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A handbook of chemical manipulation

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Supplement

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SUPPLEMENT
TO
A HANDBOOK
OF
CHEMICAL MANIPULATION.

BY
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INTRODUCTION.

IN the Preface to the original work I remarked that "Chemistry is doubtless in a transition state;" but I think that, at that time, few chemists were aware of the astonishing rapidity with which its whole face would be changed. Thanks to the profound sagacity of a resolute band of workers and thinkers, an almost chaotic mass of facts has been systematized and arranged, so that we may now be said to be rapidly on the way to that chief end of research—a complete theory. But to build a complete theory presupposes an equally complete knowledge of the constitution of substances, which can only be obtained by rigorous analytical and synthetical investigation. This involves the discovery of an immense number of new substances, all of which require to have their products of decomposition studied; and in doing so fresh substances are discovered, and so on almost *ad infinitum*. If processes were not shortened without loss of precision, even the most energetic investigators would find themselves unable to overtake the mass of labour lying before them. New methods have therefore to be devised; and it is with the view of placing a few of the more important of these before the Student that this Supplement has been written.

I have found it very difficult to determine what to select and what to reject, especially as the space at my disposal was limited. It is hoped, therefore, that those who think I have given too much attention to some subjects and too little to others will see

how impossible it is in so few pages to introduce all that I could wish.

Fortunately for the student of the present day, he is not in the position of the chemist at the time the original work was written. Apparatus of every description can be obtained cheaply and economically. In fact some of the catalogues of the principal English and Continental instrument-makers are almost encyclopædic in their completeness.

At the outset I was placed in a dilemma. Should I sacrifice advance to uniformity, or uniformity to advance? It did not take me long to decide in favour of the latter. I have therefore, in this Supplement, used the modern notation and nomenclature—first, because I believe it to be nearer the truth than the old; and secondly, because my experience of the intelligence of the students of the present day convinces me that they will, at a glance, be able to convert the old formulæ of the original work into the new.

Once more I must apologize for omissions; but where I have not been able fully to describe some new and valuable manipulations, I have at least given references to the works where they may be found.

Much of what is contained in this Supplement belongs rather to Physics than Chemistry; I am too profoundly impressed with “the connexion of the physical sciences” to allow this to trouble me. A chemist who is no physicist, or a physicist who is no chemist, is, in the present day, an anomaly.

SUPPLEMENT.

FURNACES.

SINCE this work was written, great changes have been effected in the apparatus used by chemists for obtaining high temperatures. Instead of using brick or fire-clay furnaces, which take up much space and require vigilant attention, all the ordinary operations of the laboratory may now be performed with gas. Mr. J. J. Griffin, of Garrick Street, Covent Garden, London, and Mr. Thomas Fletcher, of Museum Street, Warrington, have invented so many contrivances that it is difficult to make a selection from them. The student should procure Mr. Griffin's 'Chemical Handicraft' and Mr. Fletcher's Catalogues, where he will find all that he is likely to require, and the prices are extremely low.

Fusions at moderate temperatures.—Mr. Griffin has constructed a gas-furnace which will melt 30 lbs. of lead, or 24 lbs. of zinc, with a very small consumption of gas. The arrangement is so contrived that the pot of melted metal can be used as a bath.

Fusion of Silicates.—Another of Mr. Griffin's gas-furnaces will fuse 1000 grains of anhydrous carbonate of sodium in ten minutes. I can speak confidently of the extreme usefulness of this arrangement, as I have used it constantly, for months together, in the analysis of emeralds and beryls.

Fusions at high temperatures.—Mr. Griffin has also constructed a furnace for operations at a white heat, which leaves little or

nothing to be desired. The power of these furnaces is extraordinary. One which only consumes 20 cubic feet of gas per hour, and having a chimney only 4 feet high, will melt half a pound of cast iron in 35 minutes from the time of lighting the gas.

Mr. Fletcher has also a small furnace which, with a gas supply-pipe of only half an inch diameter, will melt silver in three minutes, cast iron in eight minutes, and cast steel in twenty-five minutes.

At page 20 of the original work a process is mentioned for the preparation of nitrite of potassium. The nitrites are now very largely employed in commerce in the preparation of certain colours. The sodium salt is that always used, and it is generally formed by the method of M. A. Girard, which consists in fusing at a low red heat nitrate of sodium with the sulphite of that metal. The sulphate produced in the reaction is removed by crystallization.

Cupellation.—Furnaces for heating muffles by gas can now be obtained, and are exceedingly convenient in many operations.

Furnaces for heating Platinum Crucibles.—It is to be observed that Remington's and Beale's furnaces are now generally superseded by those invented and sold by Griffin and Fletcher.

Methylated Spirit.—Wherever wood spirit is alluded to as a fuel or solvent in the body of the work, it is to be remembered that methylated spirit is now invariably substituted.

LAMPS.

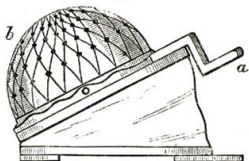
Lamps for Illuminating the Laboratory.—Where gas cannot be obtained for lighting purposes, I employ a Duplex or Silber lamp. The fuel is kerosene or paraffin-oil.

BLOWPIPE APPARATUS.

In the 'Pyrology' of Lieut.-Colonel Ross will be found numerous contrivances of interest and value to the student. Mr. Fletcher's improved Herapath and hot-blast blowpipes are also of great value.

Foot Blower for Blowpipes.—Mr. Fletcher has invented a blower which for convenience, simplicity, and cheapness leaves nothing to be desired. On working the step for the foot at *a* (fig. 1) the air is compressed and acts on a sheet of vulcanized india-rubber; this causes it to expand into a globular form as seen at *b*. The tendency of the elastic material to return to its original size causes a steady pressure upon the air of about ten ounces to the square inch. The blast is exceedingly steady. A net prevents the india-rubber from bursting.

Fig. 1.

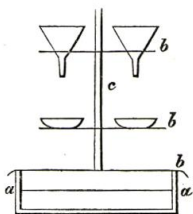


Kemp's Regulator for Water-baths, &c.—Several modifications of this useful apparatus can now be obtained from the dealers in chemical apparatus.

OPERATIONS PREPARATORY TO WEIGHING.

Desiccation over Sulphuric Acid.—Where a number of precipitates are to be dried over sulphuric acid, the student will find the apparatus represented in fig. 2 very convenient. It can easily be constructed in the laboratory. The shallow glass pan *a a* contains the sulphuric acid. The disks *b b b* may be made of sheet metal, or very coarse brass gauze or netting. Holes are cut to allow the funnels to be placed in position if sheet metal be used for the disks; if very coarse netting be used this will generally be unnecessary. In the one I employ, the vertical support was made from a piece of brass tube, and it was attached to the disks by soldering. Many different forms of this apparatus can be procured from the instrument-makers. When in use a large glass shade or bell-glass, similar to that used with an air-pump, is placed over all. The bottom edge may be ground to fit the plate of the pump, or a separate plate may be employed if it be not desired to dry the substances *in vacuo*.

Fig. 2.



THE BALANCE.

I have little to add to the matter contained in the body of the work, except that there was for a time a tendency to return to short-beamed balances with very light beams. Those introduced by Bunge are even shorter than those of Robinson, mentioned at p. 75. Their rapidity of action is their principal advantage. My friend Mr. Oertling has, however, pointed out that much the same result may be obtained by lowering the centre of gravity of the ordinary balance until the required rapidity of oscillation is obtained; but this has the effect of lessening the sensitiveness—that is to say, the index moves over a smaller arc for a given increment of weight. A more finely engraved scale must therefore be employed, and a magnifying-glass on a stand be so placed that the scale may be read off without fatigue to the eyes of the operator.

Influence of variations of the Barometer on the Weights of Substances.—F. Mohr has called attention to the errors which may occur in refined investigations from this cause. The same weights are employed in Munich 1700 feet above the level of the sea, and in London and other places at comparatively small elevations above the sea-level. A fall of the barometer of 10 millimetres, which may occur in one day, will render a kilogramme weight of rock-crystal lighter by 5·3 milligrammes. The student will do well to study Crookes's "Researches on the Atomic Weight of Thallium," in the 'Philosophical Transactions' for 1872; in this masterly investigation the influence of the barometric pressure was allowed for (see also the 'Chemical News,' November 15th, 1878).

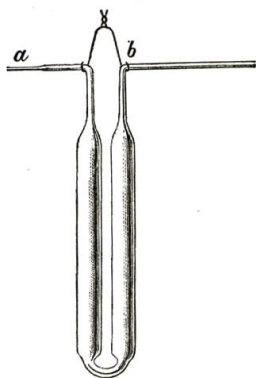
SPECIFIC GRAVITY.

An easy and exceedingly accurate method of determining the specific gravities of liquids has been devised by that able physicist Dr. Herman Sprengel*. Its accuracy is so great, even when comparatively small quantities of substance are at the operator's disposal, that it would be improper to omit an account of it. The instrument, as seen in the figure, is an elongated U-tube.

* SPRENGEL, Chem. Soc. J. [2] xi. 577.

It can be made with the greatest ease by following the directions given in the section on Glass-working, p. 399. The open ends terminate in two capillary tubes; they are bent at right angles and in opposite directions. The size and weight of the instrument depend upon the size and power of the balance at the operator's disposal. As the balances used in the laboratory usually indicate one tenth of a milligramme when loaded with 50 grammes, the instrument when filled with the liquid should not be

Fig. 3.



heavier than 1000 grains = 64.799 grammes. The instrument which Dr. Sprengel used had a length of 17.7 centimetres = 7 inches; it was made of a glass tube, having an outer diameter of 11 millimetres = $\frac{7}{16}$ of an inch. Dr. Sprengel's reason for adopting the form of a U-tube was to obtain a large surface, thus rendering the instrument sensitive to changes in temperature. A point of especial importance is the difference in the calibre of the two capillary tubes. The reason for this will appear presently. The shorter one is a good deal narrower towards the end than the longer one, the internal diameter of which is about half a millimetre. The horizontal part of the wider tube is marked near the bend with a delicate line at *b*. This line and the extremity of the opposite capillary tube *a* are the marks which limit the volume of the liquid to be weighed.

The filling of the instrument is easily effected by means of the suction-tube represented at fig. 272, p. 346. The stem should, however, be cut shorter, and a piece of india-rubber tube be fastened to it with fine wire. The narrow capillary tube is to be attached to the suction-tube in any convenient way. The hole in the cork (*a*, fig. 272) may be enlarged, and then the capillary tube may be covered by a bit of india-rubber tube and pressed in.

On dipping the wider and longer capillary tube into a liquid,

suction is to be applied to the piece of india-rubber tube fastened to the stem by wire. The suction will produce a partial vacuum, and cause the liquid to enter the U-tube by the atmospheric pressure. It would, perhaps, be better to have the wide part of the suction-tube larger than is shown at page 346, for the reason given below. If the bulb of the suction-tube be large enough, it will not be necessary to continue the suction if the end of the india-rubber tube be closed by compression between the fingers. When the bulb and the U-tube have about the same capacity, it is hardly necessary to repeat the exhaustion more than once. Without a bulb the time taken to fill the U-tube is, owing to the fineness of the capillary tubes, somewhat tiresome. The emptying of the U-tube is performed by reversing the operation and blowing into the suction-tube.

The apparatus having been filled, it is detached from the suction-tube, and placed in water of the standard temperature almost up to the bends in the capillary tubes; it is left there until it has assumed that temperature; the volume having then been carefully adjusted, the apparatus is to be removed from the bath and weighed.

Especial care must be taken to ensure the correctness of the standard temperature: a mistake of one tenth of a degree Centigrade will cause the weight of 10 c. c. of water to be estimated either too high or too low by 0.14 milligramme, giving rise to an error in the fifth decimal, thus making 100000 parts 100001.4 parts. These determinations have been made in Dupré's* apparatus, which, when furnished with a sensitive thermometer, allows the fluctuations of temperature to be fixed within 0.01.

An important feature of Dr. Sprengel's apparatus is the ease and precision with which the measurement of the liquid can be adjusted at the moment it has acquired the standard temperature; for it will be found that the liquid expands and contracts only in the *wider* capillary tube, namely in the direction of least resistance. The finer capillary tube always remains completely filled. If the liquid passes beyond the mark made at *b*, it can be brought back to its proper place by touching the point *a* with a little roll of filter-

* DUPRÉ and PAGE, Phil. Trans. 1869, p. 608.

paper. Supposing that in doing so too much liquid is removed, capillarity will correct the fault, for it is only necessary to touch the point *a* with a drop of the liquid the density of which is being determined; the capillary force acts at once throughout the mass of the liquid, and it moves forward again to, or even beyond, the mark.

This exceedingly simple yet beautiful instrument acts as a very delicate thermometer; the moment when it has reached the standard temperature of the bath may be known from the stability of the thread of liquid inside the wider capillary tube. The length of this thread remains constant after about five minutes.

While wiping the instrument, after its removal from the bath, the point *a* must not be touched, as capillarity might extract some of the liquid; otherwise the handling of the instrument requires no special precaution.

The capillary tubes need not be closed for the purpose of arresting evaporation. The error from this source does not amount, with water, to more than one twentieth of a milligramme per hour.

When the temperature of the balance-room is high, and the coefficient of expansion of the liquid is considerable, it will be better to put a small bead-shaped cap, open at both ends, over the wider capillary tube to retain any liquid which, owing to its expansion, might be lost during the weighing. Another method of overcoming the difficulty is merely to raise the standard temperature of the bath. When the cap is used, the wider capillary tube need not be longer than the narrow one.

That this method is susceptible of accuracy to the fifth decimal is obvious from the following experiments. Six weighings of the same sample of distilled water were made, three of them at 16° C., and three of them at 15° C. The instrument was filled and emptied three times, while Dupré's bath was raised and lowered to the desired temperature six times in succession. The weighings were noted after the apparatus had hung in the balance-case for ten minutes. No counterpoise in the shape of a similar U-tube was used.

