. The tube *b* is fitted tight into the larger tube by means of a cork: the cork is cut off close to the tube, and covered with sealing wax to prevent dust from adhering to it. The whole is weighed. Its increase of weight after the combustion gives the quantity of water produced.

The tube with chloride of calcium, thus prepared, is connected at the end *a* by means of a cork to the tube of combustion, *fig.* 9. The cork should be perforated by means of Mohr's cork-borer, and the aperture filed very smooth, and made to fit the end *a* very tight. It is then, with a very sharp straight-edged knife, cut so as to fit closely into the tube of combustion. According to the shape of the tube, the cork should be cut cylindrical or slightly conical. We must avoid perforating the cork with a hot wire, as most corks perforated in this way crack, and become useless.

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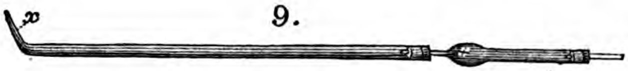

Some Chemists, according to the method of Berzelius, give to the tube with chloride of calcium, the shape represented in *fig.* 10. The tube of combustion *a* is drawn out into a point, which is introduced into the tube *b* with chloride of calcium. The junction is completed by a tube of caoutchouc, tied on both sides. After the combustion, the point of the tube *a* is cut through at *c*, the caoutchouc connecter removed, without taking away the point of *a* from the tube *b; b* is then weighed with the point; the point is taken out, washed, ignited, and weighed. Deducting the weight of the point from the whole increase of weight of *b*, we obtain the true increase of weight due to the water produced.

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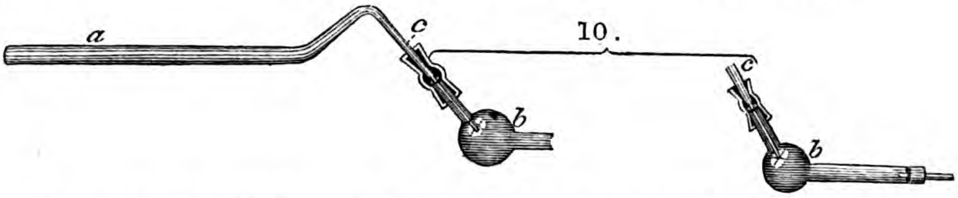

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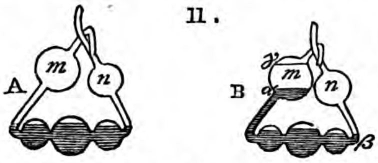
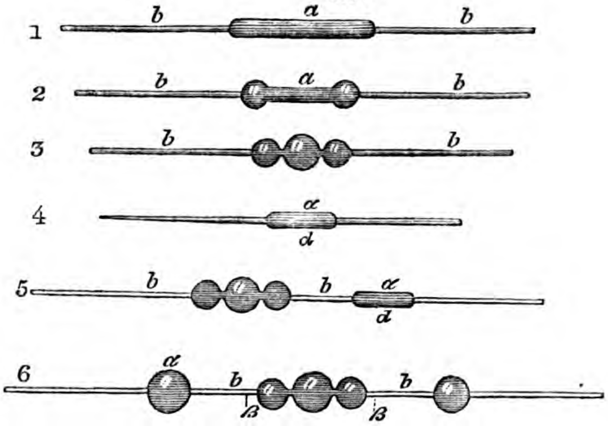


The carbonic acid formed in the combustion is collected in the apparatus, *fig.* 11, which is filled with a solution of caustic potash, in such a manner that a small bubble of air remains in each bulb. This apparatus consists of a glass tube, in which 5 bulbs are blown. It is made in the following manner. Two barometer tubes, *b b*, *fig.* 12, of $\frac{1}{6}$ of an inch wide, are soldered to a stout glass tube, *a*, 3 inches long and $\frac{1}{3}$ of an inch wide. One end being stopped up, *a* is softened at one extremity, and blown out to a bulb. The same is done at the opposite end of *a*, as may be seen in No. 2. Next, the middle part of *a* is made very hot, and blown to a somewhat larger bulb, so that the whole acquires the shape of No. 3. About an inch of a tube, α, equal to a, is now soldered to a narrow barometer tube similar to b b; one end of α is drawn out to a point, which is cut off near to d, and soldered to one of the points b—which is previously reduced to 2 inches (No. 5). α is now to be blown out to a bulb, (No. 6.) The same is done at the opposite end of β β.

12.



One of the bulbs α α may be rather smaller than the other; one however must be so large as to hold more liquid than the middle bulb of a. The tubes are now heated by a spirit-lamp close to the bulbs, β β, and are bent at an angle of 45° (*fig.* 13.) Above the bulbs, m and n, these two tubes are again bent. Here it is to be observed, that the tube o, having the larger bulb m, should be so bent that its horizontal portion, connected with the tube containing chloride of calcium, is to the left of the operator. The tubes o and p, after being sufficiently heated at α, are bent so as to cross each other, as shown at B. By attending closely to the figure, we may be certain of giving to the apparatus the best form and proportions. The sharp ends of the tubes o and p must be rounded in the flame of the spirit-lamp.

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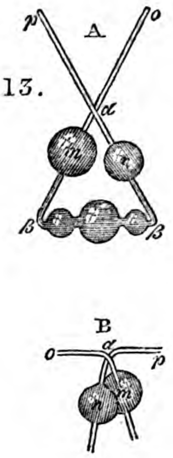

[The Apparatus thus prepared has the exact form and size represented by *fig.* 14, page 11.—W. G.]

To fill this apparatus with caustic ley, one end must be connected by a cork with the sucker, *fig.* 15; the other end of the potash apparatus is then dipped into a glass containing the ley, and the liquid drawn by suction with the mouth into the apparatus. The end of the tube which has been moistened with the ley is to be dried externally, and internally: the latter is easily accomplished by means of a small roll of filtering paper. The apparatus, when quite dry and clean, is weighed, and then joined to the tube with the chloride of calcium by means of a small tube of caoutchouc.

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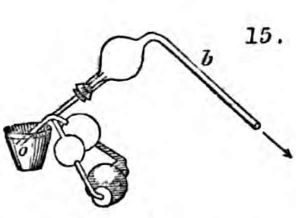
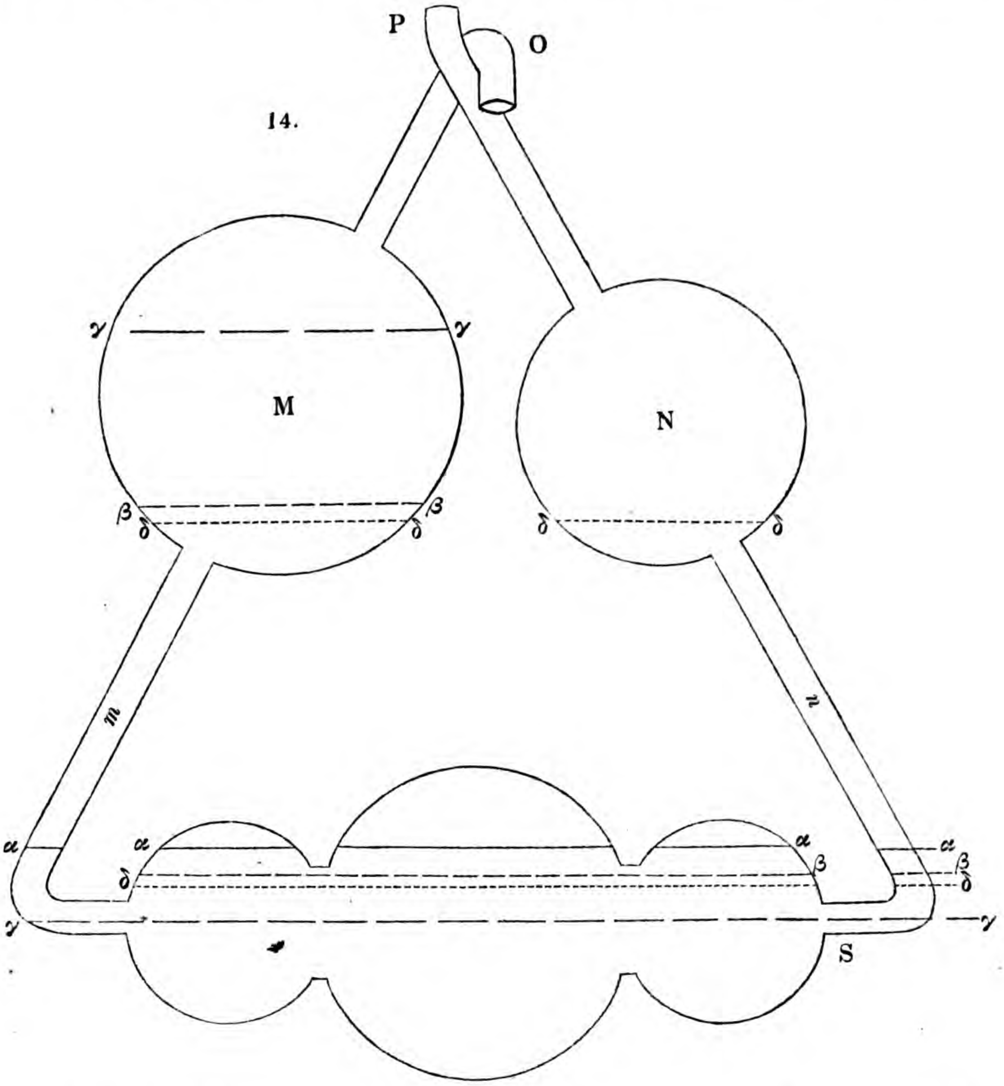


The potash apparatus, when filled with ley, commonly weighs from 750 to 900 grains. If the ley have the sp. gr. 1.25 to 1.27, it does not produce foam when bubbles of gas pass through it; and when of this strength, its absorptive power is likewise greatest. Caustic soda ley foams like soap and water, and must therefore be avoided.

14.

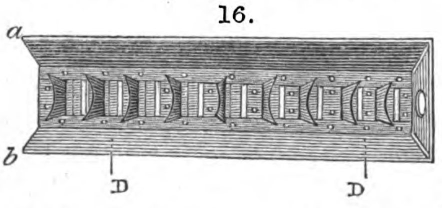


[The ley is best prepared in the following manner. Two parts of the subcarbonate of potash of the shops are dissolved in 20 to 24 of boiling water. One part of quicklime is slaked by being *covered* with hot water in any convenient vessel. In this way the whole of the lime is converted into a uniform cream, without the formation of any hard sandy particles, which occur in the ordinary method of slaking, and which are not only useless but hurtful, by preventing, from the space they occupy, and the increased proportion of lime they render necessary, the separation, by decanting, of much of the ley. The cream of lime is added in small portions to the boiling solution of carbonate of potash, which is boiled a few minutes after each addition, water being occasionally added to supply the loss by evaporation. When the whole of the lime has been added, the mixture is boiled for a short time longer, and is then allowed to cool in the pan or goblet, carefully closed with its lid. After 12 hours, nearly the whole of the ley may be decanted perfectly clear, and quite caustic, especially if the vessel has been nearly full. The carbonate of lime, when this process is followed exactly, is sandy, and occupies a very small bulk. The clear liquid is now to be rapidly boiled down in a clean iron vessel, till small crystals begin to separate. It is then allowed to cool in a stoppered bottle of green glass, when it deposits the whole of the sulphate of potash originally present in the subcarbonate; that salt being absolutely insoluble in a strong solution of caustic potash. For the above essential improvements in the preparation of caustic potash, we are indebted to the author of this treatise and to Dr. F. Mohr of Coblentz. I find that the solution which has deposited the sulphate of potash possesses the sp. gr. 1.25, and is perfectly adapted for organic analysis. As all contact with organic matter has been avoided, it is also in general colourless, and yields solid caustic potash almost white, containing no impurity except a little chloride of potassium; which of course may be avoided by using genuine salt of tartar; but which does not in the least affect the use of the potash for most purposes. The necessity for using at least 10 or 12 parts of water to 1 of carbonate of potash arises from the curious fact, noticed by Professor Liebig, that when less water is present, the potash takes back the carbonic acid from the carbonate of lime.—W. G.]

The tubes of caoutchouc are made out of thin sheets of that substance. A portion, 1½ inch long, is doubled up so as to form a tube of the size of those which it is to connect. About a line in width is now to be cut off with a very clean and sharp pair of scissors, along the length of the caoutchouc where the two sides meet. We thus obtain two smooth cut surfaces, which, if pressed together by the thumb nails, adhere so as to form a perfect junction. The tube is now pulled lengthways, so as to stretch it, several times. If we touch the fresh cut surfaces with the fingers, they do not cohere where they have been touched. It is right also to moisten the inside of the caoutchouc, before forming the tube, that its sides may not cohere. The caoutchouc tubes are fastened over the glass tubes by strong threads of silk, knotted at the ends, to prevent them from slipping.

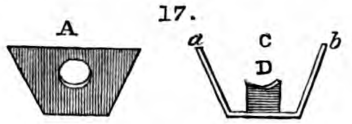
[It is more effectual to dust the inside of the tube with any fine powder, such as flour or starch—removing all that is superfluous.—W. G.]

16.



The furnace in which the combustion is carried on, is exhibited by *fig.* 16. It is made of sheet iron, 22 to 24 inches long, and 3 inches high. The bottom is 3 inches wide, and furnished with apertures which form a sort of grate; these apertures are narrow slits, running across, at an half inch distance from each other. The sides of the furnace are inclined outwards so that at the top they are 4½ inches apart. The whole rests on a large tile or paving stone, *e*, *fig.* 19, in such a manner that the two slits nearest the front are left open, while the remainder are closed by the tile. Within the furnace are placed at intervals supports of strong sheet-iron, of the form D, *fig.* 17. They must be of equal height, and must correspond with the round aperture in the front of the furnace, A, *fig.* 17. Their use is to support the tube of combustion.

17.



When we wish to increase the heat, the furnace is raised a little on one side, and a thin bit of tile is introduced at two places. This allows air to enter by all the slits in the bottom of the furnace. Good charcoal is the only fuel employed in this furnace.

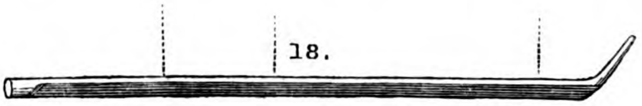
SPECIAL DETAILS OF THE METHOD.

The tube of combustion, if necessary, is washed out with water, and dried by means of bibulous paper tied round a whalebone. When the point has been drawn out and sealed, the tube is made very hot, and a long narrow tube introduced as far as the closed end. By drawing air through the narrow tube with the mouth, the last traces of moisture are soon removed. The dry tube is rinsed out with a little hot oxide of copper, which is then put aside. In order to have some measure of the quantity of oxide which is to be mixed with the substance we wish to analyse, the tube is now to be filled to three-fourths of its length with pure oxide of copper, out of the crucible in which it has been just ignited, and while it is yet hot. We must carefully avoid bringing this oxide, which is destined for the combustion, in contact with any foreign matter.

The mixture of solid substances, not volatile, with the oxide of copper, must always be made in a mortar of porcelain, (Wedgewood's ware,) of a smooth, but not polished surface, and a deep shape. The mortar is previously rubbed out with pure oxide of copper, which is put aside. The weighed substance is now shaken out into the mortar, and the tube in which it was contained rinsed out with a little oxide of copper, which is added to the substance. The latter is first rubbed with a little oxide, with which it is intimately mixed, and by degrees the whole oxide of copper is added, which had been measured in the tube.

The mixture must be made without applying any great force, for which reason the substance, before being weighed, and the oxide of copper, before the gentle ignition which must always precede its use, must be reduced to a fine powder. If the oxide of copper contain hard particles, the mixture cannot be made sufficiently intimate; and it often happens that the pestle, when pressed on such particles, springs off, whereby portions of the mixture may be thrown out of the mortar. If the mortar be placed on a sheet of glazed writing paper, it is easy to see whether any part of the mixture has been lost or not.

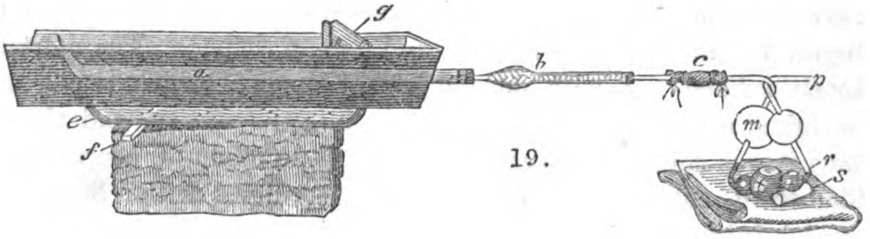
Having first introduced pure oxide of copper, so as to fill about half an inch at the closed end of the tube of combustion, we now transfer the mixture from the mortar to the tube. The mortar is rubbed out with pure oxide of copper, which is also introduced into the tube, and above the whole is put pure oxide of copper, till within one inch of the open end of the tube. In *fig.* 18 are shown the lengths of the different layers of pure oxide, mixture, rinsing from the mortar, and again pure oxide. They are marked by the dotted lines, and serve to show nearly the usual proportions.