At 16°.	At 15°.
grammes.	grammes.
U-tube + water = 41.9648	41.9675
U-tube = 23.3332	23.3332
<hr/>	<hr/>
18.6316	18.6343
Specific gravity . . 1	1.000145
grammes.	grammes.
U-tube + water = 41.9648	41.96745
U-tube = 23.3332	23.33320
<hr/>	<hr/>
18.6316	18.63425
Specific gravity . . 1	1.000143
grammes.	grammes.
U-tube + water = 41.9648	41.9674
U-tube = 23.3332	23.3332
<hr/>	<hr/>
18.6316	18.6342
Specific gravity . . 1	1.000140

The extraordinary accuracy of the above numbers requires no comment, and quite justifies Dr. Sprengel in his statement that the apparatus is perfectly capable of enabling the operator to determine, by its aid, the apparent coefficient of expansion of liquids in glass.

Sonstadt's Solution.—By dissolving iodide of mercury in a solution of iodide of potassium, a liquid may be obtained of a specific gravity as high as 3.01. Professor Church* has utilized it for the separation of mixtures of minerals.

The student is reminded that, strictly speaking, density is the weight of a unit of volume, and that specific gravity or relative density is the number expressing the relative weights of equal volumes. The two terms are, however, commonly used promiscuously.

* CHURCH, English Mechanic, Dec. 14, 1877.

SPECIFIC GRAVITIES OF VAPOURS AND GASES.

Specific Gravity of Vapours.—Since this work was written, a great number of processes for determining the specific gravities of vapours have been invented. Among them several have been devised with the intention of applying Gay-Lussac's principle to substances of comparatively high boiling-point. Natanson* invented one of the earliest, but it has not found general acceptance; and the same may be said of Grabowski's† method. It may be mentioned in passing that Gay-Lussac's method has the great advantage over that of Dumas of requiring very little substance, a matter of no small importance in some researches.

Chemists interested in this important branch of chemical physics should also read an interesting account of a modification of Gay-Lussac's method devised by Dr. W. M. Watts‡.

The apparatus (fig. 82, p. 102) for determining the specific gravities of vapours by Gay-Lussac's process has been somewhat simplified; a form very easily put together will be found in Watts's 'Dictionary of Chemistry,' vol. v. p. 367. The student will also find in the same article the full details of the author's method of rapidly determining the residual air in the balloons used in Dumas's process, and somewhat briefly described in this work at p. 100. In fact, by adopting this plan, a determination of residual air can be made in a few seconds.

When the substance, the vapour-density of which is to be determined, boils at a very elevated temperature, the processes of Deville and Troost, or of Regnault, may be employed: see the author's article on Specific Gravity in Watts's Chem. Dict. v. 373, 375.

Victor Meyer§ has determined the vapour-densities of a number of substances of high boiling-points by an ingenious method of very general applicability; it need not, however, be described, as he has quite recently published, in collaboration with Carl Meyer||,

* NATANSON, Ann. Ch. Pharm. xcvi. 301.

† GRABOWSKI, Sitz. d. Akad. Wien, l. 1866.

‡ WATTS, The Laboratory, June 29, 1867, p. 225.

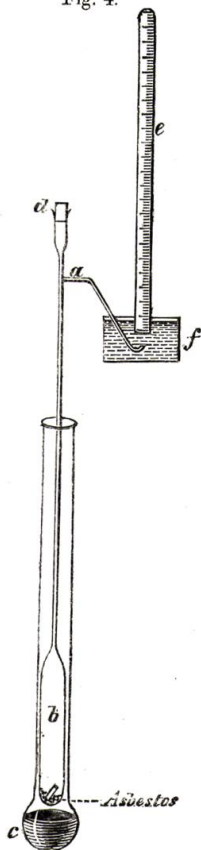
§ V. MEYER, Ber. d. D. chem. Ges. ix. 1216.

|| V. MEYER u. CARL MEYER, Ber. d. D. chem. Ges. xi. 2253.

a new, simple, and exceedingly accurate process, which appears to be superior to any that has yet been devised. It takes but little time, and does not require either the exact temperature of the bath or the volume of the vapour-flask to be known. It is, moreover, suitable for very wide ranges of temperature, from that of boiling water to melted lead. The principle depends upon the displacement by the vapour of the substance of an equal volume of air at the same temperature.

The apparatus consists of a vertical cylindrical flask, *b*, of 100 c. c. capacity. It has a tubular neck of 6 mm. interior diameter and 60 centimetres in length. The latter is expanded at the top to allow of its being closed by the caoutchouc stopper *d*. A lateral tube, *a*, of not more than 1 mm. in internal diameter, and about 140 mm. in length, is so bent as to carry the air expelled by the vapour into the graduated tube *e*, which stands in the water contained in the pneumatic trough *f*. The vapour-flask is placed inside a tube *c*, having a bulb at its lower extremity containing the fluid or substance by the vapour of which the flask *b* is to be heated. For substances which boil at very elevated temperatures the heating tube is replaced by a bath of melted lead. Before commencing the operation, a little recently ignited asbestos is placed at the bottom of *b*, to prevent its fracture when the tube containing the substance is dropped in. When the requisite temperature is reached (which, however, need not be known exactly), the

Fig. 4.



trough *f*, but is not placed beneath the graduated tube. The cork *d* being in its place, it is necessary to wait until the water in *a* remains quiescent, showing that the temperature of the vapour-flask remains steady. The substance enclosed in a small glass tube closed at one end is then introduced through the funnel, the stopper being removed for that purpose. In the act of replacing it a few bubbles of air will escape by the lateral tube *a*; they must not, however, be allowed to enter the graduated tube. After they have escaped, the tube *a* is to be placed beneath the eudiometer. When no more air escapes, the operation is finished, and the caoutchouc stopper is to be instantly removed to prevent the water in *f* from rushing back into *b*. The lower extremity of the graduated tube or eudiometer *e* is then to be closed with the thumb, and it is to be transferred to a cylinder of cold water, the temperature of which is to be accurately determined. After reposing a sufficient time to allow of the gas being of the same temperature as the water, the level inside and out of the eudiometer is to be equalized and the volume read off. Knowing the weight, *S*, of the substance, the volume of air, *V* (which, when corrected, is equal to the volume of the vapour reduced to the temperature *t* of the water surrounding the eudiometer), the barometric pressure reduced to 0° C. = *B*, and the tension of aqueous vapour at *t* being *w*, we have :—

$$D = \frac{S(1 + 0.003665 t) \times 587780}{(B - w) V}$$

There are one or two precautions which are necessary to be observed in using this apparatus. It is, of course, essential that it should be clean and dry before use. The quantity of the substance taken should not be more than sufficient to half fill the vapour-flask *b* with vapour; it is better to have even a little less.

With substances which undergo decomposition in contact with air at their boiling-points, it is necessary to perform the operation in an atmosphere of nitrogen.

The numbers obtained are remarkably accurate even with substances of the most widely differing boiling-points, as will be seen from the following table :—

	Found.	Theory.
Chloroform	4.13	4.13
Water	0.61	0.62
Mercury	6.97	6.91
Anthracene	6.01	6.15
Sulphur	6.58	6.63
Perchlorodiphenyl. . . .	17.43	17.24

Determination of Vapour-densities under diminished pressures.

—The process of Gay-Lussac has the merit of requiring very little substance* ; and as this is a point of great importance in some researches (see above, p. 13), many attempts, besides those we have already alluded to, have been made to adapt it to substances of high boiling-points. Dr. Hofmann has accomplished this end, for substances which boil at comparatively high temperatures, by the simple device of causing the vapour to be formed *in vacuo*. He effects this by diminishing the pressure on the vapour. For this purpose he uses a tube of a metre in length. The vapour is thus liberated in what, but for its presence, would be a Torricellian vacuum. The boiling-point of the substance is by this means so much lowered that substances boiling at 150° may have the densities of their vapours determined in an atmosphere of steam. By covering the measuring-tube by another, drawn out at the upper end and closed at the lower by a cork provided with a tube to allow the exit of the vapour used to heat the substance, two advantages are obtained. In the first place, the vapour of a substance of known boiling-point may be employed as the heating medium, as in Deville and Troost's method ; and, in the next, the vapour used to heat the substance may be condensed, and the resulting fluid be used repeatedly. A clear account of the way in which the operation is conducted, accompanied by an illustration, will be found at p. 24 of Schorlemmer's 'Chemistry of the Carbon Compounds.'

For other methods of determining vapour-densities see Hofmann, Ber. d. D. chem. Ges. ix. 1304, and Muir and Sugira,

* This equally applies to V. and C. Meyer's process last described.

Chem. Soc. J., Aug. 1877. In these methods the measuring-tube is not graduated.

Vapour-densities determined by a new method.—Naumann* has proposed an entirely new method of determining vapour-densities. It is founded on the well-established principle that, when substances not miscible with a given liquid are distilled with that liquid, the quantity of the two bodies in the distillate is, at a constant temperature of ebullition, in a constant ratio. Since, on the mechanical theory of gases, the vapour-tension, other things being equal, depends on the number of molecules which the vapour contains, the author sought a relation between the constituents of the distillate, expressed in molecular weight, and the vapour-tensions of these constituents in the vapour mixture. Following this out, he confirms the hypothesis. The only number he gives is that obtained with naphthalene; but the result is not satisfactory. The process is only mentioned in consequence of its novelty in principle.

Where a great number of vapour-densities have to be determined, the calculations required take up a considerable time. With the view of lessening this delay, I calculated the values of the expression $\frac{1}{1+0.00367T}$ for each degree from 1° C. to 150°. But my friend Mr. J. T. Brown has, with enormous labour, calculated the values of $\frac{0.0012932}{760(1+0.00367T)}$ and $\frac{0.00367}{1+0.00367T}$ for all the temperatures from -20° C. to 350°†. The calculation of the result of an experiment is now, therefore, a very simple matter.

Vapour-densities of substances which leave a residue on heating.—It not unfrequently happens that the substance, the vapour-density of which has to be determined, decomposes, leaving a residue in the balloon. Roscoe‡, in his well-known research on vanadium, found that the tetrachloride of that metal decomposes,

* NAUMANN, Ber. d. D. chem. Ges. x. 2098.

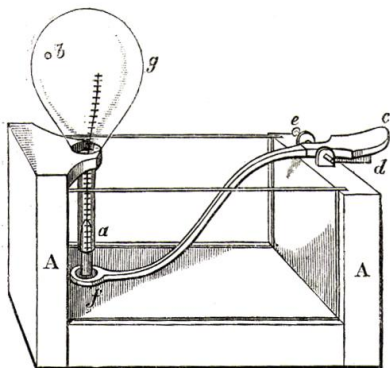
† BROWN, Chem. Soc. J. [2] iv. 72.

‡ ROSCOE, Chem. Soc. J. viii. 346.

the trichloride being formed with liberation of chlorine when the ordinary process of Dumas was used. The effect of this was that a solid residue formed and remained in the balloon. Whenever this occurs it is obvious that the number obtained by experiment will be in excess of that required by theory. To avoid this, he employs two bulbs and distils the substance from one into the other; the residue remains in the first bulb, and the determination is made in the second one. At the close of the operation, the bulbs are separated by the blowpipe.

Specific Gravities of Gases.—At page 110 I have described, very briefly, a simple and accurate process for determining the specific gravities of gases. It was devised by Bunsen *, and, as its neatness, simplicity, and accuracy have caused it to come into general use, it would be improper to omit a fuller account of it. The apparatus required can now be obtained at most instrument-makers.

Fig. 5.



The gas is weighed in a light flask, *g*, fig. 5, having a capacity of 200 to 300 c. c. The neck, *a*, which has been thickened before the blowpipe, is drawn out so as to have an aperture of the thickness of a straw. A stopper is made for it, and ground in accurately with emery and turpentine. The neck has a millimetre

* Gasometry, p. 113.

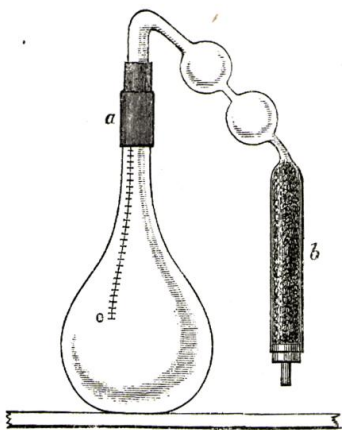
scale etched on it. The flask is to be filled with mercury by means of a funnel which reaches to the bottom. When full, the flask is removed, mouth downwards, to the mercury trough *AA*; and gas is allowed to enter until the mercury in the neck stands a few millimetres above that in the trough. The gas is dried in the flask by a small piece of chloride of calcium, *b*, which is made to crystallize on the flask, by bringing it in contact with a single drop of water, and alternately heating and cooling the glass.

In order to close the flask without warming it by the hand, the lever *cf* is employed. The stopper is so fastened in a cork at *f*, that it passes into the neck of the flask without closing it, and the lever is held in its place by a wedge *d* under the finger-plate *c*. When the apparatus has attained the constant temperature *t*, at the barometric pressure *P*, the volume *V* of the gas and the height *p* of the column of mercury above the level of that in the trough are observed with the cathetometer. If the observed volume of gas in cubic centimetres, reduced from a table of capacity, be represented by *V*₁, this volume at 0° C. and 0.76 pressure becomes, in cubic centimetres,

$$V_2 = \frac{V_1 (P - p)}{0.76 (1 + 0.00366 t)}.$$

It is now only necessary to determine the weight *G*₂ of this volume *V*₂. To do this the wedge *d* is removed; the flask is thereby closed, and by removing the pin *e* it can be removed, with the lever *cf*, from the trough. It must be most carefully freed from all adhering matters; and having attained the temperature *t*₁ of the balance-case, and the pressure *P*₁, it is to be weighed. Let *G* represent the weight in grammes. The glass stopper is then removed and replaced

Fig. 6.



by a caoutchouc tube connected with a drying-tube *b*, fig. 6. The apparatus thus arranged is placed under the receiver of an air-pump, and the air withdrawn and admitted until all the gas has been replaced by dry air. If this weight amounts to G_1 grammes, the weight G_2 of the volume of gas V_2 measured in the flask is equal to

$$G_2 = G - G_1 + \frac{V_1 P_1}{773 \times 0.76 \times (1 + 0.00366 t_1)}.$$

From this value G_2 the specific gravity is obtained by the formula

$$S = 773 \frac{G_2}{V_2}.$$

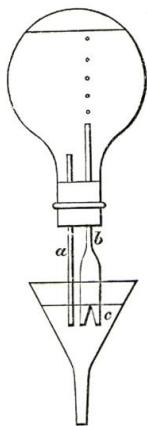
The Cathetometer.—This admirable instrument was invented by Dulong and Petit, and was first used in their researches on the dilatation of liquids. Its object is to enable the difference of level of two columns of liquid to be ascertained with precision. It may also be employed to measure the height of a column of fluid above a point which stands at a known distance from the surface of a fluid in a cistern, as at *n*, fig. 82, and *V*, fig. 85. An excellent account of its construction and mode of use will be found in the ‘Cours de Physique’ of M. Jamin, i. 36.

FILTRATION AND WASHING OF PRECIPITATES.

Rapid washing of Precipitates.—When, as frequently happens in analytical work, the liquid above a precipitate runs very quickly through the filter, the washing-tube of Berzelius, and the modification of it described at page 145, sometimes fail in affording a sufficiently rapid supply of water. To meet this difficulty I have devised the arrangement represented in fig. 7. A flask has a cork perforated with two holes fitted carefully to its neck. Through one of these holes a straight tube, *a*, passes open at both ends; into the other a tube funnel, *b*, is inserted. A slit is ground at *c*; this is easily effected by rubbing it on a stone with emery and water, or, still better, turpentine; or it may be

held for a few seconds against an ordinary grindstone. The flask is to be filled with water, or any other fluid with which it is desired to wash the precipitate, and is then to be inverted in the funnel. When the water in the latter falls below the slit at *c*, the air enters and ascends into the flask in bubbles; at the same time water descends through the tube *a* and maintains a constant level in the funnel. When properly constructed, the apparatus never fails. The slit is essential, as, without it, the bubble of air finds too much resistance to its passage. It is true that some of the precipitate is liable to find its way into the flask; but as it can always be washed into the funnel without loss, this is entirely immaterial in even the most accurate analyses.

Fig. 7.

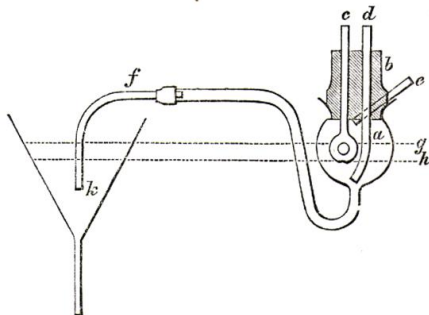


An ingenious modification of my apparatus last described has been invented by my assistant Mr. J. W. Smith. It is by no means so simple or easy to construct; but, on the other hand, when properly put together, its action is perfect. It is thus made:—A thistle funnel, *a*, fig. 8, having its bulb about $1\frac{1}{4}$ inch in diameter at the widest part, and 1 inch at the mouth, has its tube bent as in the engraving. The cork *b* is about 2 inches long, and is pierced with three holes; two of these are in the direction of its length; they serve to admit the tubes *c* and *d*. The third hole is bored diagonally, and serves to admit the tube *e*, which, therefore, allows of a free passage for air to enter the thistle funnel. The diameter of *e* should be about $\frac{1}{8}$ of an inch; *c* and *d* may also be made from tubing of the same size. The tube *c* has a bulb blown on its lower end about $\frac{1}{2}$ an inch in diameter. Two holes are made in this bulb, one at the bottom and one at the side, each about $\frac{3}{16}$ of an inch in diameter. The tube *d* is curved at its lower end to allow of its being pushed as far as possible into the thistle funnel. The cork is filed to fit the mouth of the thistle funnel, and is cemented into its place with sealing-wax. The tubes *c* and *d* are to be so adjusted that

the top of the bulb of *c* is about $\frac{1}{4}$ of an inch below the cork, the end of *d* being pushed as low down into the thistle funnel as possible, taking care that it does not touch the side so as to close the aperture.

The horizontal part of the bent tube of the thistle funnel must be above the level of the cork *a*; the proportions between the

Fig. 8.



curved and horizontal portions of the tube may be seen by inspection of the engraving. In the figure a separate piece of tubing *f* is attached to the tube of the thistle funnel by a piece of india-rubber tubing, but, if preferred, the whole may be in one piece. There are, however, circumstances which render the capability of movement in *f* a decided advantage. The lower end of *f* must be below the level of the bottom of the bulb on *c*.

The cork *b* may now have its upper end fixed in the mouth of a flask or bottle containing distilled water, and be supported by the ring of a retort or filter-stand. The flask is of course in an inverted position. This having been done, water will flow through the tube *d* into the thistle funnel, an equal volume of air entering the flask by the tube *c*. As the water rises in the thistle funnel to the top of the hole in the side of the bulb, the supply of air to the flask becomes cut off, and the flow of water through *d* ceases. The operator is now to blow gently through the tube *e*; this will force the water in the thistle funnel up the tube *f*; it will then flow into the funnel *k* containing the substance to be washed.

The tube *f* siphons the water from the thistle funnel, and delivers it into *k* in a constant stream, until the water in *k* rises to the level *g*. As the liquid runs through the filter *k*, the level of the water in *a* and *k* falls until the water in *a* reaches the bottom of the bulb, *i. e.* to the level *h*; a bubble of air now enters the bulb through the side hole, and water immediately runs through the tube *d* until the level *g* is again reached.

If it be desired to stop the action of the apparatus, it is merely necessary to close *e* with a piece of india-rubber tubing containing a short glass rod.

The advantages of this apparatus, are :—1. It never fails in working; 2. It delivers water as rapidly or slowly as may be desired; 3. Its action may be at once arrested without dismounting the apparatus, by merely closing *e*.

Filtering under increased pressure.—This may be effected in two ways, namely, by enclosing the substance to be filtered in a closed vessel and pumping the liquid upon it; or by having the mixture of fluid and solid exposed upon a filter in such a manner that the air may be removed from below. In the first case the pressure may be increased almost *ad libitum*, in the other it does not exceed that of the atmosphere.

In the earlier days of the manufacture of the aniline colours, an industry owing its first existence to the discoveries of Mr. Perkin, high-pressure filtration was generally effected in strong wrought-iron cylinders. The lower part contained an iron diaphragm pierced with numerous holes, upon this the filtering medium (stout calico or canvas) was carefully stretched. This was done in such a manner that the fluid could only escape from the apparatus after passing through the crude colouring-matter. The cylinders were heated inside by coils of steam pipe. The pressure was obtained by pumps of great power. The operation was first performed with coal naphtha to dissolve and carry away impurities, and, when these were removed, with methylated spirit to extract the comparatively pure colour. Extractors more or less resembling these have been employed in many manufacturing operations.

The pressure of the atmosphere has for many years been made

use of to facilitate filtration. In some of the arrangements, the mixture to be filtered is placed upon a suitable canvas or cloth filter; this in its turn rests upon a perforated diaphragm. A closed chamber beneath the filter is then connected with a vacuum chest. The exhaustion is sometimes effected by the condensation of steam, but more frequently by means of pumps. All these methods have been greatly improved of late years, and filter presses, worked by powerful and ingeniously contrived pumps, have come into common use; but as these are only employed in manufacturing operations, they will not be further alluded to here.

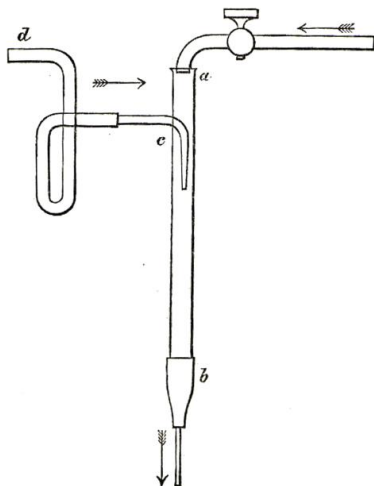
As soon as Sprengel introduced his admirable mercury-pump for the production of a vacuum, it became evident that a somewhat similar instrument could be made to work by the fall of water. Bunsen introduced a pump for the purpose of facilitating the passage of water through precipitates; and numerous modifications of his apparatus, but all on the Sprengel principle, found their way into chemical laboratories. They are now sold by all instrument-makers, and are extensively advertised in the scientific journals.

These pumps, when used for water, are exceedingly easy to make with the glass, metal, and caoutchouc tubing to be found in every laboratory. One of the simplest of the many arrangements I have seen is that of H. C. Buck*. As the journal in which the apparatus was described is, I am informed, now extinct, and as it is, therefore, unlikely to be seen by the student, I append a description of it. It consists of a piece of caoutchouc tubing *a* (fig. 9), $\frac{1}{2}$ inch in diameter and 6 inches long. At *c*, which is two inches from the upper end, a round hole is made with the aid of a punch or cork-borer, $\frac{1}{8}$ of an inch in diameter. The tube *c* is $\frac{1}{4}$ of an inch in diameter; it is bent at right angles, and is drawn out at the lower end by means of the blowpipe. The smaller end is inserted in the hole at *c*, and the tube is pressed in until the bend is just inside the caoutchouc tube. The upper end *a* of the caoutchouc tube is to be slipped over the end of the water-pipe. A $\frac{1}{4}$ -inch discharge-pipe is attached to the end

* H. C. Buck, American Chemist, April 1876.

b; this may be effected by pushing a piece of metal or glass pipe an inch long into the caoutchouc tube, and with another piece attaching the discharge-pipe. The joint may be made tight with wire or twine.

Fig. 9.



The vacuum produced will be in proportion to the height of the column of water supported in the discharge-pipe. The inventor puts the latter into the drain-pipe. Very good results, he states, may be obtained with as small a fall as 4 to 6 feet.

To complete the apparatus, a flask is taken with a well-fitting cork pierced with two holes: in one the funnel containing the precipitate to be washed is inserted, and in the other a tube bent at right angles, which is to be inserted in the caoutchouc tube *d* and fastened in the usual manner.

Another method of filtering under increased pressure has been described by Mr. H. Carmichael (Watts's 'Chemical Dictionary,' 2nd Supplement, p. 66). He obtains the pressure by the use of a more or less perfect vacuum. For this purpose he employs the

lips, a Sprengel pump, or an aspirator, according to circumstances. The process is too long to be inserted here.

An excellent water-jet aspirator has been devised by Messrs. Mawson and Swan of Newcastle. When attached to the ordinary town water-pipe, it quickly produces a vacuum capable of sustaining a column of mercury of nearly the full barometric height. It is sold at an extremely moderate price.

CRUCIBLES AND OPERATIONS AT HIGH TEMPERATURES.

Crucibles.—The plumbago crucibles made under Morgan's patent by the "Morgan's Patent Plumbago Crucible Company," York Road, Battersea, are very durable. This firm make portable furnaces of the same material. The crucibles are far superior to the old blue-pots.

Mending Platinum Crucibles.—It not unfrequently happens in the laboratory that a basin or crucible of platinum becomes injured. I have found it exceedingly easy to mend them with gold. The injured spot is to be thoroughly cleaned by sand-paper and covered with a paste of powdered borax and water. A small piece of pure gold is then to be laid on the injured part and a powerful blowpipe flame directed on it; the gold soon melts and runs into the hole. Crucibles and basins thus mended I have found to remain serviceable for many years. Platinum is eminently weldable, and if two perfectly clean surfaces are laid upon each other and tapped while white-hot with a very light hammer, they will adhere perfectly. This can easily be effected by making a mould of plaster of Paris to serve as an anvil, and heating with a table blowpipe (Garside, Chem. News, Aug. 9, 1878).

Counterpoises for Platinum Crucibles.—Extended experience has convinced me that the use of counterpoises, recommended at p. 176, § 277, is a mistake. Platinum crucibles are so liable to alter in weight, that is better to avoid counterpoises altogether.

PRESSURE-TUBE OPERATIONS.

The employment of high temperatures and pressures for the purpose of effecting reactions has now become an every-day

occurrence in laboratories; it is even a common manufacturing operation. In factories the apparatus used consists generally of cast, but sometimes of wrought iron; the metal must be of the highest possible quality. They are sometimes enamelled on the inside; but, as a rule, the enamel does not last long. They may be procured of all shapes and sizes. The more usual form is that of a cylinder with a round bottom. The cover has generally three apertures: to one is fixed a manometer or pressure-gauge; another has a tap fixed in it, and serves to enable the operator to lessen the pressure if it gets too high by letting some of the vapour escape. The third aperture admits a tube which goes nearly to the bottom of the apparatus; it projects about twelve inches from the cover, and is bent downwards. It is provided with a tap to enable a little of the liquid to be removed from the apparatus at intervals, and thus show the progress of the reaction. The cover and the top of the cylinder must be turned in the lathe so as to fit accurately. A washer is always required; it may be of lead, leather, or vulcanized india-rubber, according to the temperature used or the ingredients employed. An instrument constructed as above described is called an autoclave. They may be purchased as small as may be desired for delicate experiments; but, when only having a capacity of a litre, they are generally made of bronze, in which case they are not enamelled.

Autoclaves are exceedingly convenient in research. If not enamelled, or if the enamel has, by use, become defective, the substances to be heated under pressure may be enclosed in glass tubes of the form given at pp. 190 and 191. In this case, owing to the external pressure counteracting the internal, there is much less risk of fracture than when the tube is heated in an air- or oil-bath.

The advantage which is obtained by having an outward pressure to counteract that inside the tube is very great; in fact, according to Berthelot, alcohol or ether may be heated to 360°C . in a closed glass tube without fracture, if the pressure-tube be enclosed in an outer one containing turpentine.