18.

The cork which joins the tube of chloride of calcium to the tube of combustion, is struck with a light hammer, till it becomes soft and elastic. When the perforation for the small tube is finished, and the cork accurately fitted to the tube of combustion, the cork is placed in a covered crucible in hot sand, in order to expel from it all hygrometric moisture. It must fit very tight into the tube of combustion; but its softness allows the employment of the necessary force, without the risk of breaking the apparatus.

The tube of combustion, and that with the chloride of calcium, must be horizontal, or very slightly inclined towards the potash apparatus, so that the water which collects in the narrow end of the tube with chloride of calcium, may flow forward of itself to the chloride of calcium. For this purpose, the farther end of the furnace is made a little higher than the other, by introducing a thin bit of wood or iron below the tile at that end. *Fig.* 19 shows the whole apparatus arranged for the combustion; *a* is the tube of combustion, *b* the tube with chloride of calcium, *c* the caoutchouc tube, *m* the larger bulb of the potash apparatus, which is joined to the tube *b*, *e* is the tile, *f* a small wedge of iron introduced to give the furnace a slight inclination towards the potash apparatus.



19.

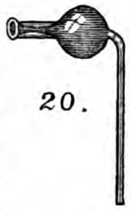
The tube of combustion, before being joined with the tube *b*, or introduced into the furnace, must be tapped smartly in the horizontal position on a flat table, in order to produce, above the mixture, (*fig.* 18,) through the whole length of the tube, a vacant space to afford a passage to the gaseous products of the combustion. Without this precaution, it often happens that the oxide of copper is thrown forwards, or that the tube at the farther end becomes choked. Innumerable analyses have shown, that, with this arrangement, the combustion is not less complete than when no vacant space is left, however rich in carbon the substance may be.

Mitscherlich screws a spiral of copper wire through the whole length of the mixture, and leaves it in the tube during the operation, with the design of interrupting the continuity of the mass; but we cannot depend on its efficiency. I repeat, that the arrangement described gives the only security for the uniform success of the analysis.

The anterior portion of the tube of combustion contains pure oxide of copper, which must be raised to a red heat before that part of the tube which contains the mixture is surrounded with glowing charcoal.

But, before beginning the combustion at all, it is absolutely necessary to be assured that all the joinings are air-tight.

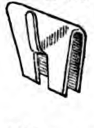
To ascertain this, a small quantity of air is sucked out of the apparatus, by means of the suction-tube, (*fig.* 20,) and the mouth; this naturally causes the ley to rise in the tube of the bulb, *m*. It is, consequently, from 1 to $1\frac{1}{2}$ inch higher in that than in the opposite tube, as may be seen in B, (*fig.* 11,) where α and β mark the level of the ley in both tubes. If this level does not remain unchanged; that is, if the liquid falls back into the middle part of the apparatus, A, *fig.* 11, air must enter the apparatus either by the caoutchouc tube, *c*, or the cork. One or both must be changed, till the liquid raised by suction to α, remains steadily at the same point.



20.

The anterior portion of the tube of combustion is now surrounded with red-hot charcoal. If the tube be quite dry, and the glass free from knots, there is no danger of its being cracked by the heat. If the oxide of copper has not been thoroughly dried, the first action of the heat causes a more or less distinct deposition of dew on the cold empty part of the tube *a*, which projects 1 inch out of the furnace. In this case, we may be quite certain that the determination of the hydrogen will give an excess.

21.



To keep the fragments of charcoal in their place, and to prevent the heat from spreading to the remaining parts of the tube *a*, the screen *g*, *fig.* 19, is employed. It is made of strong sheet iron, with a slit for the tube, and of the shape of *fig.* 21, which fits the sides of the furnace.

The screen is set up behind the anterior part of the tube, which contains pure oxide of copper. When this has been heated red-hot, the screen is moved one-half to one inch backwards, and this part surrounded with red-hot charcoal. The distance to which the screen is to be moved each time, depends on the rapidity with which gas is disengaged. So much red-hot charcoal must be put on each time, that the part of the tube, which must be completely surrounded with glowing coals, shall be quickly raised to a red heat. Even when the disengagement of gas is at first more rapid than is desirable, we must not remove the charcoal we have put on. To do so would rarely moderate the disengagement of gas, but might easily render the combustion imperfect. We must, therefore, endeavour to regulate the current of gas, by heating shorter portions of the tube at once.

The fore-end of the tube, which is empty, and projects one inch out of the furnace, must be kept during the whole operation, so hot that not the smallest quantity of water can condense within it. In this way, we can avoid any loss of water with certainty.

The combustion would proceed with perfect regularity, if we could deprive the glass of all conducting power. This is impossible, but we cannot be too careful only to heat small portions of the tube at once. The bubbles of gas must form an uninterrupted and rapid current, yet not too rapid.

When there are too few supports in the furnace, the tube sometimes bends by its own weight; but there is no danger of its being blown into holes, as the pressure of the liquid which the gas has to overcome in escaping, is too small to act on the glass, even when softened by the heat.

Mitscherlich places the tube of combustion in a gun-barrel, filed open the long way so as to admit the tube. He thus endeavours to secure a uniform heating, without melting of the tube; but in this way, we lose all the advantages of an accurate regulation of the combustion. Volatile substances, heated by the conducting power of the gun-barrel, distil over without interruption, and without undergoing combustion; and in the case of substances difficult to burn, we cannot apply the necessary heat. Mitscherlich tries to prevent the conduction of the heat along the gun-barrel by blowing on it, or surrounding it with moist cloths. But, during the combustion, our attention is taken up with matters of too great importance to permit of our occupying ourselves with attempting to keep the gun-barrel cool by blowing on it. To surround it with moist cloths is altogether inadmissible, for obvious reasons.

The position of the potash apparatus during the combustion, is shown in *fig.* 19. A bit of cork is introduced under *r*, so that this part lies a little higher than the opposite end. It is best supported on a folded towel.

When the whole tube of combustion, at the end of the operation, is surrounded with red-hot charcoal, the heat is to be increased along the whole length of the furnace. This is done below, by admitting air through all the slits, and above, by blowing the fire with a sheet of pasteboard, which is rapidly moved backwards and forwards. As soon as the disengagement of gas becomes very slow, the bit of cork is removed from the potash apparatus, which is restored to its horizontal position. *Fig.* 11, A, *page* 9.

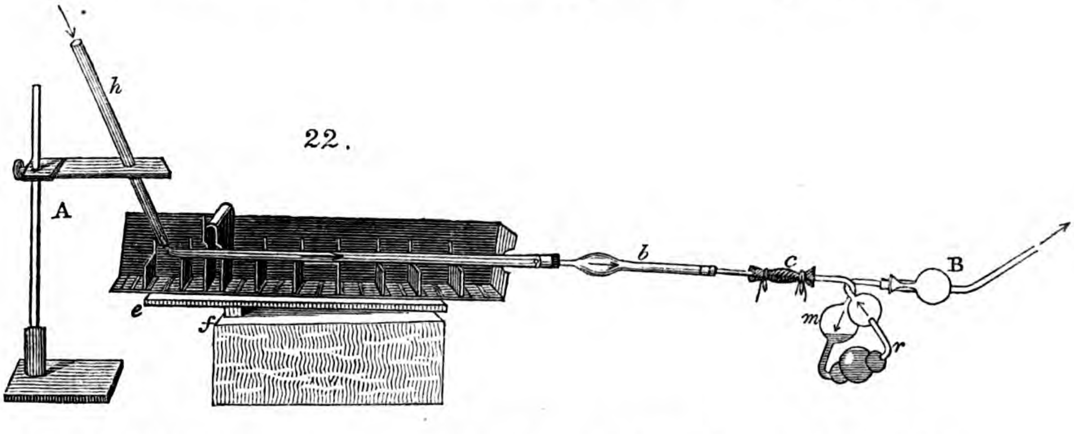
We can now see whether the combustion has been completely successful or not. If the disengagement of gas cease all at once, we are sure that the combustion has been complete. If it continue, on the contrary, at intervals for a long time, the mixture with oxide of copper has not been well made. We may then reckon with certainty on a deficiency in the determination of the carbon.

As soon as no more gas comes over, the ley rises into the bulb *m*, *fig.* 11. The size of this bulb prevents all chance of the liquid's rising into the tube *b*, and allows plenty of time for the remaining manipulations. For when the liquid has filled half of the bulb *m*, it ceases to rise. The middle part of the potash apparatus is now horizontal, and being rendered half empty by the rise of the liquid in *m*, air passes into the interior. In *fig.* 14, γ points out the beight to which the liquid can ascend. When it has reached this point, there is no further obstacle to the entrance of air.

23.

The charcoal which surrounds the farther end of the tube of combustion with its sealed point, is now removed, and the point is cut across with small pliers, *fig.* 23, at the point *x*, *fig.* 9. Over the point, when opened, is placed a tube, *h*, 15 to 20 inches long, open at both ends, supported by a stand, *fig.* 22.

The suction tube is now placed on the end of the potash apparatus, and a certain quantity of air is drawn with the mouth through the potash apparatus, which is now placed in the same position as during the combustion; by this means, all the carbonic acid and watery vapour which have remained in the apparatus are now absorbed by the ley and the chloride of calcium. *Fig.* 22 shows the apparatus at this period. The left hand holds the potash-apparatus at *r*, raising this part a little: the right hand holds the suction tube B.



22.

When the combustion has been complete, no taste is perceived in the air drawn through. When it has been imperfect, a more or less distinctly empyreumatic taste is perceived. The latter circumstance is not always a proof that the analysis has failed; for it very often happens that two analysis agree perfectly, in one of which an empyreumatic taste is perceived, in the other not. This proves how minute a quantity of empyreumatic matter suffices to communicate a taste to the air.

Berzelius proposes to avoid the suction with the mouth by employing the apparatus formerly described for producing a current of air. *See figs.* 2 *and* 4. This arrangement is inconvenient, gives unnecessary trouble, and is far from supplying the manageable delicacy of the human organ.

The air which is drawn through the apparatus contains water and carbonic acid; and both are added to the products of the combustion, unless we take means to remove them from the air before it enters the apparatus.

For this purpose, Berzelius connects the point of the combustion tube, after it has been cut, with a tube filled with dry caustic potash. This may be done, but it is a disagreeable operation, since the tube of combustion must be kept red hot while the air passes through it, in order to oxidize any traces of carbon which may be deposited on the reduced copper; while in order to attach the caoutchouc connector to the point, it must no longer be very hot. Besides, the air, which is made to pass through the potash apparatus, if dried, absorbs moisture from the ley, which it carries away; giving rise to an apparent loss of carbon. Now, if the current of dry air, as recommended by Berzelius, be continued for a quarter of an hour, it is impossible to neglect this loss, which must then be prevented by attaching to the potash apparatus another tube for collecting this moisture, and adding its weight to that of the potash apparatus.

All these troublesome and complicated arrangements may be avoided by proceeding as follows:—

The combustion being over, and the caustic ley ascending to γ, *fig.* 11, B, the potash apparatus is so inclined that the angle B is closed by liquid; the point of the combustion tube is now cut off, and air enters. The natural result of this is, that the liquid sinks in the bulb *m*, and rises in *n*, till an equilibrium is established, and a portion of liquid remains in each bulb. *See fig.* 14. The bulb *m* is full of carbonic acid gas, which is absorbed by the caustic ley; the carbonic acid gas in the tube *b* takes the place of that which is absorbed, and thus all the carbonic acid gas in the apparatus is by degrees brought into the bulb *m*, where it is so completely absorbed, that not a single bubble of gas passes through the ley.

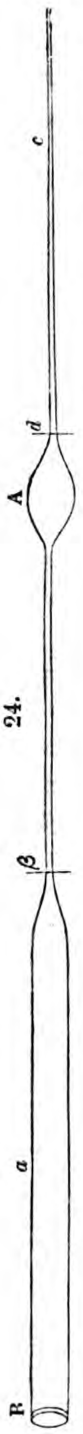
When the apparatus has stood thus for a few minutes, the air in the apparatus contains no more carbonic acid. To make all sure, however, air is drawn through by the suction tube for a few seconds; till so much has passed as is about equal in volume to the contents of the tube of combustion, *a*, and the tube with chloride of calcium, *b*.

When, as sometimes occurs in the combustion of substances very rich in carbon, a trace of carbon has been deposited on the reduced copper, and has thus escaped oxidation, it is completely oxidized by the small quantity of air now drawn through the red hot tube; and the loss of carbon from this source is avoided.

COMBUSTION OF VOLATILE LIQUIDS.

The analysis of such bodies is the most simple and easy; the results are the most exact; and beginners will do well to occupy themselves first with the combustion of such substances.

These liquids are weighed in small bulbs of glass, with a long neck, the point of which is sealed. These bulbs are easily prepared. A barometer tube, *a*, *fig.* 24, 12 inches long and $\frac{1}{4}$ inch in diameter, is drawn out before the blowpipe. The portion drawn out serves as a handle, wherewith to draw out a small portion of *a* with a long narrow neck. The point *c* is then sealed off at *d;* the portion of *a* which has been drawn off, A, is softened and blown into a bulb, (*fig.* 25.) It is then cut off at β, and the same process is repeated till a sufficient number of bulbs is procured. The moisture from the mouth, owing to the length of the tube from A to B, never penetrates into the bulb.



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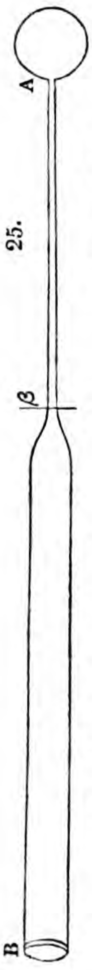


25.

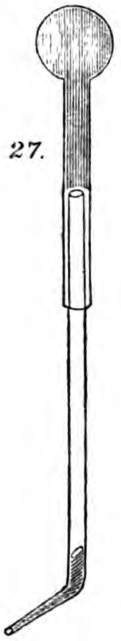
It is obvious that the portion of tube A, if wide enough, need not be blown out. Its neck is 1 to $1\frac{1}{2}$ inches long; and the sharp edges where it has been cut off must be rounded in the flame of a spirit lamp; otherwise we are in danger of breaking off little splinters after the bulb has been weighed, and while we are introducing the liquid.

To fill the bulb with liquid, it is warmed, and the open end of the neck introduced into the liquid. When by cooling a certain quantity of liquid has entered, the bulb is again warmed; the vapour which is formed expels almost the whole of the atmospherical air, and when the point is again dipped in the liquid, the bulb fills to three fourths of its bulk. The point is now sealed up, the whole is weighed, and subtracting the weight of the bulb, when empty, we have the weight of the liquid.

Before weighing the bulbs, the oxide of copper has been ignited, and, while still red hot, introduced into the tube (*fig.* 26,) which is closed with a dry cork, and allowed to become quite cold. It is not so convenient to allow the crucible to cool under a bell jar along with oil of vitriol.

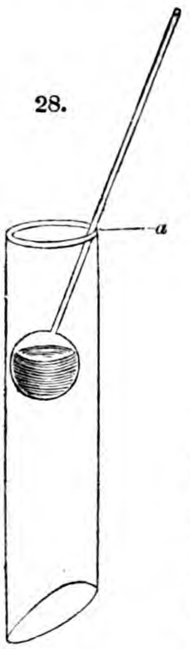
26.

27.



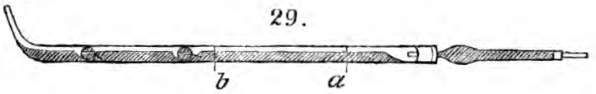
The tube, *fig.* 26, is so wide, that the tube of combustion slides easily into it. We first allow, as shown in *fig.* 27, one to one and a half inch of the perfectly dry oxide to fall into the tube of combustion, and then introduce the bulbs alternately with more oxide, so that the latter can attract no moisture. The bulbs are scratched with a sharp file on the middle of the neck, as in *fig.* 28, at *a.* They are held by the point, and when introduced into the mouth of the tube, broken across, both bulb and neck being allowed to slide down into the tube.

28.



Two bulbs, holding from 5 to 8 grains of liquid are sufficient; they are separated in the tube by a layer of oxide of copper, of 2 to 3 inches long. If the tube of combustion be 18 inches long, then there is above the uppermost bulb a layer of oxide 11 to 12 inches long. *Fig.* 29 shows the bulbs with the layers of oxide of copper.

29.



Mitscherlich is the only chemist who introduces the bulbs into the tube of combustion sealed up. He then heats, in the course of the operation, the part of the tube where they lie, till they burst. If the liquid be not very volatile, it is unnecessary to leave the bulbs closed; and if it be very volatile, this method is ill adapted to practice—for with such liquids a very sudden disengagement of vapour cannot be avoided, especially if the bulb be burst by the elastic force of the vapour, and not by the expansion of the liquid. Now when this sudden disengagement of vapour occurs, it is impossible to prevent a portion of it from escaping without undergoing combustion.

When the liquid boils at a high temperature, and is also rich in carbon, it is divided into three portions in separate bulbs, without, however, taking more than from 7 to 9 grains in all. The bulbs are separated by layers of oxide of copper.

This precaution must be attended to in analysing the essential oils, because the oxide of copper, which immediately surrounds a bulb, is seldom sufficient for the complete oxidation of the vapour; and, being itself completely reduced to the metallic state, a thin layer of carbon is sometimes deposited on its surface. Now, although this carbon may be oxidized by the air drawn through at the end of the operation, yet it is better to avoid the necessity of this rectification.

In the case of liquids which are not very volatile, the bulbs may be emptied before beginning the combustion. The tube of combustion, after being filled, is connected with the air-pump, as in *fig.* 7. When the air is rarified by a stroke of the piston, the bubble of air contained in each bulb expands, and forces out the liquid, which is absorbed by the surrounding oxide of copper.

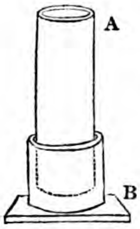
In the case of highly volatile liquids, a second screen at *b,* (*fig.* 29,) is placed between the spot where the uppermost bulb lies, and the heated anterior part of the tube. This part, containing pure oxide of copper, must, in such a case, be gradually surrounded with red hot charcoal, begining at *a*, and heating short portions at once.

From the commencement of the operation, some bits of red hot charcoal must be placed below the closed point of the tube of combustion in order that no fluid may distil into the closed end, from which it could only be expelled by a very strong heat; the liquid then boils by starts, and in little explosions, whereby some of it may readily pass away unoxidated with the gaseous products, forming a visible white cloud.

When the anterior part of the tube is red hot, the screen *b* is removed, and a piece of burning charcoal from time to time brought near the spot where the first bulb lies. In other respects the combustion is to be carried on as formerly described.

Fixed oils are weighed in the small tube, (A, *fig.* 30,) which is supported during the weighing on the stand (B, *fig.* 30,) of tinned iron. When 2 inches of oxide of copper have been introduced into the tube of combustion, the tube with the oil is allowed to slide down, with the open end upwards. By inclining the combustion tube, the oil is allowed to flow out, and we endeavour to spread it over the sides of the combustion tube as far up as the middle. The tube is then filled, as formerly directed, with oxide of copper.

30.

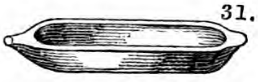


Soft fusible matters may be treated exactly in the same way.

Fusible substances which, though solid, cannot be reduced to powder, such as wax, are introduced into the empty combustion tube in weighed fragments. The tube is then heated, after being closed with a cork, till the substance melts, when it is spread along three fourths of the length of the tube, reckoning from the sealed end. When cold, the tube is filled with oxide of copper.

Such substances may also be weighed in a little glass vessel having the shape of a boat, (*fig.* 31,) which is easily made by taking a tube $\frac{1}{4}$ inch in width, softening it, and drawing it out upwards in two places, and then splitting the tube lengthways by means of a red hot point of charcoal,—(*Sprengkohle, Berzelius.*) For the combustion of such substances we must select combustion tubes somewhat wider and longer than for ordinary combustions.

31.



COMBUSTION OF SUBSTANCES VERY RICH IN CARBON, OR OF SUBSTANCES CONTAINING CHLORINE.

THERE are some substances in which it is almost impossible to determine accurately the proportion of carbon by means of combustion with oxide of copper. Such are: the different kinds of coal, indigo, ulmine, and all bodies resembling these. In the case of coal, for example, the disengagement of gas, at the end of the operation, does not cease. It becomes, indeed, gradually slower, but even an hour afterwards, when the heat has been strong, the caustic ley does not ascend.

The cause of this is, doubtless, that the combustion is unequal. The first effect of the heat is to disengage combustible gases, which reduce to the metallic state the oxide surrounding each particle; and so much carbon is left, that it cannot all be oxidized by cementation. The loss of carbon, thus occasioned, amounts to from three to five per cent.

When the substance contains chlorine, the determination of the hydrogen becomes inexact. The chloride of copper being volatile, it is impossible to prevent the deposition of some of it in the chloride of calcium tube.

For all such combustions, it is necessary to employ the chromate of lead, of which there is required rather more than half the bulk of the oxide of copper which would have been required. In other respects, the process is the same.

When the chromate of lead is used, it is necessary to give a strong heat at the end of the process. Pure oxygen is then disengaged, in which the remaining charcoal undergoes perfect combustion. But the increased heat renders it necessary to protect the tube by covering it with a thin sheet of copper, which, from its flexibility, may be easily wrapped round the tube, and which may be kept in shape by a few rings of iron wire bent round it.

The same object may be less conveniently attained, when oxide of copper is employed, by placing, in the closed end of the tube, a mixture of 1 part of chlorate of potash, and 8 parts oxide of copper. When, at the end of the operation, this part of the tube is heated, the remaining charcoal is burnt by the oxygen which is disengaged.

For substances containing chlorine, the chromate of lead is a precious, nay, indispensable means of combustion. Chloride of lead is formed, which is not at all volatile, at a red heat.

It is necessary to bestow some attention on the preparation of the oxide of copper, and the chromate of lead, as also on the choice of combustion tubes.

OXIDE OF COPPER.

This oxide may be prepared by mixing hot solutions of sulphate of copper and carbonate of soda. The pale blue precipitate of carbonate of copper is left, during from eight to fourteen days, in the liquid, and in a warm situation. At the end of that time it loses its gelatinous consistence, becoming green and crystalline, in which state it is easily washed and dried. Before being used, it must be strongly ignited, and carefully tested for sulphuric acid and soda. If it contain even a minute quantity of these, it is unfit for analyses.

The oxide thus obtained is brownish black, and forms an extremely loose, light powder, which is in the highest degree hygroscopic. Organic substances, when mixed with it, are burnt with great facility; but occasionally the mixture in the tube, when one part of it has been ignited, continues to burn spontaneously, in which case the analysis is good for nothing.

It is better to use the oxide of copper prepared from the nitrate by calcination. Its preparation is both easier and cheaper, and we are never doubtful of its purity.

To prepare it, sheet copper is ignited, and thrown, while red-hot, into cold water. All impurities on the surface peel off with the crust of oxide formed. The clean, well-washed metal is now dissolved in pure nitric acid, and the solution evaporated to dryness in a porcelain capsule. The dry salt is next ignited in a well covered hessian crucible, (care being taken not to introduce too much at once, as the salt froths up,) and the calcined mass is frequently stirred with a hot glass rod, or copper-wire, in order that no part of the nitrate may escape decomposition. Platinum crucibles must not be employed for this operation, as they are by degrees attacked and worn away when oxide of copper is ignited in them.

The ignited oxide is reduced to fine powder, and preserved in a well stopped vessel. It is compact, heavy, coal-black. Its hygroscopic condition depends on the temperature to which it has been exposed. When very strongly ignited, the oxide shrinks in bulk, becomes very hard, and loses almost all hygrometric properties. In this form, if broken into small fragments, it answers admirably, when the finer parts are removed by sifting, for the combustion of liquids, and of difficultly combustible, fatty, fusible, substances. The tube may be completely filled with it, and no tapping is required, as there are sufficient pores in the mass to yield a free passage to the gases.

To attain the same end, Dumas employs the oxide obtained by calcining copper turnings on a muffle. This oxide retains the form of the turnings, and is equally well adapted for the purpose above mentioned.

The oxide of copper, which has been used for a combustion, may be again rendered fit for use by moistening it with pure nitric acid, and igniting it afresh. Should the copper originally have been contaminated by brass solder, the oxide cannot be used for the determination of nitrogen, as the nitrate of zinc is only partially decomposed by ignition, but readily yields nitrogen or nitric oxide when heated with organic matter.

If the substance analysed have been a compound of an organic substance with a fixed base, the oxide, after the combustion, must be digested in cold dilute nitric acid, well washed and ignited.

After the combustion of a compound containing chlorine, the oxide must be redissolved in nitric acid, and the chlorine precipitated by nitrate of silver. Any excess of silver in the filtered solution is reduced by the ignition, and its presence is not injurious.

CHROMATE OF LEAD.

This substance is obtained in a state of perfect purity by precipitating acetate or nitrate of lead with bichromate of potash, and washing the precipitate carefully with distilled water. But in the state in which it is obtained by mere drying, it is not adapted for analyses. It must be strongly ignited till it begins to melt, and then reduced to a very fine powder. The ignition changes its beautiful yellow colour to a dirty brownish red, which it retains on cooling.

The chromate of lead may be used in every kind of combustion as well as the oxide of copper. The combustion takes place easily, and at a moderate heat. It is always complete, for the gases after the combustion are invariably tasteless.

Compared with an equal weight of oxide of copper, it does not contain so much oxygen available for combustion; but compared with an equal bulk, it contains nearly one half more, since its density is more than twice as great as that of the oxide of copper.

It is highly probable that the chromate of lead will be preferred to the oxide of copper in many cases, where it is desirable to determine the proportion of hydrogen with extreme accuracy. The chromate is not in the slightest degree hygroscopic, and the trace of moisture, which the substance may have attracted during the mixture, can be afterwards removed with much greater facility than in the case of oxide of copper.

COMBUSTION TUBES.

The glass of which these tubes are made, must be chosen with great care. The Bohemian potash glass, which contains no lead, is the best. Tubes of this glass never crack, even when suddenly surrounded with red-hot charcoal. It is extremely difficult to melt, and when softened, it is extremely tough. The green bottle glass of Germany cracks easily in the fire, is difficult to melt, but, when once softened, very liquid. The softened parts are blown out by the slightest pressure, and holes are formed instantly when this occurs.

The French white and green bottle glass must be rejected. The French green glass can be melted in a tube of Bohemian glass, without the form of the latter being altered.

Having now described all the precautions and manipulations which insure the performance of a trust-worthy analysis, as far as concerns the determination of carbon and hydrogen by weighing, it remains for us to describe the method of determining the carbon by the volume of the carbonic acid produced, as well as that of the nitrogen, which latter is always done by measurement. I have also to consider the degree of accuracy which is attainable in the determination of the carbon and hydrogen.

CARBON.

THE determination of the carbon by the process and apparatus above described may be rendered inexact by several sources of error. The first and most important is incomplete combustion. In repeating the analysis, this may be avoided by using a longer combustion tube and increasing the proportion of oxide of copper. The latter precaution insures a greater degree of division, and a slower combustion, which generally suffices.

A second source of uncertainty, as formerly mentioned, arises from the circumstance that the gaseous matter which, during and after the combustion, passes through the potash apparatus, carries with it a portion of water, from the caustic ley, the weight of which is thus diminished. But it is obvious that this loss of water is, in part at least, compensated by the carbonic acid of the air, so that the loss of weight varies, according to the quantity of carbonic acid present in the atmosphere.

This point has been satisfactorily cleared up by direct experiments. When the combustion tube is surrounded with red-hot charcoal, and the point broken off, *fig.* 22, without the tube *h*, the open point being also surrounded with charcoal, the potash apparatus, after 2000 cubic centimetres of air have passed through it, not only does not lose weight, but gains 18½ milligrammes (0.275 grain nearly.)

To determine the amount of water carried away by the current of air, there was connected with the potash apparatus a second similar one filled with strong sulphuric acid. It is clear, that the water carried in the form of vapour by the current of air from the caustic ley must have been condensed by the sulphuric acid.

Now the weight of the apparatus containing the sulphuric acid had increased by 14 milligrammes (0.21 grain nearly,) so that, instead of a deficiency in the carbon, there was, in this experiment, an excess; for the caustic ley had absorbed 32½ milligrammes (0.48 grain nearly) of carbonic acid from the air, and had given off 14 milligrammes of water.

When the tube *h*, 12 or 15 inches long, was placed on the point of the combustion tube as in *fig.* 22, and the experiment repeated with the same quantity of air, the apparatus with sulphuric acid again gained in weight 13.6 milligrammes, and the potash apparatus lost 5 milligrammes, (0.075 grain nearly.)

It is obvious that by this arrangement the error in the determination of carbon arising from the loss of water is completely compensated by the absorption of carbonic acid from the air.

When 200 cubic centimeters (the quantity commonly occurring in a combustion) of carbonic acid pass through the potash apparatus, the loss amounts only to half a milligramme (0.0075 grain nearly) in the weight of carbonic acid. Reduced to carbon, this amounts only to

0.000138 gramme, (0.002 grain nearly); and this loss is extended over from 0.4 to 0.8 gramme (6 to 12 grains) of the substance analysed.

Those who, at the end of the combustion, connect the point of the combustion tube with a tube of fused potash, to deprive the air of its carbonic acid, must therefore add to the weight of the potash apparatus on an average 0.0013 gramme, (0.0295 grain nearly,) for every 100 cubic centimeters of gaseous matter which pass through.

But the experiments above detailed, show that it is unnecessary to have recourse to that method; and that, in all circumstances, it is safer to follow the process I have recommended.

When the quantity of carbonic acid produced in the combustion is very large, and the bubbles follow each other with rapidity, the caustic ley becomes warm, and the loss of water is increased.

In weighing the potash apparatus, it must be observed, that when it is warm less moisture condenses on the surface of the glass than before the combustion, when it was weighed cold. This difference amounts to 0.003, or 0.004 gramme. When the air is very moist it may even reach 0.006 gramme, (0.045, 0.06, 0.09 grain nearly). It is better therefore to wait until the apparatus has cooled down.

An examination of the analysis of one or two substances possessing high atomic weights, will give the clearest idea of the accuracy with which the apparatus described enables us to determine the carbon.

It is known with sufficient certainty, that the atomic weight of the amygdalate of baryta is = 6738.829. Three analyses of this salt gave of carbonic acid 163.8, 163.5, 163.3 per cent. The mean is 163.5. The quantity calculated according to the theoretical composition of the salt is 163.7. The loss of carbonic acid is, consequently 0.002 carbonic acid, (0.2 per cent.) which is equal to 0.00055 carbon, (0.055 per cent.) There is no kind of analysis, in which greater accuracy is attainable.

This is the proper place for some remarks on the true atomic weight of carbon. The earlier determinations of Berzelius give the number 75.33. His latest experiments give 76.437. I consider the latter as the true atomic weight, determined with astonishing accuracy. Every day's experience confirms its exactness, and the following considerations will give to all chemists the same conviction.

The mean of 5 analyses of stearine give, in 100 parts of this substance, 76.084 carbon. The three highest results gave a mean of 76.306.

From the products of the decomposition of stearine we know with certainty that one equivalent of it contains 146 atoms of carbon; which, taking the atomic weight of carbon at 76.437, would give of carbon in stearine 76.21 per cent. Were the atom of carbon, as Thomson considers it, exactly 75; or 75.33, as the first experiments of Berzelius made it, the analysis, supposing stearine to contain 146 atoms of carbon, should have yielded not more than 75.85 and 75.98 per cent. of carbon.

The difference, 0.36 per cent. carbon, amounts to one atom less. But if we assume stearine to contain only 145 atoms carbon, all coincidence between the composition of stearine and that of stearic acid and glycerine, the products of its decomposition, dissappears; and we must then suppose that the analysis of one or of both of these substances is inaccurate; a supposition for which there is no foundation.

In the combustion of substances which contain sulphur, as xanthates, sulphosinapisine, &c., the weight of the carbon generally turns out too high. This proceeds from the formation of sulphurous acid, which always occurs when the mixture with oxide of copper has not been made sufficiently intimate. The sulphurous acid is absorbed by the caustic ley, and increases its weight. When we have reason to fear this source of error, we must place between the chloride of calcium tube and the potash apparatus a tube with peroxide of lead.

A concentrated solution of chloride of calcium, such as is formed in the chloride of calcium tube, does not retain any sulphurous acid, particularly when it is allowed to lie till all the liquid in it has solidified, that is, till the chloride of calcium has crystallised. The sulphurous acid which has passed through the chloride of calcium is absorbed by the peroxide of lead. The latter must not be placed between the chloride of calcium and the combustion tube, unless we mean to neglect the water in that particular analysis; as some water would be absorbed by it.

HYDROGEN.

The only error inherent to the method of analysis recommended, which affects the determination of the hydrogen, arises from the moisture of the atmospheric air which is drawn through the apparatus at the end of the combustion, with the view of bringing the whole carbonic acid in contact with the absorbing liquid.

Innumerable experiments have shown, that the amount of moisture absorbed by the chloride of calcium, when 200 cubic centimetres have passed through, never amounts to more than 0.005 or 0.006 gramme (0.075 to 0.09 grain, nearly.) This corresponds to 0.00055 or 0.00066 gramme (0.0075 to 0.009 grain, nearly) of hydrogen. This excess is divided over 0.3 to 0.5 gramme (4.5 to 7.5 grains nearly) of the substance analysed; and it is equally great, whether the substance contain much or little hydrogen. If the substance analysed be rich in hydrogen, and have a small atomic weight, this error becomes proportionally smaller. In such cases we are in no doubt as to the number of atoms of hydrogen. An example will illustrate this.