Dr. Frankland* was probably the first chemist to use autoclaves

* FRANKLAND, *Ann. Ch. Pharm.*, xcv. 30.

in this country. The form employed by him is especially adapted for heating glass tubes. It is made of one piece of wrought iron welded by means of the steam hammer. It is in the form of a cylinder, $18\frac{1}{2}$ inches long, 3 inches internal diameter, and $\frac{5}{8}$ inch thick. It has at its upper end a flange $1\frac{3}{8}$ inch broad and $\frac{5}{8}$ inch thick. It is turned in the lathe to as true a surface as possible, and has a sunken ring $\frac{1}{20}$ inch turned in it to admit a leaden washer. The cover, which is accurately fitted to the flange, has two apertures in it; to one a safety-valve is attached, the other has a cast-iron tube closed at the lower end screwed into it. The tube last described is intended to contain mercury in which a thermometer is plunged; the temperature indicated will be very nearly that of the inside of the autoclave. The cover is bolted to the flange of the cylinder by screws and nuts; and as these are forced home the leaden washer is compressed, and a joint capable of bearing a pressure of 100 atmospheres is obtained. Previous to the insertion of the pressure-tubes the cylinder is to be filled about two thirds with water.

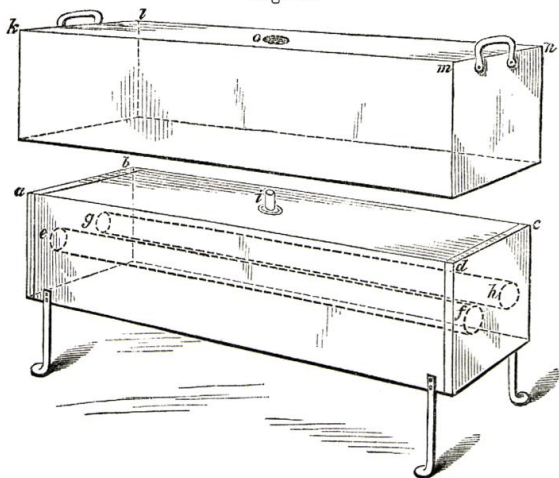
The cylinder is heated by a vertical cylindrical gas-furnace. The gas-burner is a spiral of copper or brass tube pierced with holes.

In many laboratories it is usual to heat the pressure-tubes in an air-bath. In this case it is necessary to take precautions to prevent the contents and the broken glass from being projected about the laboratory in the event of an explosion. I have seen some very narrow escapes from serious injury owing to the neglect of this precaution.

A convenient and safe air-bath for this purpose is represented in fig. 10. It consists of a rectangular sheet-iron box $abcd$; it should be 2 feet long and 8 or 9 inches broad along the line ab . It is perforated to admit two copper tubes ef and gh , having an inside diameter of $1\frac{1}{2}$ inch. The tube i serves to admit a thermometer. When the glass pressure-tubes have been placed in the copper tubes ef and gh , the cover $klmn$ is put on. The aperture o in the cover corresponds to i in the air-bath, and allows the passage of the thermometer. The length of the cover is 25 inches by $9\frac{3}{4}$ inches broad. The apparatus may be heated by one or

more Bunsen burners. It affords complete protection in the event, by no means uncommon, of a tube bursting.

Fig. 10.



An improved apparatus, which, however, I have not tried, is described very briefly in the 'Journal of the Chemical Society' for November 1877. It is an abstract of a paper by Cech*. The author, after describing the forms of digesters used in laboratories for heating substances enclosed in sealed tubes, describes his improved form of apparatus. He claims for it that it overcomes all the difficulties and dangers to which chemists are exposed by using the old form of ovens.

Cech's apparatus consists of a cylindrical sheet-iron oven riveted down one side, whereas, he says, the square iron boxes were riveted in four places. He fixes the oven in the wall leading to the chimney; by adopting this arrangement, all explosions which may occur during the heating find a vent into the flue. This part of the arrangement has undoubted advantages. It frequently happens that substances have to be exposed to a high

* C. O. CECI, *Zeitschr. anal. Chem.* xvi. 320-323.

temperature and pressure in presence of nitric acid ; if, then, an explosion take place, the atmosphere of the laboratory becomes unendurable until the ventilation has been restored. As the process of Carius* for determining chlorine, bromine, or iodine in organic substances containing much hydrogen is now frequently employed, the question of getting rid of the possibility of nitric acid vapours finding their way into the laboratory becomes important. A similar process is also used by Carius in the determination of sulphur.

DETERMINATION OF BOILING-POINTS.

The boiling-point of a body may be defined as the temperature at which the tension of its vapour is equal to the standard atmospheric pressure. When the quantity of the substance is small, the process of Mr. Chapman Jones may be employed with advantage (Chem. Soc. J., April 1878).

When the liquid, the boiling-point of which is to be determined, is not homogeneous, it is usual to put 100 c. c. into a retort and notice how much distils at each 5° or 10° C.

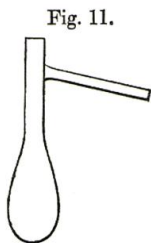
The question is constantly arising as to whether the thermometer should be in the liquid or the vapour. This has been answered at p. 224 as regards homogeneous liquids. If the liquid be not homogeneous it is impossible to give an answer which will be satisfactory in all cases. It is in commerce that disputes on this subject generally arise. If a substance be purchased on the percentage of its more volatile constituent, the seller will derive advantage from the thermometer being as far out of the liquid as possible ; if for its less volatile constituent, he will prefer it in the liquid.

In fractional distillations it should, clearly, be in the vapour, as the object of the operator is to know the boiling-point of the substance distilling over, not that of the *mélange* of substances remaining in the retort.

Retorts of the form represented in fig. 190, p. 224, are seldom used in fractional distillations or determination of boiling-points now. The tubulature should be five or six inches long, as in

* CARIUS, Ann. Ch. Pharm. cxxxvi. 129.

fig. 11. By this means the thermometer is more exposed to the heat of the vapour, and, as the fluid distils over at a lower level than the cork, the latter remains without injury for a much longer time. When the action of the fluid upon the cork is very considerable, and may thus cause inconvenience or error, the height of the tubulature of the retort above the delivery-tube may, with advantage, be made much longer than is represented in the figure.



As, during the determination of the boiling-point of water, to obtain the number 100°C . on the scale of the thermometer, the whole column of mercury is heated to that point, it is obvious that if the entire column, during an experiment, is not at the same temperature as the vapour of the fluid distilling, the boiling-point will come out too low. We must therefore apply a correction. For this purpose a second thermometer is placed so that its bulb is in contact with the stem of the thermometer in the retort; it should be halfway between the top of the mercury column of the latter thermometer and the middle of the cork. The temperature of the second thermometer is (nearly) the mean temperature of that portion of the mercury column of the principal thermometer which is not heated by the vapour of the boiling liquid. Let this temperature be t° , and the uncorrected boiling-point, directly indicated by the principal thermometer, be T° ; let N be the difference between T° and the point of the scale situated at the middle of the cork—that is to say, the length in degrees of the scale of that portion of the mercury column of the principal thermometer of which the mean temperature is t° ; lastly, let δ be the coefficient of apparent expansion of mercury in glass; the correction to be applied to the directly observed temperature T° is

$$= N(T^{\circ} - t^{\circ})\delta.$$

The value of δ may be taken as 0.0001545^* .

I have had repeated occasion to compare the results obtained

* Watts's Dict. Chem. iii. 85.

by making this correction, with those obtained by distilling with the whole of the column of mercury in the vapour. With water I find the corrected number to agree with the experiment made in the latter manner to $0^{\circ}\cdot 1$ C. With a specimen of paratoluidine the value found by distilling with the whole of the column of mercury in the vapour was $198^{\circ}\cdot 75$ C.; with the thermometer as far out of the liquid as the cork permitted, it was 194° , which, corrected according to the formula, became $198^{\circ}\cdot 25$ —the difference being $0^{\circ}\cdot 5$.

When the boiling-point of the substance does not exceed 150° C., I prefer to heat the whole column of mercury and avoid the correction; but, if much beyond that point, say 170° or 180° C., a serious error is liable to occur if the whole of the column be heated. This arises from the tendency of the mercury to distil into the upper part of the tube, thus lowering the apparent boiling-point to an unknown extent. In such a case I keep the bulb of the thermometer as far out of the liquid as possible, and make the correction.

In careful experiments it is important that the flame of the lamp should not be allowed to superheat the vapour in the retort or heat the stem of the thermometer. It is easy to adjust screens so as to eliminate this source of error.

Determination of high boiling-points.—A method of determining easily, and with an approximate degree of accuracy, the boiling-points of substances which vaporize at temperatures too high for the mercurial thermometer to be employed has been published by Messrs. Carnelly and Carleton-Williams*. The method consists in observing whether certain salts melt on exposure to the vapour of the boiling substance. As Dr. Carnelly had previously determined the melting-points of a great number of metallic salts, the way was to a large extent cleared.

For temperatures below 500° C. the substance may be boiled in an ordinary distillation flask, provided with a perforated cork, through which pass several capillary tubes containing salts which melt at known temperatures.

* CARNELLY and CARLETON-WILLIAMS, Chem. Soc. J., July 1878.

Concussive ebullition.—In cases where the remedies for this inconvenience (mentioned at page 214) are found to fail, small fragments of tobacco-pipe introduced into the liquid will often effect the desired result.

DISTILLATION.

Fractional Distillation.—Since this work was written, the importance of fractional distillation, as a method of separation, *i. e.* proximate analysis, has become more and more recognized. We no longer hear vague assertions about the breaking up of liquids into fluids of more simple constitution, against which Mansfield so strongly contended (see pp. 224 and 225). In fact without fractional distillation, not only whole fields of organic research would have to be abandoned, but the immense industries which owe their existence to the accurate separation of the aromatic hydrocarbons would cease to exist. Mansfield, whose valuable life was sacrificed to his devotion to science, was one of the first to invent an apparatus for the purpose. Since his time Coffey, Coupier, Duppa, Warren, Girard and de Laire, Linnemann, and many others have occupied themselves with this question. Rectifying stills, many of enormous size, are in use in all parts of Europe where chemical manufactures are undertaken; it is, however, in the production of alcohol and coal-tar products that they are most extensively employed. It is evident that, in this Supplement, we must confine ourselves to the consideration of one or two of these contrivances.

If we consider the principle of Mansfield's still (p. 242), we shall see that it was well adapted for the purpose for which he intended it. The outer chamber *b* being filled with water, it is plain that, if the body of the vessel *a* contains substances boiling at a higher temperature than water, they ought to condense in the head, and fall back into the still, because the head will remain at a constant temperature, namely, that of boiling water. In practice, however, this is only partially the case, because, owing to the size of the head, only a part of the vapour comes in contact with it. This fault could be remedied by repeating the operation a sufficient number of times; but this of course would

cause loss of time and fuel. The chamber *b* being open, and continual evaporation taking place from it, only a liquid of little or no value, like water, could be placed in it. Nevertheless at the time of its invention it was an important advance, for the *principle* is perfect. Let us take the case of a mixture of two substances which boil at temperatures not far apart, say aniline and toluidine. If we desire to separate them, we have only to contrive an apparatus where the vapour of the mixture shall play against a surface containing the more volatile one. It is plain that, after a time, the more volatile one, the aniline, will boil; but, as the sides of the vessel containing it will not get hotter than the boiling-point of aniline, the toluidine will be condensed and fall back, assuming that the contact be sufficient. The apparatus must also be so arranged that no loss of aniline can take place. Such an apparatus may be called a "homologue separator," because, whenever we have a sufficient quantity of the more volatile homologue to fill the condenser, we can always obtain as much more as we desire.

Guided by this idea, I have contrived an apparatus (fig. 12) of great simplicity and power; it can be made of any size, and costs but little to construct. It must be premised that all the parts are of copper or brass and brazed together.

The cylinder *a a*, through which the mixed vapours pass, contains a smaller one *b*, in which is placed the more volatile homologue. At *c* is a tubulature in which a thermometer *h* is fixed by means of a cork. The inner chamber *b* has an outlet *d* admitting the cohobating tube *g*; the latter, is, in its turn, connected with a worm or other convenient cooler. The more volatile body is therefore continually returned to *b*. The tube *f* is connected with a flask in laboratory operations, or a still when used in the factory. The product of the distillation is conveyed to a condenser by the pipe *e*.

Two or three distillations performed with this apparatus will do as much work in separation as twenty done by an ordinary retort or still.

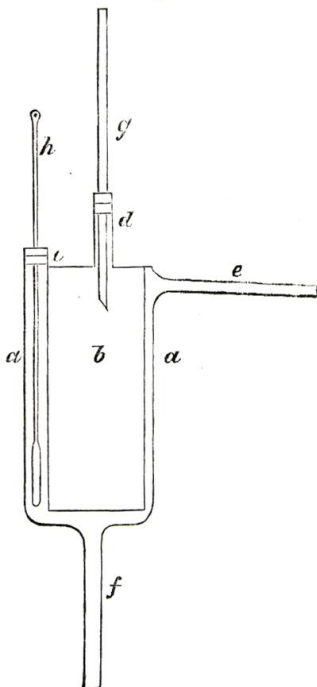
It need hardly be said that its use is not confined to the separation of homologues, but that it can be employed whenever a

substance of the proper boiling-point can be found to charge the inner cylinder. The principal point on which success with this apparatus depends is that the distance between the outer and inner vessels is not too great. On the other hand, if too small to carry away the vapours as fast as they are formed, there would be danger of some part giving way. In practice this presents no difficulty.

MM. Girard and de Laire, in their '*Traité des dérivés de la houille*' (page 341), give a description of an apparatus for the rectification of crude aniline on the large scale, which is said to work admirably.

In the apparatus used on the large scale for fractionating liquids, it is frequently so arranged that the vapour rising from the boiling liquid is partly condensed in a tube which is placed between the still and the condenser. The result of this is, that the succeeding portions of vapour have to pass through the previously condensed liquid, and thus undergo a species of washing, as in Coupier's still, which is only used on the large scale. Linemann (Watts's Chem. Dict., 2nd Suppl. 436) has contrived an effective apparatus for the same purpose. It consists simply of a long glass tube having two or three bulbs blown on it, and at an inch or two from its upper end a lateral tube at the proper angle to convey the vapour to the condenser. A thermometer can be inserted in the upper end by means of a cork. Between the

Fig. 12.



bulbs are inserted cups of platinum-wire gauze. The wire of which the gauze is made should be about the thickness of a horse-hair; the meshes should be about $\frac{3}{4}$ of a square millimetre in area. The cups are made by stamping the square pieces of the gauze in a boxwood mould. The more volatile the liquid the more bulbs and cups are required; thus, for fluids boiling below 150° C., Linnemann uses three bulbs and eight cups, 150° to 180° two bulbs and six cups, and from 180° to 250° two bulbs and five cups.