100 parts of pyroacetic spirit (acetone) when burned with oxide of copper, yield as a mean result 94.23 parts of water. The amount, calculated from theoretical composition, is 92.45 parts of water per cent. The analysis, therefore, gives 1.8 per cent. of water, or 0.2 per cent. of hydrogen, in excess. Now, the atomic weight of acetone is 366.750. Had this quantity been burned, we should have had an excess of hydro-

gen over the theoretical quantity, amounting to 0.7335; but since the atom of hydrogen weighs 6.23978, it is obvious that the error is far short of one atom of hydrogen; and that it may safely be neglected in such cases, especially as we know the source of it, and the limits within which it is confined.

But this error cannot be neglected in substances of high atomic weight which contain much hydrogen. We must subtract from the amount of water obtained 0.005 to 0.006 gramme, (0.075 to 0.09 grain nearly;) or, if we are unwilling to trust to this correction, we must break off the point before the caustic ley begins to ascend, remove the hot charcoal from about the point, and, when it has cooled sufficiently, connect it, by a tube of caoutchouc, with a tube containing chloride of calcium, or with a potash apparatus filled with sulphuric acid.

An example will render obvious the necessity for this correction. 0.3054 gramme of stearine, without correction, and without any means having been taken to desiccate the air, yielded 0.343 gramme of water: 100 parts, consequently, would have given 112.31. According to the theoretical composition of stearine, 100 parts should yield only 109.63 of water. There is, therefore, here an excess of 2.68 per cent. of water, or 0.297 per cent. of hydrogen. Now, this slight excess, calculated on the atomic weight of stearine, corresponds to somewhat more than three atoms of hydrogen.

If, however, we deduct, previously to the calculation, 0.006 gramme as hygrometic moisture, there remain for 100 parts of stearine 110.35 of water, or an excess over theory of 0.72 per cent. water, or 0.08 per cent. hydrogen; which excess, calculated on the atomic weight, amounts to less than one atom of hydrogen.

By following, therefore, the process of analysis recommended in this work, we must always be prepared for an excess of hydrogen over the truth, amounting to from 0.14 per cent. to 0.2 per cent.; and we can only consider the determination of the hydrogen as exact, when this excess does not exceed 0.2 per cent. When the analysis, without the above correction, gives exactly the theoretical quantity of hydrogen, there is much reason to doubt the accuracy of the experiment; and the formula found for the composition of the substance is erroneous, when the results of repeated analyses yield constantly less hydrogen than the formula indicates.

In publishing the weights obtained in an analysis, we must not make the above deduction, but give the numbers as they occur, since the amount of excess, due to hygrometric water, furnishes to the reader a valuable means of judging of the accuracy of the determination of the hydrogen. It is only in calculating the composition with a view to discover the formula that we are to make the correction above mentioned.*

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* *Note by the Translator.*—The statements contained in this section have excited some discussion. Berzelius, in the appendix to the last (German) edition of his system, objects

Berzelius prefers, for the connection of the combustion tube with the chloride of calcium tube, the form of apparatus, *fig.* 10, and the use of a connecter of caoutchouc, to that of a dry cork, as represented in *fig.* 9, and recommended here. This preference can only be accounted for on the supposition that he has never subjected the latter to proof. To make a good analysis with the arrangement of Berzelius is an operation which requires the hand of a master; and we must always consider it a lucky event when the analysis is safely over. The point of the combustion tube, which, in Berzelius's method, is introduced into the chloride of calcium tube, being drawn out, is easily broken by the slightest shock given to the apparatus, and we thus lose our time and trouble.

If the point does not enter deeply into the chloride of calcium tube, it also frequently happens that a drop of water rises into the space between the two tubes by capillary attraction. On untying the appara-

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to what is here said of his method, and describes minutely all the precautions and manipulations which he employs to secure accuracy. In direct opposition to the averments of the author, Berzelius declares that caoutchouc does not alter in weight by absorbing moisture; and that the cork often does give out water. Hess, also, (*Annalen der Pharmacie*, xxvi. 189,) endeavours to show that the determination of hydrogen by Liebig's method is not subject to any constant error, as stated in the text. Liebig (*Annalen* xxiii. 16,) had endeavoured to point out another source of error, namely, the usually alkaline state of the fused chloride of calcium, which, according to him, absorbed a little carbonic acid, and thus increased in weight, even when all moisture was carefully excluded. This is denied by Hess, who states that the fused chloride of calcium, although alkaline, does not absorb any carbonic acid. In a note to the paper of Hess, the author of this work has made some remarks, which appear to me so important, that I am sure the reader will approve of my transcribing them here. They place the question in dispute on its proper footing; and the admirable researches which daily proceed from Professor Liebig's laboratory, not only those of Professor Liebig himself, but those of numerous pupils, as M. M. Ettling, Schœdler, Fehling, Thaulow, Woskresensky, Gros, Regnault, Demarçay, Richardson, Campbell, &c., clearly prove the sagacity of the founder of such a school, and the great advantages derived from a simplification of the apparatus, which enables any one with ordinary care to perform an accurate analysis.—W. G.

Note by the Author to a paper by M. Hess, (*Annalen der Pharmacie*, xxvi. 192.)—As, for all chemical operations, and of course for the performance of a good organic analysis, practice is required, so this branch of analysis must be regularly acquired. I have made the experiment described by my distinguished friend a great many times, and after the cork had been carefully dried I have never observed either a gain or loss of weight. The opinion which I have expressed in the work on Organic Analysis, is founded on experience, derived from all the organic analyses which have been made by all the different experimenters in this department, the number of which must amount to several thousands. The excess of hydrogen over the theoretical quantity, may possibly, in many of these analyses, have been increased by the cork; but this excess is also observed in all the analyses in which Berzelius's method was employed. It is, therefore, independent of the cork.

The tendency of my work on Organic Analysis has been, as I have, unfortunately, had occasion to observe, misapprehended in many quarters. Berzelius has thought it necessary to correct several of my statements in reference to his method of connecting the tubes, which seemed to him erroneous. However deeply I regret to have given to one whom I so highly venerate, occasion to accuse me of injustice unintentionally done to him, this in no wise alters the view which I have taken of the processes for organic analysis.

We may attain the desired end by various means; we may choose among those which are made known; and the question is, which are we to adopt? The original method of Berzelius is excellent: no one can doubt this who recollects that we owe to him the most accurate analyses of several organic acids, and that Chevreul, by the same method, detertus, we find the inside of the caoutchouc moist, which of course causes the rejection of the determination of the hydrogen.

The cutting off the point, the removing of the caoutchouc tube without detaching the other, the igniting of the broken point, &c.—all these operations may be performed, but they are of such a nature as to expose us to accident.

The reason given by Berzelius, and those who follow his method, for requiring such an unnecessary amount of labour and dexterity, is the hygroscopic nature of the cork; which, as they say, when heated in the combustion tube, gives out the moisture it had absorbed from the atmosphere.

There is no doubt that we must give the preference to the more complicated method of connecting the tubes, if the reproach of inaccuracy cast on the simpler mode have any foundation: but experiments made expressly with the utmost care; experiments which every one who

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mined the composition of an extensive series of organic compounds in such a manner that his numbers remain to this day models of accuracy. Neither Berzelius nor Chevreul now employ this method; and the reason is plain. The former devoted eighteen months to the analysis of seven organic acids; and Chevreul was occupied for thirteen years with the analysis of the fatty substances discovered by him. With the assistance of our present methods, Berzelius would have required at the utmost four weeks, and Chevreul perhaps two years, for the same researches. Now, the advantage of our methods does not consist in greater accuracy, for, as we have seen, the old method was susceptible of the greatest exactness, but in the greater simplicity and security, with the same degree of exactness, which they afford. This, however, and no more, is the question at issue. Progress in organic chemistry is out of the question, without researches; but these include not the analysis of a single substance, but of a series of products; 60—70—100 or more analyses are not rare in the course of one investigation of this kind. I obtain in one experiment a substance of peculiar properties, which I analyse. I again procure it under somewhat different circumstances, and observe differences in the second analysis. In a third I observe further discordance; at last I arrive at the knowledge of a substance, whose properties are uniform, and whose composition explains the discordance of the first results. The last analysis alone is published; the others were merely *tests*. This is the use, then, to which a method of organic analysis must be adapted, and the greatest degree of simplicity and security of the apparatus alone render such researches possible. In this laboratory there are made annually more than 400 analyses. No sort of substance has come into our hands on which we have not had occasion to make observations of all kinds; and all the analyses are made with the same simple apparatus, with the slight modifications which suggest themselves in particular cases. Our analyses are no worse than those of the chemists who employ an apparatus constructed to insure mathematically accurate results; *which however, it does not give.* In Berlin and elsewhere, analyses indeed are made, but not researches. It is very remarkable that in the only places where researches are carried on, namely in Paris and in Petersburgh, it is not thought worth while to invent new and perfect apparatus; doubtless because chemists there go practically to work; for which, among us, pedantry and much talking leave no time. To build a great palace we require many workmen, masters and journeymen—we require simple instruments. Errors must be avoided by a strict superintendance, which is soon spontaneously and mutually established. I would rejoice to hear that blunders were made among us; for blunders are a proof that we are working. The so-called mathematically-accurate instruments, with which no better results are obtained than with our imperfect methods, profess to protect us from errors. But they deter from research; and their injurious influences on the development of organic chemistry will be long felt. The mere dread of committing errors prevents us from making discoveries. Truly if this were a matter of personal interest, it were folly to have said so much.—J. L.

desires to acquire conviction on this point may easily repeat for himself, have proved, that when the cork has been dried in a platinum crucible in hot sand, and introduced into the tube with dry fingers, this cork, while air is slowly drawn through the ignited combustion tube, gives off no water; for the weight of the chloride of calcium tube is not increased by 1 milligramme.

Daily experience shows that the determination of the hydrogen, according to the method of Berzelius, is not in the least more accurate than with the cork; nay, in most cases it may be asserted that that method gives less exact results.

There is hardly to be found a more hygroscopic substance than caoutchouc. A small tube of it dried at 212° F., increases in weight after a few minutes by 0.015 to 0.020 gramme, (0.225 to 0.3 grain nearly) and a tightly stretched bit of caoutchouc may be used as the most delicate hygrometer, instead of the slip of whalebone commonly employed.

I am opposed to the method of connection of the tubes employed by Berzelius, (and this must be especially insisted on) because, according to this method, organic analysis, *in most hands*, loses the accuracy and trustworthiness which may be given to it by the method I have recommended: and because it complicates the manipulations, thereby confining this branch of analysis to a proportionally small number of experimenters.

The determination of the hydrogen becomes inaccurate when a compound of chlorine is burnt with oxide of copper. The chloride of copper which is formed, sublimes with the current of gaseous matter, condenses in the chloride of calcium tube, and increases its weight. The more slowly the combustion goes on, the smaller is this excess of weight; but it must never be neglected. It amounts in all to from 0.01 to 0.015 gramme, (0.15 to 0.225 grain nearly.) By dissolving the chloride of calcium, precipitating the copper with sulphuretted hydrogen, and determining its quantity, this source of error may be corrected.

In the analysis of such bodies we must be particularly cautious in moderating the current of air which is drawn through the apparatus after the combustion; for if the current be made rapid, the chloride of copper may be seen passing through the caustic ley in the form of white vapours, and the nauseous metallic taste of the salts of copper, is perceived in the mouth.

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

The chloride of calcium tube must be emptied immediately after we have weighed it, if we would not lose it. If this be not done, the saturated solution of chloride of calcium which has been formed, crystallises, and infallibly bursts the tube.

DETERMINATION OF NITROGEN.

When substances containing nitrogen are analysed, the carbon and hydrogen are ascertained by the method already described, and the determination of the nitrogen becomes then the object of a separate experiment, in which everything else is neglected.

We see at once, and clearly, whether a substance contain nitrogen or not, in determining the carbon. If nitrogen be present, bubbles of gas, during the whole combustion, escape through the potash ley. If these bubbles towards the end of the combustion, are larger than an ordinary pin's head, we may be sure that the substance contains nitrogen.

We may also ascertain whether a substance contain nitrogen by melting a portion of it in a test tube with 4 to 10 times its weight of fused caustic potash. Nitrogenised substances are thus decomposed without blackening, and the whole nitrogen is disengaged in the form of ammonia, which in all cases may be easily recognised by the smell. If we are obliged to have recourse to turmeric and other tests to detect the ammonia, then the presence of nitrogen is doubtful.

In the combustion of most nitrogenised substances, the nitrogen is disengaged in the free state, and in the form of gas, mixed with the carbonic acid and watery vapour. In other cases deutoxide of nitrogen is formed; the production of which renders the determination of the nitrogen difficult, and is certain to render it inaccurate, if the utmost care be not taken to reduce the deutoxide again to the state of nitrogen.

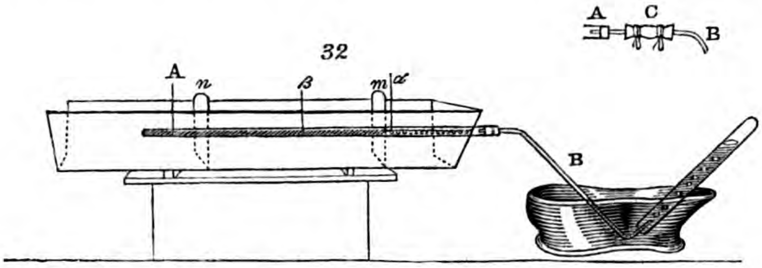
The nitrogen is always determined by measurement. Now, since nitrogen, by passing into deutoxide of nitrogen, doubles its volume, we are thus exposed to a source of error, which increases the apparent quantity of nitrogen. This error is obviated by using a combustion tube 3 or 4 inches longer than in the determination of carbon, and placing, above the anterior layer of pure oxide of copper, a layer of copper turnings, which have been ignited till their surface became black, and afterwards heated in a current of hydrogen till the crust of oxide on the surface has been completely reduced. Besides this, oxide of copper may be used for the combustion, which has already served for an analysis, and which consequently contains a considerable quantity of metallic copper.

The following rule must be attended to in the determination of nitrogen. *The more carefully and intimately the mixture with the oxide of copper has been made, and the more slowly the combustiom is made to proceed, the less danger is there of the formation of the deutoxide of nitrogen.* To give an idea of how we ought to proceed, it may here be remarked, that the combustion of a nitrogenised substance requires twice as much time as that of a substance containing no nitrogen.

The methods to be pursued in the determination of nitrogen are various, and more or less simple according to the amount of nitrogen present in the substance.

The qualitative analysis of the gaseous mixture produced in the combustion, must in all cases precede the quantitative determination of the nitrogen; for the knowledge of the relative volumes of carbonic acid and nitrogen suffices, in most cases, to enable us to calculate the amount of nitrogen, that of carbon having been previously ascertained. In these cases the employment of a special process becomes superfluous. The apparatus employed for this qualitative analysis is extremely simple; the whole operation lasts, including all the preparations, about two hours; and what we thereby ascertain determines our choice of another process, or renders all further operations unnecessary.

The substance (weighed or not weighed, this is indifferent) is mixed with forty to fifty times as much oxide of copper as would suffice for its complete oxidation. The mixture is introduced into the tube of combustion, A, *fig.* 32, so as to occupy half its length. Of the two remaining quarters of the length of the tube, one is filled with oxide of copper from β to α, the other with copper turnings from α to the mouth of the tube. The combustion tube being connected with the tube B, for collecting the gas, is placed in the furnace. The tube B may be rendered moveable by a caoutchouc connecter, C; it reaches into the mercurial trough, and is barely covered with mercury.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The screen *m* is put on at α, and then both the metallic copper and the oxide of copper are raised to a full red heat; the slits in the bottom of the furnace as far as α, being exposed, so that the heat may be strongest in the anterior half of the tube. If the tube be not of Bohemian glass, this part of the tube must be wrapped in thin sheet copper, tied on with copper wire: otherwise, the pressure, even of a small column of mercury, blows out the heated part, and causes a hole in the tube.

As soon as the copper and oxide are fully red hot, the second screen, *n*, is so placed, that a length of one inch of the tube, *from the closed end*, is exposed, and this is surrounded with red hot charcoal. The combustion is thus begun at the closed end; the gaseous matter disengaged expels all the atmospheric air from the apparatus, and by this means the whole is filled with the gaseous products of the combustion alone. The combustion is now carried on as usual, beginning at α, and proceeding gradually towards the closed end, by moving the screen, *m*, backwards half an inch at a time, surrounding each $\frac{1}{2}$ inch with glowing charcoal, &c. The gas, produced at this period, is collected in graduated tubes, $\frac{1}{2}$ inch in diameter, and 12 to 15 inches long, accurately graduated into equal parts, whether cubic inches, or cubic centimetres, or arbitrary measures, but all strictly uniform in each individual tube.

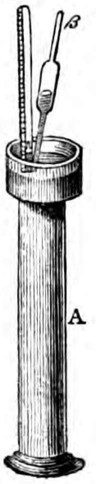
When the first tube is three-fourths full of gas, it is to be lifted out of the mercury, and air allowed to enter it. As this air, in a few seconds, mixes with the gas, it furnishes a very delicate test of the presence of deutoxide of nitrogen. Should $\frac{1}{1000}$th of this gas be present, the well-known red vapours of nitrous acid are instantly seen, which, if in very small proportion, give a yellow colour to the gas, when viewed through a great thickness, as by looking through the tube horizontally from end to end.

Sometimes deutoxide of nitrogen occurs at the beginning, and not after some time, because the oxide at α is reduced and assists the deoxidising agency of the turnings. The above-described test of the purity of the gas must be tried at the beginning, middle, and end of the combustion. If the formation of deutoxide of nitrogen has been observed throughout the whole operation, either the mixture of the substance with the oxide has been imperfect, or the combustion has been too rapid, or else it is necessary to increase the proportion of copper turnings.

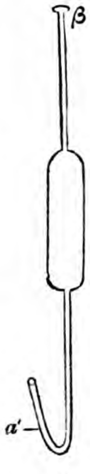
It is not worth while in this case to finish the experiment: it teaches nothing, gives rise to false notions of the composition of the substance, and only raises doubts of the accuracy of the next better analysis.

We obtain in all 6 or 8 tubes of gas, whose united volumes amount to from 300 to 600 cubic centimetres; and we have now to determine the relative volume of the nitrogen and carbonic acid. For this purpose, the tubes are carried, one after the other, into the cylinder with mercury, (*fig*. 33,) which is widened out at the top, the mercury within and without is brought to a level, and the volume of gas noted.

33.



34.



By means of the pipette, *fig*. 34, which is filled with caustic ley, and closed at α with mercury, the ley is introduced into the tube to the depth of some lines. This is generally done by applying the mouth to β, and producing a slight pressure, not more than sufficient to force out some of the ley.

When the bent point of the pipette is 1½ inch long, and reaches above the mercury into the tube, we have only to raise the graduated tube in the mercury, so as to cause a slight vacuum within, when the pressure of the atmosphere causes the ley to flow into the graduated tube.

By gently moving up and down the graduated tube, all the carbonic acid is rapidly absorbed, and nothing but nitrogen is left. The open end of the tube is easily broken, owing to the weight of the mercury. This accident may be entirely avoided, by holding the tube so that its mouth is constantly in contact with the side of the cylinder while we are moving it up and down. The mercury without and within is now again brought to a level, and the volume of gas noted.

Let the volume of gas in the 6 tubes be = 620, and let the remainder, after the action of the caustic ley, be = 124; 496 vol. of carbonic acid have consequently disappeared. Hence, in this case, the volume of the nitrogen is to that of the carbonic acid, as 124 : 496, or as 1 to 4.

We may now proceed, in a variety of ways, to calculate the nitrogen contained in the substance from the relative volumes, *it being presupposed, that the quantity of carbonic acid yielded by a given weight of the substance is known.* Either we convert the weight of the carbonic acid into volume, and divide this by the number expressing the relative proportion; the quotient gives the corresponding quantity of nitrogen by volume. For example, 0.100 gramme of caffeine yield by combustion, by weight, 0.180 grammes of carbonic acid. The gaseous mixture which caffeine yields by combustion, contains nitrogen and carbonic acid in the proportion by volume of 1 to 4. Now, 1000 cubic centimetres of carbonic acid gas weigh 1.97978 gramme,—0.180 gramme of carbonic acid, therefore, corresponds to 91.85 cubic centimetres. Dividing this number by 4, we obtain the number 22.85 cubic centimetres, which are to 91.85 as 1 to 4. These 22.85 cubic centimetres are calculated as nitrogen. We know that 1000 cubic centimetres of nitrogen weigh 1.26 gramme. Hence, 100 parts of caffeine contain 28.834 of nitrogen, and 49.796 carbon.

Or, to avoid this tedious calculation, if we remember that 1 vol. carbonic acid represents 1 atom of carbon, and 1 vol. nitrogen gas, 2 atoms of nitrogen, (1 atom English,) since the quantity of carbon, and the relative volumes of carbonic acid and nitrogen are known, we calculate the nitrogen from the atomic weights.]

Caffeine, according to the determination of the carbon, contains 49.796 per cent. of carbon. It also yields carbonic acid and nitrogen in the proportion of 4 to 1; consequently, it contains carbon and nitrogen in the proportion of 4 atoms carbon to 2 nitrogen, (1 atom English.)

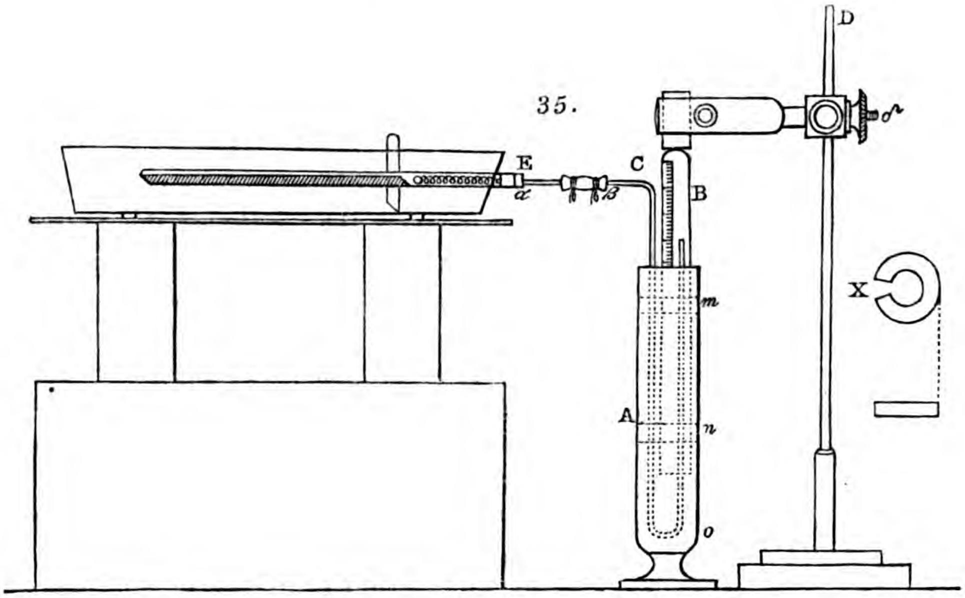
Therefore, as 4 × 76.437 (the atomic weight of carbon) is to 2 × 88.518 (the atomic weight of nitrogen,) so is 49.796 : x. That is, 305.748 : 177.036 :: 49.796 : x = 28.834, = the quantity of nitrogen in 100 parts.

The above described qualitative determination of nitrogen furnishes complete security, and is exact for all nitrogenised bodies, in which the nitrogen is to the carbon in no proportion smaller than 1 to 8.

As a control over this qualitative method, the nitrogen may be determined quantitatively by means of the following apparatus. *Fig.* 35.

It consists in a cylinder with a foot, *fig.* 35, A, in which three rings of cork, X, are glued, one at the bottom, the others at *m* and *n*. These rings serve to protect the small graduated bell-jar B, in its movements. The tube C, through which the gases enter the bell-jar, has two vertical and parallel limbs, the ascending one of which must have the same height as the jar, while the other passes outside the jar through slits in the cork rings, X. The tube C is now placed in the cylinder, the bell-jar is put down to the bottom of the cylinder over the tube, and the cylinder

35.



filled with mercury. The jar and tube are both kept firm in their places by means of the holder D, so that the mercury cannot displace them. The arm δ of the holder is moveable up and down the rod, D, and may be fixed by a screw at any convenient height. To the tube C is joined, by a tube of caoutchouc, the short tube E, the use of which is to allow a little motion without the risk of fracture of the apparatus. E, again, is joined to the combustion tube by means of an air-tight cork.

The substance is weighed and introduced into the tube in the manner formerly described. Before heating the tube, we must ascertain that all the joinings are tight. This is done by raising the bell-jar till the mercury stands an inch higher within than without. Its height is marked, and if it do not change in a quarter of an hour, no air enters by α or β. We may then begin the combustion, first bringing the mercury without and within the bell-jar to a level, and noting the volume of the atmospheric air in the jar, the temperature, and the height of the barometer.

The gas produced in the combustion enters the jar and displaces the mercury; but by raising, as it may be required, the wooden arm δ, we can preserve the mercury always at the same level, and thus avoid any internal pressure on the combustion tube.

When the combustion is over, and we perceive no more increase of the volume of gas in the jar, the charcoal is removed, and the whole is allowed to cool. The level of the mercury, which changes during the cooling, is restored; the temperature and height of the barometer are noted, and the volume of gas measured. To obtain the true volume of the disengaged gases, we now deduct from the gross volume the volume of air in the jar at the commencement of the operation, and reduce the residue to the normal temperature and pressure, provided neither temperature nor pressure have changed during the experiment. If they have changed, the reduction must be performed separately for each portion of gas—that is, for the original air, and for the gross volume at the end of the combustion.

We now know the sum of the volumes of nitrogen gas and carbonic acid gas yielded by a given weight of the substance. We know, further, from a previous analysis, the weight of the carbonic acid. The latter, being reduced to volume, is deducted from the mixed gases to obtain the volume of the nitrogen, which is then reduced to weight. The volume of nitrogen must bear to the volume of carbonic acid a simple ratio, and, indeed, the same indicated by the qualitative analysis. If the two do not agree, one or other of the analyses is erroneous, and must be repeated.

For example, 0.100 gramme of caffeine burnt in this apparatus, yield at 0° C. and 28″ bar., 114.06 cubic centimetres of gases. The same quantity of caffeine, burned in the apparatus, *fig.* 19, gives 0.180 gramme of carbonic acid, corresponding, at 0° and 28″ bar., to 91.21 cubic centimetres of carbonic acid gas. Hence, 0.100 gramme of caffeine yields $114.06 - 91.21 = 22.85$ cubic centimetres of nitrogen $= 28.836$ per cent.

The quantity of substance which may be analysed in this apparatus, depends on the size of the bell-jar. For each per cent. of nitrogen and carbon we must calculate 1 cubic centimetre in the bell-jar, and, over and above, a free space of from 15 to 20 cubic centimetres, to allow for changes of volume from changes of temperature. If the bell-jar, for example, holds only 100 cubic centimetres, we can only measure in it the gases from 0.060 gramme (0.9 grain nearly) of caffeine, or of 0.09 to 0.1 gramme of morphine (1.35 to 1.5 grain nearly,) if the jar contain at first 15 cubic centimetres of air. These jars commonly hold from 200 to 250 cubic centimetres; but it is easy to see, that in all these cases, the quantity analyzed is very small, and that the errors of manipulation or of observation have, under all circumstances, a great influence on the amount of nitrogen obtained; so that, when the quantity of nitrogen in the substance is very small, this apparatus ceases altogether to give exact and trustworthy results.

One principal source of error here is the softening of the combustion tube by the strong heat employed, whereby it loses its shape, which of course affects the volume of gas in the bell-jar. This occurs very readily, where the level of the mercury has not been very carefully regulated. It is advantageous to enclose the lower half of the tube along its whole length in a half cylinder of thin sheet copper, lined with fine charcoal powder to prevent adhesion. A sheet of platinum as long as the tube, and only just broad enough to keep it from bending, answers still better.

DIRECT DETERMINATION OF THE NITROGEN.

In the analysis of substances containing a very small proportion of nitrogen, the whole amount of the nitrogen gas is ascertained by a special operation. For this purpose we employ the apparatus, *fig.* 35, arranged in the following manner. Into the closed end of a combustion tube, 18 inches long, is introduced a layer of dry hydrate of lime, (slaked lime) of 2 to $2\frac{1}{2}$ inches. There must be at least 60 to 80 grains of it. Above it is placed 1 inch of oxide of copper, then the mixture of the substance with oxide of copper; the other divisions, *fig.* 36, point out the oxide of copper used for rinsing out the mortar after the mixture; above this, pure oxide of copper; and, lastly, copper turnings.

36.

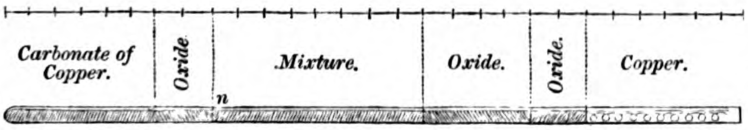
The combustion tube is connected with another in the shape of a large chloride of calcium tube with two bulbs; the bulb α is empty, the other bulb and the wide part of the tube are filled with fused hydrate of potash. By means of a tube of caoutchouc, this apparatus, after the combustion tube has been placed in the furnace, is connected with the gas tube and gasometer, *fig.* 35, and the combustion carried on as usual. When the absorbtion tube is 12 inches long, and the wide part of it $\frac{1}{3}$ of an inch in diameter, it holds about thirty times as much potash as is sufficient to absorb the whole carbonic acid produced, so that nitrogen alone enters the gasometer.

If the hydrate of lime be gently ignited at the end of the combustion, the water it contains is converted into vapour, and drives all the carbonic acid before it into the graduated tube. After the cooling, the combustion tube contains only watery vapour which condenses; any traces of carbonic acid being absorbed by the quick lime.

Before the combustion there was in the gasometer a known volume of air, after the combustion that volume is increased, and the increase gives exactly the volume of nitrogen that has entered the gasometer. This is measured, and after being corrected to the normal temperature and pressure, is reduced to weight.

This apparatus is exposed to a constant error, which is unavoidable. We always obtain by it too little nitrogen, which obviously arises from this, that the oxygen of the air in the tube takes part in the combustion, and the volume of gas in the gasometer is thus diminished. By a series of the most careful analyses of nitrogenised substances of known composition, the limits of this error have been ascertained, and when we add 1 per cent. to the nitrogen obtained in this way, the sum expresses exactly the true quantity of nitrogen in the substance.

When the apparatus next to be described is employed, there is always obtained an excess of nitrogen, and this excess, in good analyses, amounts to 1 to $1\frac{1}{2}$ cubic centimetres of the whole volume obtained; when deutoxide of nitrogen occurs, this excess is greater. But when a nitrogenised substance is analyzed, both in the manner last described and in that about to be mentioned, the mean of the results (one giving an excess and the other a deficiency) approaches as nearly to the true amount of nitrogen as it is possible to do at present, in cases when its quantity is small. A combustion tube being chosen, 24 inches long, 6 inches at the closed end are filled with carbonate of copper; above this, 2 inches are filled with pure oxide of copper; next, the mixture of the substance with oxide of copper; next, another layer of pure oxide; and lastly, a layer of copper turnings. In *fig.* 38, these layers are marked. The combustion tube is connected by a cork with the three-limbed tube, *fig.* 39, the cork being covered with melted sealing wax. One limb of the tube is joined to the small air pump, *fig.* 37, B, the other with a bent tube 30 inches long, A, which dips into a small mercurial trough, D.