The result of using the wire gauze is, that the vapour condenses in the bulbs and on the surface of the wire faster than it can pass through the gauze; the vapour which follows has thus to pass through a stratum of fluid, and thus undergoes the process of washing previously alluded to.

The exact form of Linnemann's apparatus need not be strictly adhered to. The bulbs are not really necessary, nor need the gauze be of platinum. Dr. Armstrong uses a straight wide tube, narrowed at the lower end to fit into a flask. Through a wide cork at the upper end of the tube containing the gauze is passed a lateral tube and a tubulature for the thermometer; this part of the apparatus is in one piece. Its form may be seen by looking at fig. 325 *upside down*. The part *a b c* should be bent slightly downwards. He uses from 12 to 24 trays of copper-wire gauze, at intervals of about half an inch. The fractionating power of a column made in this manner is very remarkable, and it enables complex organic mixtures to be separated in a state of purity hitherto unapproached. It also enables the boiling-point to be determined accurately. This arises partly from the purity of the substance obtained, and partly from the metal trays effectually preventing over-heating of the vapour.

DETERMINATION OF MELTING-POINTS.

A great many methods of determining melting-points have been published at various times; but the following is so accurate, easy, and requires so little substance that it may safely be recommended. A piece of glass tube, about $\frac{1}{4}$ inch in diameter or less, is drawn out at the blowpipe until it forms a tube of

rather less than a $\frac{1}{16}$ inch. In the act of drawing out two melting tubes are formed at once. They are to be closed at the lower ends.

The substance, the melting-point of which is to be determined, should be in small fragments. If the fragments are angular, so much the better. A clean glass beaker is then charged with water for temperatures below 100° C., and with colourless oil of vitriol for higher ones. It is to be supported by a ring of the retort-stand over an Argand burner. The substance is to be broken into very small fragments, one of which is to be dropped into the small part of the tube. A piece of copper wire is then to be twisted round the larger part of the tube, and the end is to be bent into a hook. The tube is then to be hung in the vessel of water or vitriol. The substance should be about halfway between the top and bottom of the liquid. Heat is then to be applied, and the liquid is to be slowly stirred with a delicate thermometer. The substance is to be narrowly watched, and any rounding of the angles is an announcement that the melting-point is almost reached. At last the substance will suddenly become fluid and run into the narrow tube. The mercury in the thermometer may then be read off. One or two duplicate observations are to be made, but always with fresh substance. This is because any change in the appearance of the fragment can only be observed before it has lost its form. When once it has melted into the tube it is almost impossible to get an accurate observation again. The imminent approach to the melting-point is signalled by different substances in different ways. With some it is shown by a peculiar semitransparency, followed, generally, by a rounding of the angles. This is the reason why irregularly-shaped fragments have so much advantage over round ones. The smaller the tubes the more accurate will be the result, and, after some practice, they may be made almost capillary. The wide tube may be from half an inch to an inch in length, the small one $1\frac{1}{2}$ or 2 inches. If the operator select a very small tube, a magnifying-glass may be used with advantage.

Some chemists do away with the wider part of the tube altogether. I myself greatly prefer the addition of the wide part:

it enables the wire by which the tube is hung in the fluid to be attached easily, and it serves as a funnel by which to introduce the substance.

In determining melting-points no pains must be spared in purifying the substance. A trace of impurity will often render the result utterly valueless. If it will crystallize from any menstruum, it should be purified repeatedly in that manner; and when the melting-point is no longer raised by two or three crystallizations the substance may generally be regarded as pure.

VOLUMETRIC MANIPULATION.

On a new Indicator for use in the Volumetric determination (Titration) of Acids and Alkalies.—It has been shown by G. Lunge that the dimethylamido-azo-benzolsulphonate of ammonium of Griess and Witt forms an admirable substitute for litmus in the determination of acids and alkalies. This substance is known also as the orange 3 of M. Porrier of Paris. As it is unaffected in its indications by carbonic acid or sulphuretted hydrogen, boiling the solution is unnecessary; this is a great advantage where a large number of estimations have to be made. In my own experience I have found that, in consequence of this property, four operations can be made with the new indicator in the same time as one with litmus. Different specimens of the latter substance somewhat vary in their sensitiveness to acids; that with which I worked in my comparative study of the two indicators ceased to react with sulphuric acid when more dilute than one part to fifty thousand of water. The orange 3, on the other hand, remained sensitive to one part of sulphuric acid to one hundred thousand.

The solution of the orange is made by dissolving one centigramme in 100 cub. centims. of distilled water. This quantity is sufficient for 500 alkali determinations.

From one to two tenths of a cubic centimetre of the solution are used in each analysis. When this small quantity is added to the solution containing the alkali to be tested, there is no perceptible coloration as long as it is alkaline, but the faintest trace of

acid turns the solution a pale but distinct pink tint ; this is easily seen by placing the beaker upon a sheet of white paper.

The best way of applying the test is, after each addition of acid from the burette, to allow a drop of the indicator to fall on the surface of the liquid in the beaker after the contents have been well stirred. The reason for this is that the indicator is distributed over a small space and, being less diluted, the pale pink tint is more distinctly observed. The accuracy obtainable may be seen from the following Table.

DETERMINATION OF CARBONATE OF SODIUM VOLUMETRICALLY,

Standard Sulphuric Acid 1 cub. centim.=0.051176 gramme of Carbonate of Sodium.

Carbonate of sodium taken.	Standard sulphuric acid used.	Percentage of carbonate of sodium obtained.	Indicator.
grammes. 0.4655	cubic centimetres. 9.07	99.71	Litmus.
0.9344	18.20	99.68	„
1.0646	20.75	99.75	Orange 3.
0.6739	13.15	99.86	„

The numbers obtained with ammonia and a standard hydrochloric acid were even nearer. This, perhaps, arose from increased experience in the use of the tests.

Glass Stopcocks for Burettes.—I have said, at p. 263, that the use of a glass stopcock adds to the expense of the burette without increasing its efficiency. I wish to withdraw this statement. A greatly extended experience has taught me that glass stopcocks are indispensable with some of the solutions now used in titration ; and it is better in every respect to avoid those made of caoutchouc.

Correction of Footnote at page 271.—It is hardly necessary to

say that the nature of the reaction between turpentine and bromine has been the subject of repeated investigations since the footnote was written.

Note on Litmus.—A good account of the present state of our knowledge on this subject will be found in Watts's Chem. Dict. iii. 730.

GAS MANIPULATION.

Ozonized Turpentine.—It is now stated that the oxidizing property of the terpenes is not due to peroxide of hydrogen or ozone, because it is destroyed at the boiling-point of turpentine oil, viz. 160°C ., at which temperature ozone and peroxide of hydrogen are permanent*.

Apparatus for Sulphuretted Hydrogen.—A vast number of contrivances for yielding sulphuretted hydrogen whenever wanted have been invented. Those of William Griffin and Kipp are among the best; they may be obtained at any instrument-makers. The one figured in the text (p. 281) is, however, very effective; the washing-tube *e* may be replaced by a washing-bottle with advantage.

Preparation of Carbonic Acid.—Kipp's or Kemp's apparatus (fig. 219) for yielding a supply of sulphuretted hydrogen may be employed equally well for carbonic acid by substituting lumps of marble for sulphide of iron.

Preparation of Oxygen Gas.—When oxygen gas is to be prepared from chlorate of potassium and oxide of manganese, a little of the mixture should always be tried in a test-tube. If there be any deflagration the mixture is to be rejected, as it would indicate the presence of charcoal in the manganese. Several serious accidents and one or two deaths have arisen from omitting this precaution. The manganese had been wilfully adulterated with charcoal powder for the sake of the extra profit.

Oxides of Nitrogen.—The names of the oxides of nitrogen have now been modified. The student will do well to read Hofmann's 'Modern Chemistry' on this and other subjects. It is a work of immense value to all commencing the study of chemistry.

* KINGZETT, Chem. Soc. J. [2] xii. 511.

Decomposition of Water by Sodium.—Instead of letting the sodium wrapped in paper ascend to the top of the tube containing water, it is much better to use a wire gauze spoon and, holding it with the convex surface upwards, carry it under water to the mouth of the inverted jar or tube. The hydrogen ascends and displaces the water. Sometimes it is desired to show at one and the same time the decomposition of water by the metal, and the alkaline nature of the soda formed. To do this, instead of water alone, a solution of litmus reddened by a trace of acetic or hydrochloric acid is used, and a piece of sodium wrapped in paper is passed up. As the water is decomposed, the gas accumulates in the tube, and the reddened litmus solution is turned to blue. In repeating this experiment I have often had the tube shivered to pieces; the student is therefore cautioned against doing it in this manner. The bluing of the reddened litmus can be shown afterwards.

EUDIOMETERS.

A modification of Bunsen's method of gas analysis has been made* whereby the operator is rendered independent of variations in the barometer or thermometer which may occur during the experiment. In this way of working, the gas at the time of its volume being read off is always saturated with vapour, and the ordinary calculations for reducing the observed volume to standard temperature, pressure, &c. become unnecessary. In order to accomplish this result, the elasticity of the gas is maintained constant. For details the student is referred to the original memoir.

The same chemists† have now modified the apparatus just described by introducing a separate absorption-tube or laboratory-vessel, as in the apparatus of Regnault described at p. 324 and that of Frankland and Ward given at p. 331. This alteration enables them to use liquid reagents, and thus obtain their results more quickly than could be done with solid absorbents, as in their former apparatus and as in the process devised by Bunsen.

* WILLIAMSON and RUSSELL, Proc. Roy. Soc. ix. 218.

† WILLIAMSON and RUSSELL, Chem. Soc. J. [2] ii. 238.

A still greater simplification* has been made by Russell. He abolishes the absorption-tube altogether, and performs the absorptions in the measuring-tube itself.

Estimation of Carbonic Acid in Carbonates by Weight.—In spite of the vast number of contrivances which were known at the time of writing the original work, as many more have been devised during the last 10 or 15 years. Some of them are very elegant, and could only be made by highly skilful glass-blowers. This remark applies especially to those of Kipp and Rohrbeck; but, as they do not give more accurate numbers than can be obtained with the apparatus of Will and Fresenius (fig. 271, p. 346), they need not be described here. They can, however, if desired, be obtained of any instrument-makers.

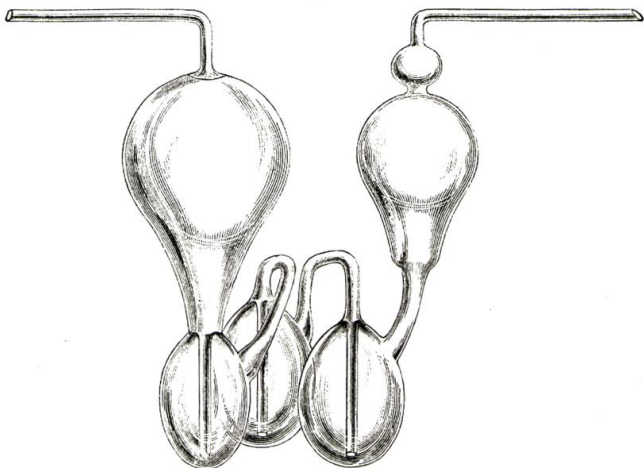
MANIPULATION CONNECTED WITH ORGANIC ANALYSIS.

The Potash-tube.—I have nothing to add to what has been said (p. 350) as to Liebig's potash-tube. It is capable, if properly used, of giving quite as accurate results as any other. Nevertheless Geissler's potash-tube has for some years been much employed in English and Continental laboratories. Its form is shown in fig. 13. It has, as may be seen, three lower bulbs, which are connected by tubes like Woulfe's bottles. I found it exceedingly useful in a particular case where Liebig's bulbs were inadmissible. I allude to the detection of traces of carbon in emeralds and beryls. In this case the three bulbs were filled to the usual height with a solution of hydrate of barium. The gas being sent through the bulbs at a regular rate, certain conclusions were able to be drawn by noticing whether the whole of the carbonic acid was absorbed by the fluid in one bulb, or whether there was sufficient to render the second one milky. It would be possible to construct an apparatus on this principle which would allow of rough approximations to the quantity of carbonic acid in the atmosphere of rooms, theatres, &c. being made in a few minutes. The principal precaution re-

* RUSSELL, Chem. Soc. J. [2] vi. 128.

quired would be to ensure absolute uniformity in the volume of the gas passing through.

Fig. 13.

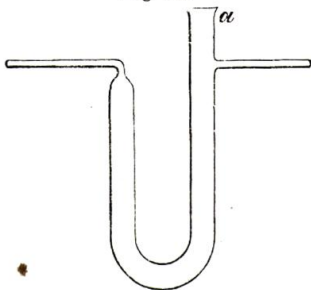


Dr. Otto N. Witt has pointed out to me that Geissler's potash-tube is unable to absorb all the carbonic acid produced in the combustion of some nitro-compounds which contain much oxygen. The substances he alludes to burn instantaneously; the potash-apparatus, under these circumstances, is not only unable to absorb all the carbonic acid produced, but it is also unable to give it a sufficiently rapid passage. The result is loss of carbonic acid from two sources, namely insufficient absorption and a sudden rise of pressure in the combustion-tube, against which even india-rubber corks are unable to contend at the temperature they are exposed to during the analysis. He obviates this difficulty by the use of soda-lime. Mulder*, it is true, has long ago used soda-lime for absorbing carbonic acid in organic analyses; but his *modus operandi* is different. The soda-lime properly granulated not only offers an easy passage for the gas, but so eagerly

* Zeitschrift f. analyt. Chem. i. 2.

absorbs it, that even the most rapid stream is at once taken up. Dr. Witt makes his soda-lime tubes of the form seen in fig. 14. After filling the tube through *a* with soda-lime, he closes with a cork which, owing to the use of the lateral tube, has no perforation, and is therefore more protected against escape of gas through defective corks &c. than when the usual form is employed. Dr. Witt employs two soda-lime tubes for each combustion: the first generally takes up all the carbonic acid formed, and the second only serves as an extra precaution; it never increases more than six decimilligrammes.