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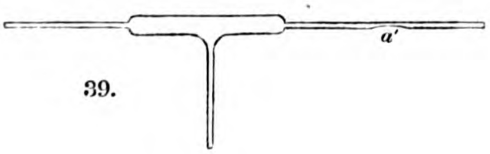

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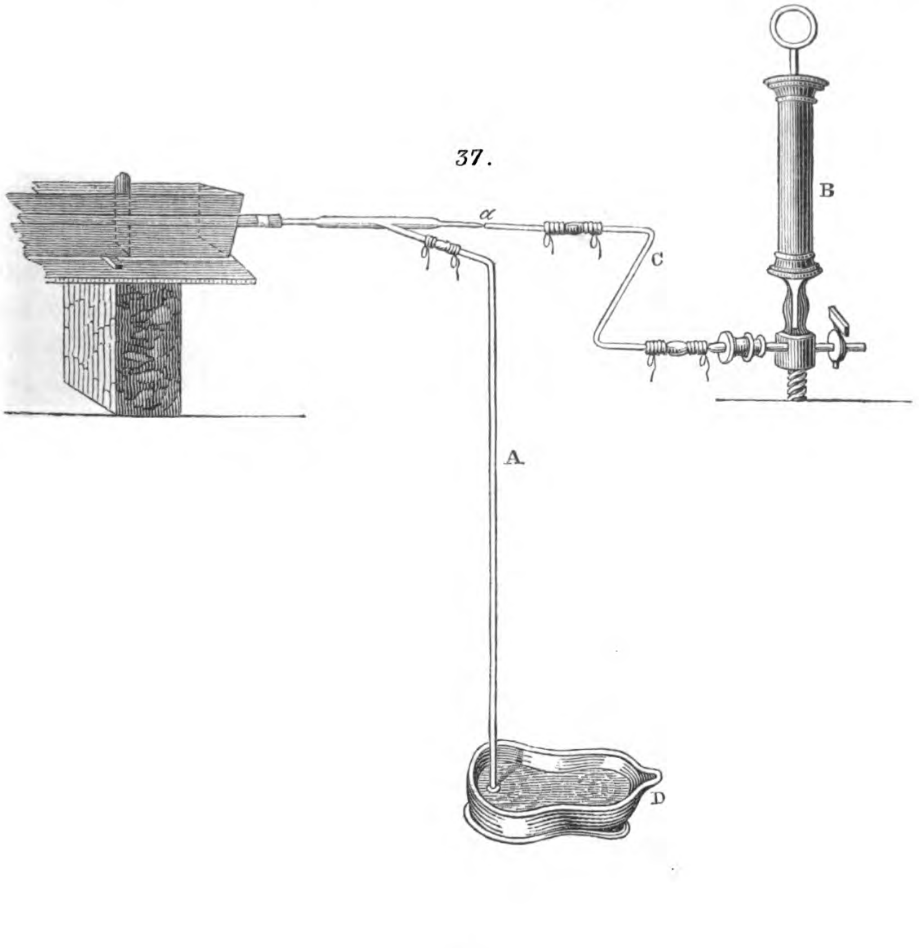
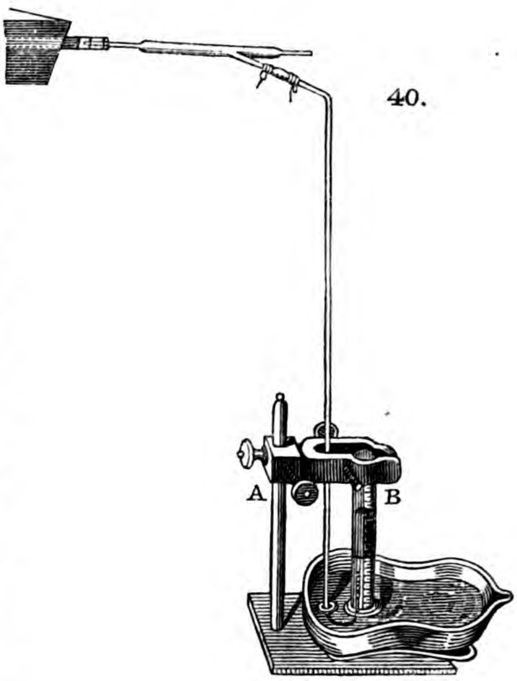


Both joinings are made with caoutchouc tubes. The three-limbed tube, *fig.* 39, is somewhat drawn out at *a*. The apparatus is now exhausted, the mercury rises to 27 inches. If it falls, some one of the joinings is not air tight. A screen is now placed behind the oxide of copper at *n*, *fig.* 38, and the half of the carbonate of copper farthest from the closed end of the tube is surrounded with a few red hot bits of charcoal. Pure carbonic acid is instantly disengaged, the mercury sinks, gas escapes at the end of the tube. The apparatus is now exhausted a second time; carbonic acid is again disengaged, and this is repeated four or five times, or till the bubbles of gas, when received in a tube of caustic ley, are almost completely absorbed, and leave a scarcely perceptible trace of air. The air is now expelled from the apparatus. The part *α* of the three limbed tube, *fig.* 39, previously drawn out, is now sealed with a spirit lamp flame, and the air pump, together with the S formed tube of connection C, removed. A graduated tube B, of about 100 cubic centimetres capacity, half filled with mercury and half with caustic ley, is now fixed by the holder A, *fig.* 40, over the mouth of the long bent tube. The combustion is now carried on as usual; nitrogen and carbonic acid are evolved, the latter is absorbed by the ley, and thus nitrogen alone is collected in the graduated tube.



40.

When the combustion is over, and the tube has been heated as far as *n*, *fig.* 38, the gas remaining in the apparatus still contains some nitrogen, which must be brought into the graduated tube, *fig.* 40, B. One half of the carbonate of copper has served to expel the atmospheric air, the other half now serves to force all the residual gas into the graduated tube. The closed end of the tube is, therefore, now surrounded with red-hot charcoal, and 300 or 400 cubic centimetres of gas disengaged and passed into the graduated tube; by which means the whole of the residual gas is swept out.

When no farther absorption takes place in the graduated tube, especially when it is shaken, its mouth is closed with a ground glass plate, and it is opened under water in a large jar. The mercury and caustic ley descend, and their place is occupied by water.

The gas is measured, noting the temperature and pressure, the correction for the tension of water is made, the volume reduced to the normal temperature and pressure, and the weight of the nitrogen calculated from its volume.

Berzelius proposes to dispense with the air-pump altogether, by passing a current of carbonic acid gas through the apparatus for a long time before the combustion, so as to remove all the atmospheric air. If we would not expose ourselves to the risk of serious error, we cannot omit the use of the air-pump: for, without exhaustion, the air contained in the pores of the powder is not removed by the current of carbonic acid. This air amounts to from 8 to 9 cubic centimetres in the ordinary bulk of the mixture; and this is often more than the nitrogen contained in 0.5 to 0.6 grammes of substance.

Mitscherlich proposes to introduce the mixture into the tube without carbonate of copper; to exhaust the apparatus, to conduct the combustion as usual, to receive all the carbonic acid and nitrogen in a graduated bell-jar, to measure their volume, and to absorb the carbonic acid by hydrate of potash. He thus obtains the relative volumes, from which the weight of the nitrogen may be calculated.

But if we reflect that by the first action of heat on all organic substances, volatile products are formed, which are only completely burned when they pass *slowly* over red hot oxide of copper; and if we consider that when combustion occurs in vacuo, the gases evolved expand rapidly therein, we must expect incomplete combustion at the beginning of this process. Besides, there remains, at the end, a certain quantity of nitrogen in the tubes which is not measured; and, farther, the volume of the hydrate of potash must be estimated and deducted from that of the gas. This method was suggested by the analysis of uric acid; but for this substance, so rich in nitrogen, it is not required; and it is hardly to be recommended for substances which contain very little nitrogen.

The apparatus I have described may be also used for the combustion of substances in vacuo, with the object of ascertaining, by the qualitative analysis of the gases, (rejecting, of course, the first portions,) the relative volumes of carbonic acid and nitrogen—and this with the exclusion of the air of the apparatus. Here the carbonate of copper is not required. But in substances which contain very little nitrogen, we cannot depend on the determination of the relative volumes, even when we operate with the utmost care.

We must never neglect, in all determinations of nitrogen, to subject the accuracy of our weights to a most rigorous scrutiny. It is indifferent, as is well known for ordinary analysis by weight, whether the weights be accurate or not, provided they agree among themselves. But when the weights with which we weigh our substances are not true to the standard, we are exposed to serious errors in reducing the volumes of the gases to weights.

METHODS OF CONTROL FOR ORGANIC ANALYSES.

ALL the precautions which insure an accurate result having now been described, we have yet to consider some methods which are occasionally employed to check the determinations of the carbon and the hydrogen.

In the case of substances having a small atomic weight, and in which, consequently, the numbers of atoms of the elements stand in a very simple relation to one another, no further control is necessary than the accurate determination of the atomic weight. The case, however, is very different with bodies of considerable atomic weight—in which a trifling difference in the determination of the atomic weight sometimes corresponds to more than half an equivalent of carbon, and often to more than 3 atoms, or 1½ equivalent of hydrogen. With such bodies we must not neglect the following methods of checking the result:—

Control for the Carbon.—If the substance enter into combination with a nitrogenised body, as, for example, with ammonia or nitric acid, the combustion of such compounds, when the proportion of the nitrogenised substance is known, gives, through the relative volumes of carbonic acid and nitrogen gases obtained, a strict control for the carbon. The volumes of the two gases are to each other as the equivalents of carbon and nitrogen in the compound.

A second method of checking the carbon in acids of high atomic weight, consists in the combustion of one of their salts, whose base retains carbonic acid, although ignited with oxide of copper, as, for example, baryta does. We obtain less carbonic acid than when the substance itself is burned with oxide of copper, and, of course, exactly one atom less. The quantity of carbonic acid retained by the base may be determined, and its weight should be to that of the carbonic acid obtained in the same experiment as 1 to the remaining atoms of the carbon of the acid analyzed. Both taken together should give the number of atoms of carbon in the substance. For example, the acid in the amygdalate of baryta contains 40 atoms of carbon. This salt, by combustion with oxide of copper, yields a certain quantity of carbonic acid, which is to that retained by the baryta as 39 to 1. Added together they give 40. In a similar manner must the atomic weights of all fatty acids be checked.

Control for the Hydrogen.—The hydrogen of the organic alkalies may be checked by the analysis of the salts they form with muriatic acid. Since muriatic acid undergoes no decomposition in combining with these bases, the quantity of hydrogen obtained should always be, if calculated on the weight of the base, greater by 2 atoms, or 1 equivalent, (the quantity contained in the muriatic acid,) than that furnished by the analysis of the base separately. With substances like stearic and oleic acids, there is always some uncertainty in the determination of the hydrogen; and we must here choose that number of atoms which corresponds most closely with the minimum of hydrogen obtained. The surest means of acquiring certainty in such cases, consists in the separation of the substance into new products, and the analysis of such products. The hydrogen of these must bear a distinct and obvious relation to that of the substance from which they proceed. If we cannot point out such a relation, some doubt must still remain.

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

THE methods hitherto described give the composition of the substances analyzed in a known weight, but do not decide on the number of atoms of the elements of the compound. We may indeed ascertain their relative number, when we are able to decompose the substance into products of known composition. But this has been hitherto possible with but few; and the determination of the proportion in which the substance combines with the known atomic weight of another body, remains, as yet, the most important step towards ascertaining the true composition, and checking the numerical results of the analysis.

If the substance be an acid, its atomic weight is ascertained by the analysis of one of its salts. Its combination with oxide of silver, oxide of lead, or baryta, is best adapted for this purpose. Salts of silver, when they can be formed, are preferable to all others; they are always anhydrous, and leave, when ignited, pure metallic silver, from which the atomic weight may be easily calculated. Many salts of silver, when heated, are decomposed with a slight explosion; in these the silver must be determined by converting the oxide into chloride. Some have recommended to moisten the salt with oil of turpentine, and set it on fire, which prevents explosion; but oxalate and fumarate of silver, besides other salts, explode in spite of this precaution, which can only serve its purpose in few cases.

Berzelius analyzes salts of lead in a very convenient and expeditious way. He places the salt in a small thin capsule of porcelain, and heats it sharply at the edge, where the salt commonly takes fire, and continues to glow till nothing is left but a mixture of oxide of lead and metallic lead. The weight being taken, it is moistened with acetic acid, and washed by decantation, first with water, and lastly with alcohol, and again dried. The loss is oxide of lead, the final increase of weight in the capsule is metallic lead.

In forming compounds of lead, we must bear especially in mind the property possessed by insoluble salts of lead, of combining with salts otherwise soluble, which may be present, and are apt to be precipitated at the same time.

If the acid form an acid and a neutral, or a neutral and a basic compound, the analysis of such compounds gives a new means of fixing the true atomic weight; but all that could be said on this head must be obvious to every one acquainted with general analysis.

Compounds of baryta answer very well. With bodies of high atomic weight the analysis of salts of lime is exposed to serious errors, from the low atomic weight of that base.

The combustion of the acid, and of one of its anhydrous salts, determines the amount of water present in the form of hydratic water.

The determination of the water of crystallisation of the salts analyzed, is of great importance in organic analysis, and must never be neglected where it can be performed.

The capacity of saturation of the organic alkalies may be ascertained by means of the drying apparatus formerly described—(*figs.* 1 and 2, pages 4 and 5.) The organic base is placed in the middle portion of the vessel, and, its weight in the dry state being known, dry muriatic acid gas is introduced through *a*. The combination takes place easily, rapidly, and with disengagement of heat. Several of the bases melt, others remain porous; in all cases a certain quantity of muriatic acid, not essential to the compound, remains, and must be removed. For this purpose we proceed, just as if we wished to dry the compound. The apparatus is surrounded with boiling water, and dry air passed through till the weight becomes constant. The increase of weight in the apparatus gives the quantity of muriatic acid which has entered into combination.

If it be thought necessary to ascertain whether, during the combination, water may not have been given off, which would diminish the apparent quantity of the muriatic acid, a known weight of the salt must be dissolved in water, and the muriatic acid determined as chloride of silver.

[NOTE.—In a paper lately published by Professor Liebig, (Annalen der Pharmacie XXVI.) he has proposed a new method of determining the atomic weight of organic bases, which appears decidedly preferable to the above. All the vegetable alkalies in the state of muriates, form double salts with bichloride of platinum, analogous to the compounds of bichloride of platinum with muriate of ammonia, and with the chlorides of potassium and sodium; with this difference from the latter, that the salts formed by muriatic acid with the vegetable bases are true muriates, containing all the oxygen of the base, and all the hydrogen of the muriatic acid, thus adding one more to the numerous analogies existing between the vegetable alkalies and ammonia. These double salts, which are easily obtained pure, are readily analyzed by ignition. They leave metallic platinum, from which their composition may easily be calculated. This is only one of the numerous improvements in organic analysis for which we are indebted to the author of this work, and which have been the main cause of the astonishingly rapid progress lately made in this department of chemistry.—W. G.]

Many organic substances, without being exactly acids, combine with oxide of lead; and by this combination a certain portion of water is occasionally separated, which would not have been separated by heat. By the analysis of the pure substance and of these compounds with oxide of lead, we may learn all that we wish to know of the number of atoms of the elements of the substance.

Other substances combine neither with acids nor with oxides, but they crystallize with water. In such cases the water of crystallization must be determined with the utmost care. We can calculate from it, with the same precision, the single, double, or half atomic weight of the substance, &c.—which, of course, depends on the number of atoms of water with which the substance combines.

EXAMPLES.

COMPOSITION OF AMYGDALIC ACID.—DETERMINATION OF ITS ATOMIC WEIGHT.

1.089 amygdalate of baryta, decomposed by sulphuric acid, yield 0.234 sulphate of baryta. The atomic weight of the sulphate of baryta is 1458.05. That of amygdalate of baryta is therefore obtained by the proportion

0.234 : 1.089 :: 1458.05 : 6783.37.

Control.—1.002 amygdalate of baryta yield, by calcination, 0.182 carbonate of baryta. Calculated from this, the atomic weight is 6790.00. Mean of the two = 6786.68.

0.668 of the same salt yield 1.068 carbonic acid, or 159.88 per cent. 0.7235 yield 1.148 carbonic acid, or 158.60 per cent. 100 parts therefore yield, as a mean result 159.24 carbonic acid.

Further, 0.668 amygdalate of baryta yield 0.302 water, and 0.7235 yield 0.326 water.

When a salt of baryta is burned with oxide of copper, carbonate of baryta is left, the carbonic acid of which must be taken into the calculation. From one of the above experiments it appears that 100 parts of amygdalate of bartya leave, after calcination, 18.17 carbonate of baryta. These 18.17 parts contain 4.0718 carbonic acid. 100 parts of amygdalate of baryta yield, therefore, in all, 159.24 + 4.0718 = 163.3118 carbonic acid.

We calculate now the results for 100 parts amygdalate of baryta—what is wanting of the 100 is oxygen. The above experiments show that 100 parts of the salt contain,

Carbon,	45.157
Hydrogen,	5.014
Baryta,	14.098
Oxygen,	35.731
	100.000

Next, in order to find the composition of the acid, and the number of atoms of its elements, we calculate how much carbon, hydrogen, baryta, and oxygen are contained in the sum of the atoms of all the elements, that is, in the atomic weight already found.

100 parts contain

45.157;	consequently	6786.68	contain	3064.660	Carbon.
5.014;	......	6786.68	...	340.284	Hydrogen.
14.098;	......	6786.68	...	956.706	Baryta.
35.731;	......	6786.68	...	2424.948	Oxygen.
100.000				6786.598	

3064.660 is the *sum of the weights* of the atoms of carbon in 1 atom of the salt. This number, divided by the weight of 1 atom of carbon, must give the *number* of atoms of carbon; and so on for the other elements.

$\frac{3064.660}{76.437}$ .... = 40.09 atoms Carbon.
$\frac{340.284}{6.2398}$ .... = 54 atoms Hydrogen.
$\frac{956.706}{956.88}$ .... = 1 atom Baryta
$\frac{2424.948}{100}$ .... = 24 atoms Oxygen.

Consequently the formula for the salt, as deduced from the above analysis, is

$$C_{40}\ H_{54}\ O_{24}\ Ba\ O.$$

The comparison of the composition in 100 parts, given by the formula, with the numbers obtained experimentally, will now show how near the result of the analysis comes to the theoretical composition.

			In 100 parts.
40 atoms Carbon......................	=	3057.48	45.28
54 atoms Hydrogen....................	=	336.949	4.99
1 atoms Baryta.......................	=	956.880	14.17
24 atoms Oxygen......................	=	2400.000	35.56
Atomic weight of the formula	=	6751.309	100.00

The usual method of calculating the number of atoms in the organic substances analyzed, is exactly that now explained; the formula thus obtained being the closest expression of the numbers found by experiment. The accuracy of the formula must now be subjected to a strict examination.

In the example above given, the actual result of experiment agrees as closely as can be expected with the theoretical result, according to the formula adopted. As far as regards the carbon, oxygen, and baryta, or in short, all the elements, except the hydrogen, this is sufficient security for the correctness, both of the formula and the analysis; but if we bear in mind what has been said of the determination of hydrogen, we perceive that this *exact* coincidence proves the substance to contain *less* hydrogen than that formula indicates.

It was formerly stated that, in bodies of high atomic weight, a correction is required for the hydrogen; this, in the above calculation, has been omitted.

But if we now deduct, from the water actually obtained in each analysis, 6 milligrames (0.09 grain, nearly) as foreign to the substance, we have, from 0.668 amygdalate of baryta, 0.296 water, and from 0.7235, 0.320 water; or adding both together, from 1.3915 of the salt, 0.616 water. Hence 100 parts of the salt yield 4.91 hydrogen, that is, less than the formula requires. Adopting now the formula $C_{40}\ H_{52}\ O_{24}\ Ba\ O$, the salt will contain 4.81 hydrogen per cent.; and this calculated result agrees with the *corrected* experimental one as nearly as can be expected in experiments of this nature.

From what has been said, we may conclude, with sufficient certainty, that the amygdalic acid does not contain more than 52 atoms of hydrogen, and that, consequently, the atomic weight of the salt is really only 6738.829.

It is obvious that the errors of observation in this analysis tend to diminish the apparent quantity of carbon. Now if the salt, with an atomic weight of 6786.68, only contained 39 atoms of carbon, its composition must be expressed by the formula $C_{39}\,H_{54}\,O_{25}\,Ba\,O$; which would give for the atomic weight of the salt the number 6874.872; a number approaching even more nearly to that found by experiment than the above calculated one, 6738.829. But in this case, the salt would contain only 43.35 per cent. carbon; whereas the quantity obtained, 45.157 per cent., is undoubtedly below the truth.

Here, then, a difference of $1\frac{3}{4}$ per cent. in the carbon is equal to a difference of 1 atom of that element, and it is easy to see that the loss of carbon must not, in a substance like this, exceed 0.87 per cent., if we wish the result to be free from doubt.

If we subtract, from the atomic weight of the salt that of one atom of baryta, we obtain the atomic weight of the acid; thus $6738.829 - 956.88 = 5781.949$; from which number we can calculate the composition of the acid in 100 parts.

In the calculation and control of an organic base, its atomic weight is ascertained by the quantity of acid with which the base forms a definite compound; in other respects, the calculation is the same.

The number of organic substances which do not combine with some other substance of known atomic weight, and whose composition, therefore, cannot be subjected to any control, is exceedingly small. With such substances, we must be contented to ascertain the relative proportions of the atoms of their elements, and to express these in the simplest form. Maunite, for example, belongs to this class of bodies. 2.735 parts yielded by combustion 4.097 carbonic acid, and 1.770 water; which gives for 100 parts,

Carbon	39.7259
Hydrogen	7.7210
Oxygen	52.5531
	100.0000

If the atomic weight of maunite were 100, then

$\frac{39.7259}{76.437}$ would give the number of atoms of Carbon.

$\frac{7.7210}{6.2398}$ the number of atoms of hydrogen, and

$\frac{52.5531}{100.000}$ the number of atoms of oxygen.

But, as its atomic weight is unknown, the quotients express the relative proportions of the numbers of atoms of these elements in maunite. The quotients are,

0.518............Carbon.
1.238............Hydrogen.
0.525............Oxygen.

We see at once, that the number of atoms of carbon in maunite must be equal to the number of atoms of oxygen; for the numbers 0.518, and 0.525 differ very slightly. We observe likewise, that the number of atoms of hydrogen must be greater than that required to make up, with the oxygen, the composition of water. For if hydrogen and oxygen were present in the proportion which constitute water, 525 of oxygen would require 1050 of hydrogen; but we have 1238, that is, very nearly one-sixth more. For one atom of oxygen, therefore, there are present 2.36 atoms of hydrogen; or, expressing this proportion in the nearest whole numbers, maunite contains, for 3 atoms oxygen, 7 hydrogen and 3 carbon.

The analysis of crystallised cane sugar gave the following results for 100 parts:—

Carbon.........42.301.........$\frac{42.301}{76.437} = 0.553.$
Hydrogen...... 6.454.........$\frac{6.454}{6.2398} = 1.034.$
Oxygen.........51.501.........$\frac{51.501}{100.000} = 0.515.$

Here we see that the number of atoms of hydrogen is exactly twice as great as the number of atoms of oxygen; and consequently, that sugar contains these elements in the proportion to form water. The number of atoms of oxygen is to the number of atoms of carbon, as 0.515 to 0.553; in whole numbers, as 11 to 12. If then, we assume sugar to contain 11 atoms of oxygen (the smallest whole number) its composition will be expressed by the formula $C_{12}\ H_{22}\ O_{11}$.

A great many organic bodies, the atomic weight of which cannot be directly determined, are decomposed, when brought in contact, under certain circumstances, with other substances, such as acids or alkalies, into new products, whose composition either is already known, or can be easily ascertained. These decompositions furnish valuable means of determining the constitution and controlling the analysis of such bodies. Sugar, for example, in contact with ferment, is resolved into carbonic acid and alcohol; oxamide, in contact with acids or alkalies, is resolved into oxalic acid and ammonia. It is obvious, that when we have determined, in these instances, the quantity of carbonic acid and oxalic acid produced, and have satisfied ourselves that in the former case no other product besides alcohol, and in the latter none except ammonia, is formed; we can, from these data, determine the composition of these substances with absolute certainty.

A very important means of testing the composition of an organic compound of unknown atomic weight, is furnished by the hypermanganate of potash. This salt, gently heated with a soluble organic substance, is resolved into peroxide of manganese, oxygen, and potash. The oxygen enters into combination with the organic matter, and when the latter is in excess, it rarely happens that the carbon is oxidized so as to form carbonic acid. But organic acids are produced, and invariably in the proportion necessary to neutralize the potash ; for the solution remains neutral. The acid chiefly formed is the oxalic; in many cases the formic. Both are easily determined; and from their quantity and that of the hydrated peroxide of manganese, the composition may be ascertained. For example, a pure solution of sugar, warmed with this salt, yields neutral oxalate of potash, and peroxide of manganese, in the proportion of 1 atom of the former to 2 of the latter; from which it is easily demonstrated that sugar contains oxygen and hydrogen in the proportion to form water.

[NOTE.—This experiment was first made by the Translator and M. Horace Demarçay, in 1835, and has since been confirmed by the Author of this work, and by M. Pelouze. As the hypermanganate of potash has thus become a useful re-agent in organic analysis, an account of the process by which the Translator prepares this salt will not be considered out of place; more especially as a number of experimenters have found some difficulty in preparing it from the account inserted in the " Records of Science " for 1836.

Native peroxide of manganese *in very fine powder*, and fused potash, are taken in the proportion of 3 atoms of each; and chlorate of potash in the proportion of one atom. The fused potash is dissolved in a small quantity of water, and the other substances added to the solution. The whole is dried up by a moderate heat, and the dark green mass is then powdered, and heated for half an hour to a *very low red heat* in a platinum crucible. The heated mass is then dissolved in a very large quantity of boiling water, and when the solution has become of a pure deep red, it is decanted from the hydrated peroxide which separates, and evaporated rapidly till small black crystals appear on the surface. On cooling, a large number are deposited. They are easily purified by recrystalization, when they become larger and acquire a bronze colour. In the hands of the Translator this process never fails, and from good oxide of manganese a quantity of crystals equal to half the weight of the oxide employed may easily be obtained. The principal causes of failure would appear to be, impurity of the oxide of manganese, or using it in a coarse powder, or, finally, applying too strong a heat.—W. G.]

Many indifferent azotized substances, in contact with alkalies, are resolved into ammonia and an acid, whose atomic weight can be determined. Such bodies are caffeine, asparagine, amygdaline, &c., the atomic weight of which may easily be deduced from the quantity of the acid, or of a salt of the acid, of known atomic weight, which is produced. For example, 1.357 parts of amygdaline produce 1.592 amygdalate of baryta.

The atomic weight of this salt is 6738.829. Hence 1.592 : 6738.829 : : 1.357 : 5797 = the atomic weight of amygdaline.

DETERMINATION OF THE SPECIFIC GRAVITY OF THE VAPOURS OF VOLATILE SUBSTANCES, AS A MEANS OF ASCERTAINING THE NUMBER OF ATOMS OF THEIR ELEMENTS.

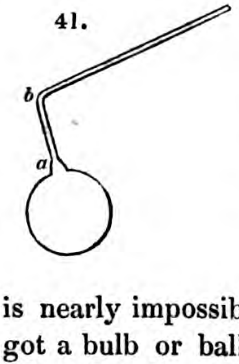
In the analysis of a volatile substance, the determination of the specific gravity of the vapour is a most valuable means of control over the analysis by combustion. The process, which is followed for this purpose, is that of Dumas, first rendered practical by that distinguished chemist, and by him also first applied, with the happiest results, to this object. The description of it, given by Dumas, in his "Traité de Chimie," embraces all the precautions which can ensure an accurate result.

The apparatus is simple in a high degree, and the whole operation is easily performed without requiring any great expenditure of time, or any peculiar dexterity in the operator. The problem to be solved is to ascertain the weight of a known volume of the vapour.

For this purpose, a convenient vessel, filled with dry air, at a known temperature and pressure, is weighed: the fluid or volatile substance, the specific gravity of whose vapour we wish to ascertain, is then introduced, and heated to from 50° to 75° beyond its boiling point, till it is entirely converted into vapour; the temperature is noted, the vessel hermetically sealed, and again weighed. We know now the weight of the vessel, when filled, both with air and with vapour. After reducing both to the same temperature and pressure, the weights of both are easily calculated, if the volume, that is, the capacity of the vessel, be ascertained. The specific gravity of the vapour is ascertained by dividing the weight of a known volume by that of an equal volume of air at the same temperature and pressure.

The following is the process in detail:—A flask of the capacity of 20 to 35 cubic inches, *fig.* 41, (10 to 18 fluid ounces), clean and dry, is chosen. It is connected with the air pump and the apparatus, *fig.* 5, *p.* 6. Air is now alternately pumped out, and re-admitted, by which means it is soon filled with dry air.

41.

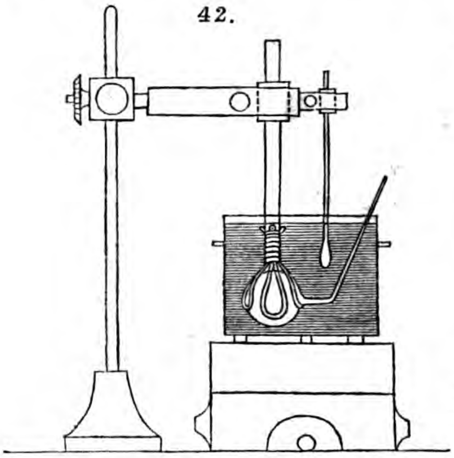


The neck of the flask is now drawn out at *a*, before the blow pipe, to a narrow tube, 6 or 8 inches long, which is bent at *b*; the point is cut across with a sharp file, and the cut edge rounded in the flame. The glass must not split when softened, otherwise it is nearly impossible to seal it up quickly when required. We have now got a bulb or balloon with a drawn out point. It is now weighed, and allowed to lie on the scale till its weight no longer increases by the deposition of moisture on the external surface of the glass.

To introduce the liquid or the melted volatile solid, the bulb is gently warmed, so as to expel a portion of air, and the point immersed in the fluid substance. As the heated air contracts, the liquid rises into the bulb; this may always be quickly accomplished by moistening the bulb with a little ether. The quantity of liquid introduced varies with the size of the bulb: 80 grains may be mentioned as the minimum, 160 as the maximum quantity required. If the substance should solidify in the neck or the narrow tube, these must of course be previously warmed.

The balloon is now placed in a bath of water, chloride of calcium, chloride of zinc, &c., which must always be heated to a temperature 50° to 75° beyond the boiling point of the substance. The bath may be previously heated to the required degree; there is no fear of cracking the bulb. A very exact thermometer shows the temperature of the bath.

42.



43.

The bulb may be supported in the bath in a variety of ways. *Fig.* 42 shows one method. *Fig.* 43 is the support for the bulb.

As soon as the temperature of the bath rises a few degrees above the boiling point of the substance, a stream of its vapour issues from the point of the tube. This gradually diminishes, and after 15 or 20 minutes, a flame brought near the point is not moved in the least. Should any drops of liquid have condensed on the neck or tube where it is out of the bath, they must be removed. This is easily done by approaching a glowing coal; and then, by means of a spirit-lamp and blow-pipe, the point is suddenly softened, while the vessel remains in the bath; it closes hermetically with facility.

The iron vessel containing the bath is now removed from the fire, the closed bulb is taken out, washed, dried, and weighed with the precautions formerly described.

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

For this purpose the point is immersed in mercury, and is cut near the neck, under the mercury, with a sharp file. When the tube is broken off, the vacuum caused by the condensation of the vapour at the ordinary temperature, is instantly filled by mercury. In general a small bubble of air is left, but in many cases the mercury entirely fills the bulb. The volume of the mercury is equal to that of the vapour at the temperature at which the bulb was sealed. To determine it, the mercury is measured in a graduated vessel. The bulb is now entirely filled with water, and the water measured in like manner. The difference between the volume of the water, and that of the mercury, gives the volume of the small quantity of air, if any, which remained.

From the data thus obtained, the specific gravity of the vapour may be calculated. The following example will illustrate this calculation. It is taken from the Analysis of Carbonic Ether, by Professor Ettling:—

Boiling point of carbonic ether, 258° F. The balloon with dry air weighed 47.77 grammes; the temperature of the air was 65.5 F.; the height of the barometer 331.8 centimetres. The bulb, after the experiment, was found, when filled with water, to have a capacity of 290 cubic centimetres, = the volume of air contained in it. 290 cubic centimetres of air at 65.5° and 331.8 B. give, at 32° and 336. bar., 267.7 cubic centimetres of air, which weigh 0.34776 gramme. Subtracting this weight from the weight of the bulb with dry air, there remains 47.42224 grammes for the weight of the bulb alone. The bulb was heated in a bath of chloride of zinc, and sealed at the temperature of 292° F. and 331.8 bar., and it now weighed 48.431 grammes. The mercury which entered the bulb after the experiment, measured 289.5 cubic centimetres at the temperature of 65.5° F. and 332 bar. Subtracting the weight of the empty bulb from that of the bulb when filled with the vapour, we have for the weight of the vapour 1.00876 grammes. If its volume, at 292° and 331.8 bar., be assumed to have been 289.5 cubic centimetres, this would give, at 32° and 336 bar., 182.98 cubic centimetres. This volume of vapour, then, weighs 1.00876 grammes; consequently, 1000 cubic centimetres would weigh 5.5129 grammes. Now, 1000 cubic centimetres of air, at 32° and 336 bar., weigh 1.299075 grammes. Hence, the specific gravity of the vapour of carbonic ether is $= \frac{5.5129}{1.299075} = 4.243$.

This determination is certainly exact enough for controlling the analysis of carbonic ether; but the calculation may yield a false result under certain circumstances: for example, if a correction be not made for the small quantity of air left behind. Since the mercury which entered the bulb in the above experiment was only 289.5 cubic centimetres, while the capacity of the bulb was 290 c. c., there was left 0.5 c. c. of air, which was weighed along with the vapour. The true weight of the vapour is therefore got by subtracting from 1.00876 gramme the weight of 0.5 c. c. air, at 32° and 336 bar., which is 0.00062 gramme. The remainder is 1.008135 gramme.

But the volume of the mercury which entered the bulb does not, moreover, express the true volume of the vapour at 292°: for the 0.5 c. c. air at 292° expanded by 0.23 c. c., and, therefore, occupied at that temperature the volume of 0.73 c. c. The volume of the vapour in the above calculation, was, therefore, taken too high by 0.23 c. c. Its true volume was, 289.5 — 0.23 = 289.27 c. c. It is easy to see that, in the above example, these corrections hardly affect the result; but where the air left exceeds 2 c. c., it must be taken into the calculation as now explained.

The process just described is not susceptible of perfect accuracy. The volumes which are measured and weighed, are too small. If we take very large bulbs, the apparatus becomes difficult to manage, and requires large and perfectly exact balances. But all this is unnecessary for the object in view. It is enough if the two first decimals agree with the calculated theoretical specific gravity. In no case can we reckon on the accuracy of the third decimal. For this reason it is superfluous to take into account the expansion of glass and a correction of the mercurial thermometer. The determination of the specific gravity of the vapour of camphor by Dumas, will show how slight are the changes made by these corrections on the result of experiment.

Dumas found that specific gravity, without these corrections, to be 5.356, and after making the corrections, to be 5.337. The difference between the results of two experiments is, however, always greater than this: so that we may save ourselves the trouble of these calculations.

APPLICATION OF THE KNOWLEDGE OF THE SPECIFIC GRAVITY OF A BODY OF UNKNOWN ATOMIC WEIGHT AS A CONTROL OVER THE ANALYSIS.

The composition of carbonic ether was ascertained in the usual way. The highest numbers gave in 100 parts 51.3075 carbon, 8.5802 hydrogen, and 40.1121 oxygen. These numbers correspond to the formula $C_5 H_{10} O_3$.