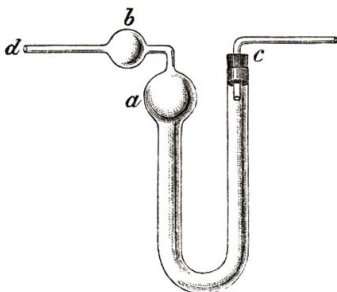
Fig. 14.



Dr. Witt prepares the soda-lime for this purpose thus:—Slack 200 grammes of the best flare-lime to a dry powder. Add 400 cub. centims. of syrupy caustic-soda solution, make into a paste; dry quickly in a large copper dish protected from the access of carbonic acid, and granulate by constant stirring.

Chloride-of-Calcium and Sulphuric-Acid Tubes.—The form of chloride-of-calcium tube represented in fig. 66 is very seldom used

Fig. 15.



now. It has the disadvantage of frequently requiring to be emptied and recharged; the water formed during the analysis also

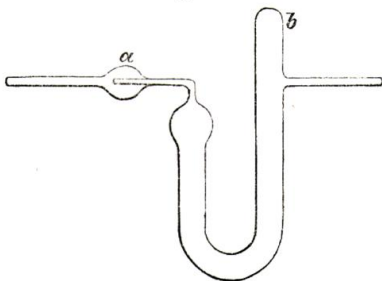
dissolves the chloride, which then crystallizes, frequently stopping up the tube. The apparatus shown in fig. 15, charged with fragments of pumice-stone saturated with monohydrated sulphuric acid, has great advantages over the old chloride-of-calcium tube. The pumice-stone should be broken into fragments about the size of pepper-corns or No. 4 shot. The bulb *a* is then to be filled with asbestos. This is easily done by selecting some that is very soft and free from lumps. It is then to be rolled into a ball and introduced at *c*, the cork and tube being removed for the purpose. The ball having been pushed into the tube, the thumb is placed over the opening, and as good a vacuum as possible is made by sucking at *d*. On suddenly removing the thumb the asbestos will be forced towards the bulb *a*. A few repetitions of the suction will enable the operator to introduce as much asbestos as may be desired. The pumice-stone is then to be warmed in a porcelain dish with strong sulphuric acid; this will decompose any carbonates or chlorides which may be present. The purified pumice-stone may then be transferred to the tube. When so much has been added that it reaches within half an inch of the cork at *c* another plug of asbestos is inserted; the cork and tube may then be put in their places, and rendered perfectly air-tight by sealing-wax.

The bulb *b* in fig. 15 has a very important use. The greater part of the water formed in the analysis condenses in it, and at the end of the operation (that is to say, after being weighed) may be expelled by a sharp jerk. By this means it is evident that the sulphuric acid will be diluted more slowly, and the tube comparatively seldom require recharging.

Dr. Witt has devised a chloride-of-calcium tube which is very convenient under certain circumstances. The tube is originally open at *b* (fig. 16) to enable it to be filled with chloride of calcium. When sufficient has been inserted, the part *b* is to be closed before the blowpipe. As all the water collects in *a* except that which is volatile at the temperature of the room in which the combustion is made, it can be shaken out when the analysis is finished. He finds that the tube may be used more than a hundred times before requiring recharging. It serves equally well for pumice-

stone and sulphuric acid, which, as a rule to which there are few exceptions, is preferable to chloride of calcium for the reasons given at p. 45.

Fig. 16.



When the substance is to be burned in a current of air or oxygen, or in both, the straight tube (fig. 66) is quite inadmissible, the current of air or gas would be very liable to pass over so short a distance too rapidly to allow of complete desiccation. The hydrogen would then be liable to come out too low; and this is one of the worst faults that can occur in an organic analysis.

Corks for Combustions.—Wooden corks, if the expression may be permitted, are now very rarely employed in organic analyses. They have been completely superseded by vulcanized india-rubber. They should be selected of several sizes, so as to enable all the combustion-tubing used in the laboratory to be fitted; or, still better, let the combustion-tubing be carefully selected in three sizes only, as directed at p. 356, and then only three sizes of combustion-corks will be required.

The above precautions, if followed, will save much trouble, because it is not easy to cut caoutchouc corks in such a manner as to perfectly preserve their form. When it is required to cut them down, the knife must be very sharp and be wetted with solution of caustic soda. The caoutchouc cork may be readily pierced with a cork-borer moistened with solution of caustic soda. It is, perhaps, hardly necessary to remind the student that, if no solution of soda be at hand, the combustion-potash will do as well.

Some chemists, instead of an alkaline solution, use oil to facilitate the use of the cork-borer. The caoutchouc combustion-cork should be well rubbed with black-lead before being inserted in the combustion-tube; this will prevent it from adhering during the heating, and it will therefore enable it to be removed with ease after the operation.

Combustion-tubes.—As organic analyses are now almost always made in a gas-furnace, the very hardest and best quality of glass tubing must be selected. If protected by a hemispherical trough running the whole length of the furnace, and lined with asbestos, the tube may be used several times in succession.

It has been said (p. 382) that when nitrogen determinations are made very frequently, gun-barrels are frequently substituted for glass tubes. To show how easily they may be worked, I may mention that, many years ago, I made five nitrogen determinations a day for months together in gun-barrels. Of course the process used was that of Varrentrap and Will, but using a standard solution of sulphuric acid. The use of iron is advocated for combustion-tubes by Cloez*. He uses a tube of 1.15 metre long and 0.020 to 0.222 in diameter. He covers the inside with a layer of oxide. For this purpose he heats it to redness and passes steam through it. It projects 0.2 metre beyond the furnace both at the anterior and posterior ends. In the middle is placed the cupric oxide in a granular condition. This cupric oxide may be kept in its place by copper foil, and into each end is pushed a semicylindrical gutter or tray of sheet iron; it has a wire attached for facilitating extraction.

If the substance to be analyzed contains nitrogen, the anterior tray, which is two decimetres in length, is filled with metallic copper. If the substance contains chlorine or sulphur, the copper is replaced with chromate of lead; if the substance be difficult to burn, the tray is filled with cupric oxide or chromate of lead. When the arrangement is complete the tube is heated to redness; a slow stream of air is sent through it, so as to render the contents perfectly dry. The cupric oxide, in the hinder tray, when

* CLOEZ, Ann. Ch. Phys. [3] lxviii. 291.

sufficiently cool, is mixed with the substance to be analyzed in an iron capsule. The carbonic-acid apparatus and the hydrogen tube are then attached to the anterior part of the apparatus, the tray containing the substance having been previously put in its place. The combustion is carried on in the usual manner in a current of air. Of course the precautions universally taken to remove moisture and carbonic acid from the air are not omitted.

Reduced Copper turnings.—The fact that copper turnings and gauze, when reduced in hydrogen, occlude some of the gas, is undoubtedly true; but, at the same time, I think that the error from this source has been sometimes exaggerated. That the occluded hydrogen, when heated in air or oxygen, forms water, is proved by the fact that, at the commencement of the heating, and long before the substance is reached, a dew is formed in the front of the tube which is gradually carried into the hydrogen apparatus. This, according to my experience, is invariable; but, on the other hand, I have found in hundreds of analyses the excess of water not to exceed one or two tenths of a per cent.

Some substances tend much more than others to have their nitrogen converted into nitric acid and oxides of nitrogen, which are arrested in the potash-bulbs. This often occurs with products containing a very moderate percentage of nitrogen. I have known platinum salts, containing 3 or 4 per cent. of nitrogen, obstinately to yield much more carbon than that required by theory; while substances containing 13 or 14 per cent. gave, with the *same amount of copper*, less than one tenth of a per cent. in excess. The nitrate of lepidine, a substance which would be supposed to yield high hydrogens and carbons, gave, in three analyses, the following numbers:—

	I.	II.	III.	Mean.
Carbon	57.69	58.40	58.24	58.11
Hydrogen	4.93	4.90	4.98	4.93
Nitrogen
Oxygen

While theory requires :—

Carbon	58·25
Hydrogen.....	4·86
Nitrogen	13·59
Oxygen	23·30
	<hr/>
	100·00

Now, in this case, a long column of reduced copper gauze was used, so that the occluded gas might have been expected to yield a very high result in hydrogen, whereas the mean of three experiments only gives 0·07 in excess.

My friend Dr. O. N. Witt has pointed out to me that Leitzenmayer* heats the plugs of reduced copper gauze before use to 200°–250° C. in an air-bath. This will produce a slight film of oxide. He then heats them to dull redness in a tube sealed at one end, and having a very fine orifice at the other; the occluded hydrogen at this temperature will attack the oxide and reduce it. This completely agrees with my own experience, as I have repeatedly observed, with plugs of gauze which had in the process of drying become somewhat dulled, that the moment heat was applied to the front of the tube they regained their lustre, and a dew was simultaneously deposited on the cool part of the combustion-tube.

It is probable that the amount of hydrogen occluded varies with the temperature at which the reduction is effected.

Stein states that the reduced copper used in the analysis of substances containing nitrogen becomes oxidized when the substance is burnt in a stream of oxygen; he therefore uses silver in its stead. Calberla† has shown that that metal completely reduces nitrogen-dioxide to free nitrogen, but has no effect whatever on carbonic acid. Silver also arrests any chlorine and bromine the substance may contain. It has been attempted even to determine those elements quantitatively in this manner; but, as far as I have been able to ascertain, the results are variable.

It is a remarkable fact that the organic analyses of the present

* LEITZENMAYER, Ber. d. D. chem. Ges. xi. 306.

† CALBERLA, Bull. Soc. Chim. [2] x. 382.

day, in spite of the numerous alterations in the apparatus used by some chemists, are, as a rule, not more accurate than those published fifteen or twenty years ago.

Some chemists, in spite of the beautiful simplicity and accuracy of the process of Liebig, are endeavouring to return to methods resembling, more or less, those of Gay-Lussac and Thénard and Prout. Some of these will be dealt with very briefly. Ladenburg* determines the carbon directly by the quantity of carbonic acid formed; and the amount of oxygen consumed is also noted, so that the hydrogen is found from the difference between the total quantity of oxygen consumed and that required for the combustion of the carbon. The oxygen is obtained from iodate of silver mixed with strong sulphuric acid. The mixture alone, even when heated to 300°C. , does not give off either iodine or oxygen; but, if an organic substance be present, carbonic acid and water are formed by reduction of the iodic acid; the hydriodic acid and iodine, formed at the same time, react on the iodic acid present in large excess as silver salt, so as to produce iodine and water.

Another method, still more resembling that of Gay-Lussac and Thénard, inasmuch as the substance is mixed with chlorate of potassium, has been devised by Schulze†. If this process were to prove accurate in the hands of ordinary manipulators, it would, under certain circumstances, prove invaluable, inasmuch as he only uses 0.010 to 0.012 grm. of substance. The mixture is burnt at a low red heat in a combustion-tube, from which all air has been removed. The gases produced are transferred to a eudiometer and analyzed. The total volume is first determined, and the amount of carbonic acid is estimated in the usual way. The carbonic acid occupies the same volume as the oxygen contained in it; consequently, after burning of a carbohydrate ($\text{C}_n\text{H}_{2m}\text{O}_m$), the volume of the oxygen in the eudiometer corresponds to the oxygen in the chlorate of potassium; if, on the other hand, the volume of gas is greater, the substance must

* LADENBURG, *Ann. Ch. Pharm.* cxxxv. 1; also *Watts's Chem. Dict.* 1st Supplement, p. 143.

† SCHULZE, *Bull. Soc. Chim.* [2] viii. 263.

have contained more oxygen than that required to burn the hydrogen in it; if smaller, the substance must contain more hydrogen than a carbohydrate.

Estimation of Oxygen in Organic Compounds.—Maumené*, instead of oxide of copper, uses litharge containing 25 per cent. of phosphate of lime; this is added to prevent fusion. In addition to the carbonic acid and water obtained in Liebig's process, he obtains metallic lead. After the analysis the contents of the tube are mixed with twice its weight of pure litharge and fused. By this means the reduced lead is converted into a fused button, which has to be cleaned and weighed. The oxygen of the substance is found by deducting the oxygen, equivalent to the lead, from that contained in the carbonic acid and water.

Von Baumhauer† has published two processes for determining carbon, oxygen, and hydrogen simultaneously, which, in his hands, have certainly given admirably accurate results.

In the first process he takes a glass combustion-tube, open at both ends. One end is connected with the ordinary apparatus of Liebig for determining carbonic acid and water. The substance is mixed with oxide of copper. The two ends of the apparatus are connected with graduated glass tubes. That at the posterior end is filled with oxygen gas. When the combustion is finished, the oxygen is passed through the combustion-tube, and by this means the reduced copper is reoxidized. When the apparatus has cooled to the temperature of the atmosphere, the volume of the gas in the graduated tubes is noted. The potash-bulbs and the chloride-of-calcium or sulphuric-acid tube are then weighed. Correct the apparent volume of the gas for temperature and pressure, and deduct the volume found after the combustion from what had been observed before the process: the difference gives the quantity of oxygen required to reoxidize the copper. Now calculate the quantity of oxygen in the carbonic acid and water formed, and deduct from their sum the oxygen required to reoxidize the copper: the remainder is the oxygen contained in

* MAUMENÉ, Compt. Rend. lv. 432.

† VON BAUMHAUER, Ann. Ch. Pharm. xc. 228; also FRESSENIUS, 'Quantitative Analysis,' 6th edit. 479; Watts's Chem. Dict. i. 239.

the substance analyzed. As, from the nature of the apparatus the total amount of gas in it cannot be exactly determined, any great variation in the temperature and the height of the barometer would seriously affect the results. Any alteration in the form, and therefore capacity, of the combustion-tube would also introduce error.

Von Baumhauer* has modified the above method with the view of attaining greater accuracy; but it is not shown that greater accuracy has been obtained by the sacrifice of simplicity; and it must not be forgotten that in delicate analyses complication is the fruitful mother of error. There are, however, so many cases in modern chemical research where the direct determination of oxygen is of great importance, that it would be improper to omit the most refined methods; the more especially as they will be eventually simplified, without sacrificing accuracy. A combustion-tube, similar to that employed in the first process and 70 or 80 centimetres long, is packed as follows, commencing at the front end:—1. A plug of copper turnings 20 centimetres in length. 2. 20 centimetres of fragments of porcelain, washed with hydrochloric acid and ignited. 3. 25 centimetres of coarse-grained oxide of copper, previously strongly ignited; this layer is kept in its place by plugs of asbestos. 4. The substance contained in a porcelain or platinum boat, or, if a liquid, in a glass bulb, which is pushed into the tube to within 5 centimetres of the oxide of copper. If the substance be solid and difficult of combustion, it is mixed with oxide of copper and placed in the porcelain or platinum boat. 5. At a distance of 6 or 7 centimetres behind the substance, a few grammes of iodate of silver are placed in a porcelain boat. The posterior end of the combustion-tube is connected (by means of a tube containing ignited copper turnings with a U-tube filled with pumice-stone soaked in sulphuric acid, and a second containing chloride of calcium and soda-lime) with two gasometers, one filled with pure nitrogen, the other with hydrogen. Before attaching the hydrogen apparatus and the potash-tube, the front part of the combustion-tube,

* VON BAUMHAUER, *Zeitschr. anal. Chem.* v. 141.

containing the 20 centimetres of copper turnings, is heated, and a slow stream of hydrogen is passed through until the copper is completely reduced. The hydrogen is then displaced by nitrogen. The potash-bulbs and the hydrogen-tube (by which we always mean the apparatus for collecting the water formed in the analysis) are then attached, and the porcelain boat and the oxide of copper are heated in a slow stream of nitrogen. When the whole apparatus is filled with nitrogen, and the potash solution is also saturated with that gas, the potash-bulbs and the hydrogen-tube are removed, weighed, and again replaced in their previous position. The substance is now to be carefully heated, the stream of gas continually being kept up. As soon as the substance is completely burned, or, at least, completely carbonized, the iodate of silver is gradually heated, by which proceeding the remaining carbon is burnt, and the reduced copper reoxidized, the excess of oxygen being retained by the copper turnings. When the iodate of silver is completely decomposed, the stream of nitrogen is continued for some time; the potash-bulbs and hydrogen-tube are then removed and weighed. The fire is now removed from all parts of the tube except where the copper turnings are, but the stream of nitrogen is still kept up. When the oxide of copper is quite cold, a weighed chloride-of-calcium tube is attached, and a stream of hydrogen is sent through the apparatus. The excess of oxygen given off by the iodate of silver, and which had been absorbed by the copper turnings, is thereby converted into water; and this weight corresponds with the quantity of oxygen contained in the iodate of silver, more than was necessary for the combustion of the substance.

Let us now see what greater exactitude Von Baumhauer attained with this process over the first and comparatively simple one. The substance was in each case oxalic acid.

	1st process.	2nd process.	
	Found.	Found.	Calculated.
Carbon	26.71	26.73	26.66
Hydrogen	2.28	2.21	2.23
Oxygen	71.32	71.39	71.11
	<hr/> 100.31	<hr/> 100.33	<hr/> 100.00

Any chemist who has had much experience in organic analysis will see, from the above numbers, that the difference between the two analyses is too slight to enable him to pronounce in favour of the more complex process.

A process for the determination of the oxygen in organic compounds has been devised by Stromeyer*. It depends upon the determination of the amount of copper reduced during the combustion. The residue is heated with a solution of ferric chloride and hydrochloric acid, or ferric sulphate and sulphuric acid. The ferrous chloride or sulphate is determined with permanganate. For details, the student is referred to the original memoir, or to Fresenius's 'Quantitative Analysis,' 6th edit., p. 479.

A. Mitscherlich† has invented three processes for organic analysis. The first has this peculiarity, that the combustion is made in a current of chlorine. The mode of proceeding may be briefly described as follows:—When an organic substance is heated to redness in chlorine free from oxygen, the hydrogen is converted into hydrochloric acid, and may be determined in that form; but the oxygen unites with its carbon, or with charcoal added, forming carbonic oxide and carbonic acid, from which the amount of the oxygen in the substance may be calculated. The combustion-tube is of porcelain, 0·6 metre long, and 9 millimetres internal diameter, and is half filled with charcoal. If the substance is not volatile below 150° C., it is enclosed in a glass tube open at both ends; if volatile below 150° C., it is placed in a glass apparatus of peculiar construction. The gases are enclosed in a graduated jar immersed in water, and are passed into the combustion-tube by a tube attached laterally to that conveying the chlorine. The gases produced by the combustion are passed into Mitscherlich's absorption-bulbs. The hydrochloric acid, produced from the combustion of the hydrogen, is absorbed by a concentrated solution of nitrate of lead, which, according to Mitscherlich, does not absorb free chlorine. The carbonic acid

* STROMEYER, *Annal. d. Chem. u. Pharm.* 117, 247.

† A. MITSCHERLICH, *Pogg. Ann.* cxxx. 536, and *Bull. Soc. Chim.* [2] x. 378; also *Watts's Chem. Dict.* 1st Supplement.

is absorbed by potash; but it must be first freed from chlorine by passing the gases through an alcoholic solution of stannous chloride or ferrous sulphate. The carbonic oxide is absorbed in a series of bulbs filled with a solution of cuprous chloride and hydrochloric acid. I think that this method of absorbing the gases is liable to error.

2. In determining carbon, sulphur, the halogens, and nitrogen, the substance is heated in a current of hydrogen, and the mixture of the vapour of the substance, or the products of its decomposition, is burnt in a current of oxygen. The process will not be further described, as it appears to contain certain sources of error. The student desirous of studying it can find the method at length in the references given.

3. Mitscherlich describes also a third and simplified method, by which carbon, hydrogen, and oxygen can be determined in a single operation. In this process the substance is burnt with platino-chloride of potassium, which, under the circumstances given, parts with its chlorine when heated with organic substances.

The substance is introduced into a porcelain tube filled with a mixture of pumice-stone and platino-chloride of potassium, enough of the latter being added to contain about 8 grammes of platinum. The air of the apparatus is driven out by a current of nitrogen gas, and the tube is heated to redness. The water is absorbed by phosphoric acid, hydrochloric acid by nitrate of lead, free chlorine by stannous chloride, and carbonic acid by potash. The products of the combustion are driven into the absorbing-apparatus by a current of nitrogen; the whole is left to cool; and the various pieces of apparatus for absorption are weighed.

The porcelain tube is again heated to redness, and a current of oxygen gas is passed through it; the carbon left is converted into carbonic acid, which is absorbed in the same apparatus. To avoid loss of carbon from the formation of a solid difficultly oxidizable chloride, a glass tube containing oxide of copper is introduced into the porcelain tube, and the vapours of the chlorinated body are passed over it and the carbon is burnt completely.

The combustion-tube, after the operation, contains a mixture of pumice-stone, metallic platinum, and potassium chloride. By passing a current of chlorine through it the author states that it becomes fit for a fresh analysis.

It not unfrequently happens, in organic research, that the substances are exceedingly difficult to procure in quantity; and the difficulties of the investigation are increased when, as is quite common, certain of the elements contained in it yield accurate numbers, while one refuses to give a correct result. In such a case we should advise the student to determine the carbon, hydrogen, and oxygen by Baumhauer's first process; the other elements, if present, such as sulphur, chlorine, bromine, &c., separately by the processes given in manuals of analysis.

Combustion of substances which leave a residue on distillation.—It has been stated, at p. 371, that liquids and other substances which have a very high boiling-point, and leave a residue in the bulbs, may be weighed, and placed in the combustion-tube, in a short tube supported, while on the balance-pan, by a small stand of tin plate. A longer and more extended experience has shown me that, with all the precautions there given, even when the combustion is carried on in a current of oxygen gas, a trace of carbon may remain unburnt at the bottom of the tube. This probably arises from the oxide of copper filling the tube, and preventing the oxygen from coming in contact with the carbon. From whatever source the error may arise, it can be prevented by dropping into the tube a small fragment of chlorate of potassium. At the end of the analysis enough oxygen will be liberated to convert the carbon into carbonic acid. The results of a combustion should always be mistrusted if even a trace of reduced copper be found at the bottom of the tube after the analysis. Where many analyses have to be made on the same substance, a scratch with a diamond should be made on the tube; this will enable nearly the same quantity to be used in each combustion, and save time in the preparations for the analysis. The most inexperienced need hardly be told that this does not do away with the necessity for an accurate second weighing.

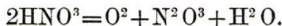
Combustion of very volatile liquids.—Since writing the ac-

count of the way in which I burn very volatile liquids, described at p. 372, and shown in section in fig. 294, I have had much more experience of it, and I still consider it more rapid and accurate than any other plan that I have yet tried. Even isoprene*, which boils at 37° C., and has the troublesome property of leaving a film of carbon in the bulbs, gave, as a mean of five combustions:—

	Found.	Calculated.
Carbon.	88.0	88.2
Hydrogen	12.1	11.8

The excessive volatility of this substance, rendering it necessary to keep all the apparatus and materials very cold, made an exact determination of the hydrogen as difficult as that of the carbon.

Estimation of Sulphur, Iodine, Chlorine, and Bromine in Organic substances.—The method of burning organic substances containing sulphur is described at p. 376; since that description was written, Carius† has described a new and excellent method of determining sulphur and the halogens in organic substances. He treats them with nitric acid, of a specific gravity of 1.5, in sealed tubes. The acid is prepared by heating pure red fuming nitric acid of a specific gravity of 1.57 in an open flask. It is better, however, to grind a glass tube to the neck of the flask and to convey the fumes out of the laboratory. As to the quantity of the acid required for the purpose it should be about twice that required by the equation



The operation is a short one, never more than an hour and a half, and even then the first half-hour is expended in attaining the proper temperature. This temperature depends upon the substance to be acted on, and varies between 150° C. and 330° C. For example, substances which are readily attacked do not require a heat higher than from 150° to 200°. Substances belonging to the aromatic series will require from 250° to 260°; wood-charcoal disappears rapidly at the same temperature; traces

* Phil. Trans. 1860.

† CARIUS, Ber. d. D. chem. Ges. iv. 697.

of organic matter, however, remain in the solution; but if the temperature be raised to 300° , all the carbon present is converted into carbonic acid. Graphite takes two hours at from 300° to 330° to convert all its carbon into carbonic acid.

The combustion-tubes should be from 18 to 20 inches in length, and about half an inch internal diameter. The quantity of nitric acid should not be more than 4 grammes to an internal capacity of 50 cubic centimetres. This quantity is workable with ease, as even mercaptan, which requires more acid than most substances, only requires 4.4 grammes of nitric acid for 0.24 gramme of substance.

We have described above, at p. 29, an apparatus which enables tubes containing corrosive acids to be heated under pressure without danger to the operator.

When the oxidation of the organic matter and the sulphur or halogen is complete, the combustion-tube is opened and cold water is cautiously added; nitric oxide is then freely evolved, and care must be taken against loss of liquid by spirting.

If sulphur is to be determined, it will be found that, owing to the small amount of nitric acid used, the sulphate of barium will easily be freed from nitrate of barium by washing with boiling water. Chlorine, bromine, or iodine are determined by adding nitrate of silver to the contents of the tube after washing out into a beaker. When iodine is to be estimated and nitrate of silver is added to the contents of the tube in the necessary excess, the two melt into a yellow mass: this must be heated for two or three hours in the dilute acid to remove the nitrate.

We have said that Stein and Calberla prefer silver to copper in front of the combustion-tube when nitrogenous substances are to be burnt. The latter, as we have said, asserts that chlorine and bromine are completely arrested by silver. Kraut* remarks that when substances containing chlorine, bromine, or iodine are analyzed with oxide of copper in a current of oxygen, a plug of metallic copper should be placed in the front of the tube followed by a roll of silver leaf 5 inches long. The silver will retain the whole of the halogen, even when oxygen is passed over it, and

* KRAUT, *Zeitschr. anal. Chem.* ii. 242.

may be used many times before its surface requires to be renewed by reduction in a stream of hydrogen. I can confirm this, having seen many analyses made in this manner.

Determination of Nitrogen.—An excellent process for determining nitrogen has been devised by Dr. Maxwell Simpson*. It has the advantage of being available even with the most difficultly combustible nitrogenous organic compounds. In some respects it resembles Dumas's process, but the apparatus used is very different; for a description of it the reader is referred to the original memoir, or the other references given.

My friend Mr. J. T. Brown has rendered a great service to all those who do many nitrogen-determinations by calculating the expression $\frac{\cdot 0012562}{(1 + 0\cdot 00367 T 760)}$ for all values of T, from 0° to 30° C.†

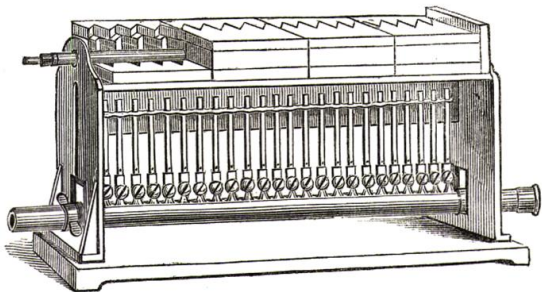
Gas-Furnaces for Organic Analyses.—The furnace invented by Dr. Hofmann (p. 390) is now quite superseded. Even Dr. Hofmann himself has abandoned it in favour of another form. There are at least twelve, and probably a still greater number of other forms. The one I use myself is Griffin's, and I have never had an accident with it due to any fault in the furnace. It consumes a moderate amount of gas, and any temperature can be obtained which the hardest combustion-tubing will endure. As I am unable to find any fault with it, it is the only one which I shall describe. It is represented in perspective in fig. 17. In common with most of the combustion-furnaces of the present day it is heated by a row of Bunsen's burners; they are placed so near each other that no part of the combustion-tube escapes being heated; and, if only the commonest care be taken with the stop-cocks which supply the burners, any amount of heat can be given to any part of the combustion-tube, from a heat far below redness to one capable of fusing the hardest tubing that can be obtained. Above the flame from the burners is placed a double row of fire-clay tiles of a peculiar form, which we shall describe

* SIMPSON, Chem. Soc. J. vi. 299; Fresenius's Quant. Anal. 6th edit. p. 489; Watts's Dict. Chem. i. 243.