The specific gravities of carbon vapour, hydrogen, and oxygen, are to each other as their atomic weights. It is obvious, therefore, that in one volume of carbonic ether vapour, the volumes of carbon, hydrogen, and oxygen, must be found in the ratio of 5, 10, and 3, or in multiples or submultiples of these numbers, according to the condensation; the proportions cannot vary.

We now inquire how much carbon, hydrogen, and oxygen are contained in 4.243, the weight of one volume of carbonic ether vapour.

100 parts contain

51.3075 Carbon,	therefore	4.243	contain	2.1769.
8.5802 Hydrogen,	......	4.243	...	0.3645.
40.1121 Oxygen,	......	4.243	...	1.7018.

The number 2.1769 expresses the sum of the weights of the volumes (the specific gravities) of carbon vapour in one volume of the vapour of carbonic ether. Dividing this number by the weight of one volume of carbon vapour (its specific gravity) $= 0.84297$, we obtain the number of volumes, namely, $2\frac{1}{2}$.

The specific gravity of hydrogen is 0.0688. Hence $\frac{0.3645}{0.0688} = 5$ is the number of volumes of hydrogen; and as the specific gravity of oxygen is 1.1026, $\frac{1.7018}{1.1026} = 1\frac{1}{2}$ is the number of volumes of oxygen in one volume of carbonic ether vapour. It is easy to see that $2\frac{1}{2}$, 5, and $1\frac{1}{2}$, are to each other as 5, 10, and 3, whence it may be inferred that the analysis and the formula deduced from it are correct:

5 volumes Carbon, $= 5 \times 0.84279 = 4.2139$.
10 volumes Hydrogen, $= 10 \times 0.0688 = 0.6880$.
3 volumes Oxygen, $= 3 \times 1.1026 = 3.3078$.

The sum of all is . . . 8.2097.

The number 8.2097 is to the specific gravity found by experiment, very nearly as 2 to 1. Hence, in one volume of the vapour of carbonic ether, there must be contained $\frac{5}{2}$ volumes carbon, $\frac{10}{2}$ volumes hydrogen, and $\frac{3}{2}$ volumes oxygen; this is the proportion of $2\frac{1}{2}$, 5, $1\frac{1}{2}$, above obtained. The weight of one volume of carbonic acid is 1.524: that of 1 volume of ether is 2.58088. The sum of both is 4.10488. Hence one volume carbonic ether vapour contains one volume carbonic acid, and one volume of the vapour of ether, condensed into one volume.

TABLES.

Names of the Gases.	Specific Gravities.	Absolute Weights in Grammes of Cubic Centimeters of the Gases. Thermometer, 32° F., or 0° C.; Barometer, 0,76 Meter, or 30 Inches.								
		1000.	2000.	3000.	4000.	5000.	6000.	7000.	8000.	9000.
Atmospheric Air	1,00000	1,29907	2,59814	3,89721	5,19628	6,49535	7,79442	9,09349	10,39256	11,69163
Carbonic Acid CO_2	1,52400	1,97978	3,95956	5,93934	7,91912	9,89890	11,87868	13,85846	15,83824	17,81802
Nitrogen N	0,97600	1,26790	2,53580	3,80370	5,07160	6,33950	7,60740	8,87530	10,14320	11,41110

Names of the Gases.	Specific Gravities.	Absolute Weights in Grains, of Cubic Inches of the Gases. Thermometer at 32° F., Barometer at 30 inches.								
		100.	200.	300.	400.	500	600.	700.	800.	900.
Atmospheric Air	1,0000	32,854	65,708	98,562	131,416	164,270	197,124	229,978	262,832	295,686
Carbonic Acid CO_2	1,5240	50,069	100,138	150,207	200,276	250,345	300,414	350,483	400,552	450,621
Nitrogen N	0,9760	32,066	64,132	96,198	128,264	160,330	192,396	224,462	256,528	288,594

Before calculating the weight of a given volume of gas by this table, the volume must be reduced to what it would be at 32° F. and 30 inches Barometer. The weights of gases are commonly given at 60° F. in English works, but I have retained the normal temperature used on the Continent, as it is just as easy to reduce the volume from the observed temperature to 32° as to 60°. The normal pressure, 30 inches, or 0,76 metre, is the same in England and on the Continent.—*W. G.*

FOUND.		REQUIRED.		1	2	3	4	5	6	7	8	9
Carbon,	C	Cyanogen,	$N_2 C_2$	2,15805	4,31610	6,47415	8,63220	10,79025	12,94830	15,10635	17,26440	19,42245
Carbonic Acid,	CO_2	Carbon,	C	0,27651	0,55302	0,82952	1,10603	1,38254	1,65905	1,93556	2,21206	2,48857
Carbonate of Baryta,	$Ba O, CO_2$	Carbonic Acid,	CO_2	0,22414	0,44828	0,67242	0,89656	1,12070	1,34484	1,56898	1,79312	2,01726
Carbonate of Baryta,	$Ba O, CO_2$	Baryta	Ba O	0,77586	1,55172	2,32758	3,10344	3,87930	4,65516	5,43102	6,20688	6,98274
Carbonate of Lime,	$Ca O, CO_2$	Carbonic Acid,	CO_2	0,43708	0,87416	1,31124	1,74832	2,18540	2,62248	3,05956	3,49664	3,93372
Carbonate of Lime,	$Ca O, CO_2$	Lime	Ca O	0,56292	1,12584	1,68876	2,25168	2,81460	3,37752	3,94044	4,50336	5,06628
Chloride of Potassium,	KCl_2	Chlorine,	Cl_2	0,47466	0,94932	1,42398	1,89864	2,37330	2,84796	3,32262	3,79728	4,27194
Chloride of Sodium,	$Na Cl_2$	Chlorine,	Cl_2	0,60344	1,20688	1,81032	2,41376	3,01720	3,62064	4,22408	4,82752	5,43096
Chloride of Silver,	$Ag Cl_2$	Chlorine,	Cl_2	0,24670	0,49340	0,74010	0,98680	1,23350	1,48020	1,72690	1,97360	2,22030
Chloride of Silver,	$Ag Cl_2$	Muriatic Acid,	$Cl_2 H_2$	0,25366	0,50732	0,76098	1,01464	1,26830	1,52196	1,77565	2,02928	2,28294
Chloride of Silver,	$Ag Cl_2$	Silver,	Ag	0,75330	1,50660	2,25990	3,01320	3,76650	4,51980	5,27310	6,02640	6,77970
Chloride of Silver,	$Ag Cl_2$	Oxide of Silver,	Ag O	0,80903	1,61806	2,42709	3,23612	4,04515	4,85418	5,66321	6,47224	7,28127
Lead,	Pb	Oxide of Lead,	Pb O	1,07725	2,15450	3,23174	4,30899	5,38623	6,46348	7,54072	8,61797	9,69521
Muriatic Acid,	$H_2 Cl_2$	Chlorine,	Cl_2	0,97258	1,94516	2,91774	3,89032	4,86290	5,83548	6,80806	7,78064	8,75322
Nitrogen,	N_2	Ammonia,	$N_2 H_6$	1,21147	2,42294	3,63441	4,84588	6,05735	7,26882	8,48029	9,69176	10,90323
Nitrogen,	N_2	Cyanogen,	$N_2 C_2$	1,86351	3,72702	5,59053	7,45404	9,31755	11,18106	13,04457	14,90808	16,77159
Oxide of Lead,	Pb O	Lead,	Pb	0,92829	1,85658	2,78487	3,71316	4,64145	5,56974	6,49803	7,42632	8,35461
Oxide of Lead,	Pb O	Oxygen,	O	0,07171	0,14342	0,21513	0,28684	0,35855	0,43026	0,50197	0,57368	0,64539
Silver,	Ag	Oxide of Silver,	Ag O	1,07391	2,15082	3,22472	4,29863	5,37253	6,44644	7,52034	8,59425	9,66815
Sulphate of Baryta,	$Ba O, SO_3$	Baryta,	Ba O	0,65628	1,31256	1,96884	2,62512	3,28140	3,93768	4,59396	5,25024	5,90652
Sulphate of Potash,	KO, SO_3	Potash,	KO	0,54067	1,08134	1,62201	2,16268	2,70335	3,24402	3,78469	4,32536	4,86603
Sulphate of Lime,	$Ca O, SO_3$	Lime,	Ca O	0,41532	0,83064	1,24596	1,66128	2,07660	2,49192	2,90724	3,32256	3,73788
Water,	$H_2 O$	Oxygen,	O	0,88889	1,77778	2,66666	3,55555	4,44444	5,33333	6,22222	7,11110	7,99999
Water,	$H_2 O$	Hydrogen,	H_2	0,11111	0,22222	0,33334	0,44445	0,55556	0,66667	0,77778	0,88890	1,00001

CHLORINE.

Cl_1	221,325	Cl_8	1770,600	Cl_{14}	3098,55	Cl_{20}	4426,5
Cl_2	442,650	Cl_9	1191,925	Cl_{15}	3319,875	Cl_{21}	4647,825
Cl_3	663,975	Cl_{10}	2213,25	Cl_{16}	3541,2	Cl_{22}	4869,150
Cl_4	885,3	Cl_{11}	2434,575	Cl_{17}	3762,525	Cl_{23}	4090,475
Cl_5	1106,625	Cl_{12}	2655,900	Cl_{18}	3983,850	Cl_{24}	5311,8
Cl_6	1327,95	Cl_{13}	2877,225	Cl_{19}	4205,175	Cl_{25}	5533,125
Cl_7	1549,275						

CARBON.

C_1	76,435	C_{16}	1222,960	C_{31}	2369,485	C_{46}	3516,01
C_2	152,870	C_{17}	1299,395	C_{32}	2445,92	C_{47}	3592,445
C_3	229,305	C_{18}	1375,83	C_{33}	2522,355	C_{48}	3668,880
C_4	305,74	C_{19}	1452,265	C_{34}	2598,790	C_{49}	3745,315
C_5	382,175	C_{20}	1528,7	C_{35}	2675,225	C_{50}	3821,75
C_6	458,610	C_{21}	1605,135	C_{36}	2751,660	C_{51}	3898,185
C_7	535,045	C_{22}	1681,570	C_{37}	2828,095	C_{52}	3974,620
C_8	611,480	C_{23}	1758,005	C_{38}	2904,53	C_{53}	4051,055
C_9	687,915	C_{24}	1834,440	C_{39}	2980,965	C_{54}	4127,490
C_{10}	764,350	C_{25}	1910,875	C_{40}	3057,4	C_{55}	4203,925
C_{11}	840,785	C_{26}	1987,31	C_{41}	3133,835	C_{56}	4280,36
C_{12}	917,220	C_{27}	2063,745	C_{42}	3221,027	C_{57}	4356,795
C_{13}	993,655	C_{28}	2140,18	C_{43}	3286,705	C_{58}	4433,23
C_{14}	1070,090	C_{29}	2216,615	C_{44}	3363,14	C_{59}	4509,665
C_{15}	1146,525	C_{30}	2293,05	C_{45}	3439,575	C_{60}	4586,1

Ammonia, ...	$N_2 H_6$	 214,47
Baryta, ...	$Ba O$	 956,88
Lead, ...	Pb	1294,50
Oxide of Lead,...........	$Pb O$	1394,50
Muriatic Acid,............	$H_2 Cl_2$	 455,14
Chloride of Potassium,..	$K Cl_2$	 932,57
Chloride of Silver, ...	$Ag Cl_2$	 1794,26
Lime, ...	$Ca O$	 356,02
Carbonic Acid,............	$C O_2$	 276,44
Carbonate of Baryta,...	$Ba O , C O_2$	1233,32
Carbonate of Lime, ...	$Ca O , C O_2$	 632,46
Oxide of Copper, ...	$Cu O$	 495,70
Sulphuric Acid, ...	$S O_3$	 501,16
Sulphate of Baryta, ...	$Ba O , S O_3$	1458,05
Sulphate of Lead, ...	$Pb O , S O_3$	1895,66
Sulphate of Potash,......	$K O , S O_3$	1592,25
Sulphate of Lime, ...	$Ca O , S O_3$	 857,18
Silver, ...	Ag	1351,61

Water,......$H_2 O$ =	Aq.	112,48	Aq_7	787,36
	Aq_2	224,96	Aq_8	899,84
	Aq_3	337,44	Aq_9	1012,32
	Aq_4	449,92	Aq_{10}	1124,80
	Aq_5	562,40	Aq_{11}	1237,28
	Aq_6	674,88	Aq_{12}	1349,75

SULPHUR.

S_1	201,165	S_4	804,66	S_7	1408,155	S_9	1810,485
S_2	402,330	S_5	1005,825	S_8	1609,32	S_{10}	2011,65
S_3	603,495	S_6	1206,99				

NITROGEN.

N_1	88,52	N_6	531,12	N_{11}	973,72	N_{16}	1416,32
N_2	177,04	N_7	619,64	N_{12}	1062,24	N_{17}	1504,84
N_3	265,56	N_8	708,16	N_{13}	1150,76	N_{18}	1593,36
N_4	354,08	N_9	796,68	N_{14}	1239,28	N_{19}	1681,88
N_5	442,6	N_{10}	885,2	N_{15}	1327,80	N_{20}	1770,40

HYDROGEN.

H_1	6,23975	H_{39}	243,35025	H_{77}	480,4607	H_{114}	711,33150
H_2	12,4795	H_{40}	249,59	H_{78}	486,7005	H_{115}	717,57125
H_3	18,71925	H_{41}	255,82975	H_{79}	492,94025	H_{116}	723,811
H_4	24,959	H_{42}	262,0695	H_{80}	499,18	H_{117}	730,05075
H_5	31,19875	H_{43}	268,30925	H_{81}	505,41975	H_{118}	736,2905
H_6	37,4385	H_{44}	274,549	H_{82}	511,6595	H_{119}	742,53025
H_7	43,67825	H_{45}	280,78875	H_{83}	517,89925	H_{120}	748,77
H_8	49,918	H_{46}	287,0285	H_{84}	524,139	H_{121}	755,00975
H_9	56,15775	H_{47}	293,26825	H_{85}	530,37875	H_{122}	761,2495
H_{10}	62,3975	H_{48}	299,508	H_{86}	536,6185	H_{123}	767,48925
H_{11}	68,63725	H_{49}	305,74775	H_{87}	542,85825	H_{124}	773,729
H_{12}	74,877	H_{50}	311,9875	H_{88}	549,098	H_{125}	779,96875
H_{13}	81,11675	H_{51}	318,22725	H_{89}	555,33775	H_{126}	786,2085
H_{14}	87,35650	H_{52}	324,467	H_{90}	561,5775	H_{127}	792,44825
H_{15}	93,59625	H_{53}	330,70675	H_{91}	567,81725	H_{128}	798,688
H_{16}	99,836	H_{54}	336,9465	H_{92}	574,057	H_{129}	804,92775
H_{17}	106,07575	H_{55}	343,18625	H_{93}	580,29675	H_{130}	811,1675
H_{18}	112,3155	H_{56}	349,426	H_{94}	586,5385	H_{131}	817,40725
H_{19}	118,55525	H_{57}	355,66575	H_{95}	592,77625	H_{132}	823,647
H_{20}	124,795	H_{58}	361,9055	H_{96}	599,016	H_{133}	829,88675
H_{21}	131,03475	H_{59}	368,14525	H_{97}	605,25575	H_{134}	836,1265
H_{22}	137,2745	H_{60}	374,385	H_{98}	611,4955	H_{135}	842,36625
H_{23}	143,51425	H_{61}	380,62475	H_{99}	617,73525	H_{136}	848,606
H_{24}	149,754	H_{62}	386,8645	H_{100}	623,975	H_{137}	854,84575
H_{25}	155,99375	H_{63}	393,10425	H_{101}	630,21475	H_{138}	861,0855
H_{26}	162,2335	H_{64}	399,344	H_{102}	636,4545	H_{139}	867,32525
H_{27}	168,47325	H_{65}	405,58375	H_{103}	642,69425	H_{140}	873,565
H_{28}	174,713	H_{66}	411,8235	H_{104}	648,934	H_{141}	879,80475
H_{29}	180,95275	H_{67}	418,06325	H_{105}	655,17375	H_{142}	886,0445
H_{30}	187,1925	H_{68}	424,303	H_{106}	661,4135	H_{143}	892,28425
H_{31}	193,43225	H_{69}	430,54275	H_{107}	667,65325	H_{144}	898,524
H_{32}	199,672	H_{70}	436,7825	H_{108}	673,893	H_{145}	904,76375
H_{33}	205,91175	H_{71}	443,02225	H_{109}	680,13275	H_{146}	911,0035
H_{34}	212,1515	H_{72}	449,262	H_{110}	686,3725	H_{147}	917,24325
H_{35}	218,39125	H_{73}	455,50175	H_{111}	692,61225	H_{148}	923,483
H_{36}	224,631	H_{74}	461,7415	H_{112}	698,852	H_{149}	929,72275
H_{37}	230,87075	H_{75}	467,98125	H_{113}	705,09175	H_{150}	935,9625
H_{38}	237,1105	H_{76}	474,221				

GLASGOW:
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