† J. T. BROWN, Chem. Soc. J. [2] iii. 211.

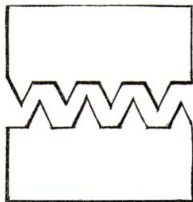
presently. They rest upon two thick plates of iron, reaching from end to end of the furnace, which are fastened to stout upright iron supports. A simple contrivance at the back of the tiles prevents

Fig. 17.



them from falling out of their places. Upon the two plates of iron, which we have above alluded to, are placed two rows of fire-clay tiles with triangular points (fig. 18), and so arranged that, as the points of one tile correspond to the hollows in the other, they can be placed at any distance from each other: this gives the operator complete control over the heat, as, if placed very closely together, scarcely any flame reaches the combustion-tube; and if at a considerable distance, the whole power of the Bunsen's burner is exerted upon the tube. The triangular points of the fire-clay tiles answer to the grate of the furnace upon which the combustion-tube rests. These tiles are 4 inches long, 2 inches wide, and $\frac{1}{2}$ inch thick.

Fig. 18.



Upon the grate just described is placed another double row of tiles of the same length and breadth as the former ones, but 1 inch in thickness instead of $\frac{1}{2}$ an inch. They are placed on each side of the combustion-tube, and keep it in its place, as seen in fig. 19. The flame of the Bunsen's burners penetrates through the hollows between the points. As a rule, these tiles are kept close to the

combustion-tube, but they may be moved to any distance to and from it which the exigencies of the operation may require. On the top of the last-described double row of fire-clay tiles, another double row like the first, fig. 18, is placed. The use of these is important, because, if put closely together, they make the flame reverberate upon the top of the combustion-tube, and thus equalize the heat of the top and bottom of the tube. The illustration, fig. 20, shows the general arrangement of the combustion-tube and the tiles, as seen in cross section. The combustion-tube is

Fig. 19.

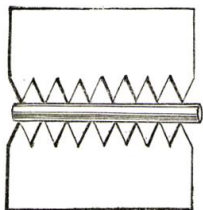


Fig. 20.

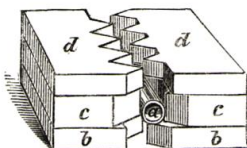


Fig. 21.



seen at *a*, supported by the first layer of tiles of the form seen in fig. 18; *c c* are tiles of the shape given in fig. 19, and which keep the combustion-tube in its place. The tiles which cause the flame to reverberate down upon the combustion-tube are seen at *d d*, and they are, as we have said, of the form of those shown in fig. 18.

To prevent the over-heating of the iron plate at the end of the furnace, and, consequently, of the corks, a perforated clay plate, represented in fig. 21, is placed at each extremity of the furnace. After the gas has been lighted a short time, all the points of the fire-clay tiles become red hot; but whether a dull or bright red, depends upon the arrangement of the tiles and the amount of gas turned on. If the bottom row of tiles be removed further from each other, the tube will have the blue flame playing direct upon it, and the heat will become so great that care must be taken to prevent it being melted. As far as my personal experience with this apparatus goes, and it is considerable, nothing is easier than to obtain any heat required, high or low.

The horizontal main-pipe can either be supplied with gas at one end or both: I have always found one end quite sufficient;

the other end can then be closed with a cap which is provided for that purpose.

The stopcocks can be opened, shut, or adjusted either with a long-beaked pair of pliers or with a clamp provided for the purpose. One or the other must be provided, as, when the combustion is well advanced, the heat radiated downwards is too much for the fingers to bear.

As the heat of the furnace is very intense towards the end of the combustion, it is necessary to protect the tube, so as to prevent it blowing out. This may be done by laying it in a trough of sheet iron with a layer of asbestos at the bottom. I myself, however, prefer a tube of coarse iron-wire gauze, especially in the analysis of very volatile liquids, as I find that the trough or gutter of sheet-iron conducts the heat to the bulbs (or rather bulb, for I use but one, § 602), and thus sometimes causes the distillation to commence too quickly. After the analysis is over, a sheet-iron trough, reversed, should be placed over the Bunsen's burners to prevent dirt falling into them.

As regards the gas-holders, and the apparatus for collecting the water and carbonic acid, the arrangements already described in § 625 will do very well. The chloride-of-calcium tube B, p. 391, should, however, be replaced by a U-tube of the same form, filled with fragments of pumice-stone, moistened with monohydrated sulphuric acid.

I have, of late, replaced the gasometers with very large india-rubber bags standing each on its own table, and having pressure-boards which can be weighted to any desired extent. By the use of bags of this kind I have had a supply of oxygen, hydrogen, or air carried to each laboratory; and in some researches this is a great convenience. A few staples, a good supply of tin or lead gas-tubing, and a few stop-cocks, will enable the operator, or his assistant, to put the gas-supply apparatus up themselves with greater ease, rapidity, and accuracy than if they employed a workman.

It is hardly necessary to remind the operator that the combustion is almost invariably commenced in a current of air, the oxygen being reserved for the end of the operation.

The small glass trays or boats described in § 604 I have long abandoned in favour of platinum. The platinum boats have the great advantage of enabling not only the carbon and hydrogen, but also platinum, gold or ash, to be determined at the same operation.

When it is required to prepare a large quantity of oxygen, I take 30 or 40 gallon sheet-iron cylinders, such as are used for the carriage of aniline or other chemicals, and convert them into gasometers for storage; the india-rubber bags or the laboratory gasometers can be filled from them with the greatest ease.

The perforated tile (fig. 21) is also made with a slit instead of a circular hole for those who prefer that form. It has the advantage of being more readily removed without moving the combustion-tube.

CUTTING GLASS.

By a gas-flame.—The method of cutting glass by spring-coals or pastilles, given at p. 402, is exceedingly convenient where there is no gas supply; but where gas can be obtained the following method is preferable:—Draw out a piece of the hardest glass, and, at the same time, thicken it until the aperture will only admit a very fine needle. Connect it with the gas-pipe by an india-rubber tube, and so adjust the tap of the latter that you have a flame not larger than a hemp-seed. This flame is perfectly manageable and will cut any thing, from a carboy holding ten gallons to the smallest flask.

GALVANIC BATTERIES.

Since this work was written, a vast number of batteries have been invented for different purposes. It would be quite out of place to describe or even enumerate them all, as, in many cases, they are of a very limited application.

Smee's Battery.—We have nothing to add to what we have said about this excellent and cleanly arrangement, except that it is about the most constant of all batteries with only one cell.

Grove's Battery.—This form has retained all its old popularity, where an exceedingly powerful electromotive force is required.

Daniell's Battery.—The strength of the dilute sulphuric acid was given, in the body of the work, the same as for Smee's battery, namely 1 to 12. It is better to be somewhat more

*See from
Simple
Myer*

dilute than this, namely, 1 of acid to 20 of water. If properly put together, it will often work electric apparatus not requiring very high electromotive force for 12 months at a time.

Bunsen's Battery.—This form of battery comes next in electromotive force to Grove's, and is therefore much used for the electric light, where it is not convenient to employ dynamo-electric machines. It is usual now to make the carbons in the form of a square prism.

Leclanché Battery.—This is a battery intended for currents of low electromotive force but great constancy. It has the peculiarity of becoming very weak for a time after being used, but it recovers itself on standing. It consists of two cells. The inner one is porous and contains a rod of carbon with a leaden top-piece, to which is attached a binding-screw; the cell is then nearly filled with equal parts by volume of manganic dioxide and gas-retort carbon in fragments. When the fragments nearly fill the cell, pitch is poured in until it is quite filled. But while the pitch is being poured in, two iron rods are placed vertically on opposite sides of the porous cell, and touching the carbon and manganese. After the pitch has solidified the rods are removed, leaving two holes; they allow of the escape of air, and enable the exciting fluid to rise in the porous cell. The latter is then placed in an earthenware or glass outer cell, and a saturated solution of sal-ammoniac is poured in to within an inch and a half of the top of the inner cell. A zinc rod, to which a copper wire is attached, is then placed in the outer cell and the battery is complete. The time they keep without requiring to be re-charged is remarkable. I have had them in action for 12 months, and yet they still did their duty to perfection.

The Bichromate Battery.—This, like Smee's, is a one-cell battery, with two carbons and one zinc. It has great advantages for lecture illustration, as it evolves no offensive gases, and it is very convenient for persons who are conducting investigations, as it enables them to obtain a strong current at a moment's notice. It is generally made in the form of a flask with a very wide neck. The flask has a brass cap attached to its neck, through the centre of which a wire slides, which carries a binding-screw at the upper

end. To the lower end is attached an amalgamated zinc plate. The method of amalgamating zincs for batteries is described at p. 419. When not in use, this movable wire enables the zinc plate to be drawn up into the neck of the instrument; and as the exciting liquid only reaches its commencement, it is evident that when the zinc plate is in the neck there is no action going on. The brass cap has two other wires in it ending in binding-screws, one of which is on each side of the central one carrying the zinc. Each wire carries a plate of gas-retort carbon; therefore when the battery is in action, the two carbon plates are parallel to, and one on each side of, the zinc.

It is evident, from what has been said, that the size of the plates is only limited by the size of the neck of the flask. The power of arresting all action on the zinc in a moment is a very great convenience. Its elegance of form recommends it for use on the lecture-table. The bichromate battery is charged with a solution prepared as follows:—A quantity of boiling water proportionate to the size of the flask is poured upon an excess of bichromate; if, therefore, all the bichromate dissolves, more must be added until it is evident that the salt is in excess. When it is somewhat cooled add one tenth part of oil of vitriol. It must be remembered that pouring oil of vitriol into hot, or even warm, solutions always involves more or less danger; the sulphuric acid tends to combine with water with great avidity, and so much heat is given out that dangerous explosions often occur and the corrosive acid is thrown about. The acid must therefore be added to the bichromate solution very slowly and with constant stirring. The plates must be reamalgamated from time to time, as may be required.

Byrne's Pneumatic Battery.—A battery of extraordinary powers is described under the above name by Mr. Wiesendanger*. I have as yet had no experience with it; but if it has only a portion of the power attributed to it, it will considerably modify our views as to the loss by polarization in batteries generally. One plate is compound, and made up of platinum, lead, and copper; the other is a

* WIESENDANGER, *English Mechanic*, Dec. 6, 1878.

sheet of zinc. As in the battery last described, only one solution is employed, namely, a saturated aqueous solution of bichromate of potash with one tenth of its volume of sulphuric acid added to it. Each cell contains perforated tubes through which air is pumped into the liquid. The exciting liquid is thus in a continual state of commotion, therefore lessening internal resistance and perfectly preventing polarization. With such a battery of four cells (the size of the plates is not stated), pieces of platinum wire several feet in length have been raised to a white heat and fused.

Meidinger's Battery.—Daniel's battery, in spite of its excellent qualities, has one defect—the copper is, in time, deposited upon the porous cell, gradually rendering it useless. This has caused the introduction of several forms of battery in which the porous cell is dispensed with; they are known under the general name of gravity-batteries. A cylinder of copper rests at the bottom of the cell, and another of zinc rests on a shoulder in the cell some inches higher up, or on projections made for the purpose. The lower cylinder—the copper one—is immersed in a saturated solution of sulphate of copper, and the zinc one in a solution of sulphate of magnesia. They remain separate in virtue of their different specific gravities. A flask full of crystals of sulphate of copper is then filled with solution of sulphate of magnesia, a cork containing a glass tube, open at both ends, is fitted to the flask, and the latter is inverted in the cell. The mouth of the glass tube must reach the solution of sulphate of copper, and should be, when in its place, about halfway between the top and the bottom of the copper cylinder. The sulphate of magnesia dissolves some of the sulphate of copper, and by becoming denser than the sulphate of magnesia in the cell, causes a constant flow in two directions through the tube in the neck of the flask; the heavier liquid which contains sulphate of copper descends, while the sulphate of magnesia ascends, and in its turn dissolves more sulphate of copper and again descends. This goes on until nothing but a saturated solution of sulphate of copper exists in the lower part of the cell, in fact up to the tube in the neck of the flask. Two wires are used as terminals: one is attached to the zinc in the upper part of the arrangement, the other to the copper; the latter

is insulated wherever it touches the liquid by gutta percha. This battery has very little power, but is useful where a weak but constant current is required for a long time. If the circuit is not very frequently closed it will act for many months. For myself, when requiring a low but constant power, I greatly prefer the Leclanché cell.

A great number of other batteries are now in use for special purposes. M. Gaiffe has invented a chloride-of-silver battery for use in medical electricity. Messrs. De La Rue and Müller have also, and I believe previously to M. Gaiffe, invented a chloride-of-silver battery which they have made use of in their important researches. Menotti has devised a form of Daniel's battery. It has a plate of copper at the bottom of the cell; this is covered with sulphate of copper, a layer of sand is placed above this, and the zinc is placed on the top.

The student desirous of knowing all the kinds of batteries in use should consult the catalogues of the various scientific instrument-makers; but there are very few researches which may not be carried out with Bunsen's, Daniel's, or the Leclanché. I prefer the latter to the gravitating batteries on the Daniel principle, from the fact that it may with safety be used anywhere; and the solution of sal-ammoniac, if spilt, is neither corrosive nor poisonous. This is especially important, as weak batteries are so much employed for electric bells, microphones, and other apparatus used in the house.

MISCELLANEOUS OPERATIONS.

To the student ardently desirous of pursuing the study of chemistry and physics experimentally, I cannot sufficiently recommend the study of Professor A. F. Weinhold's 'Introduction to Experimental Physics'*. If one may be permitted to refer to personal considerations, I can truly say that if such a work had existed in my student days, much labour and vain searching through libraries in search of information would have been saved. As I have no personal knowledge of either author or translator,

* Translated by Benjamin Loewy, F.R.A.S. Longmans, Green, and Co., 1875.

this tribute to their labours will, at least, have the merit of sincerity.

Caoutchouc tubes.—The remarks at p. 437 are no longer applicable. Excellent black tubing can now always be obtained from the instrument-makers, perfectly adapted for making the junctions in organic analyses. By using fine copper wire, well annealed, tight joints can always be obtained even with the most complicated systems of apparatus.

Soldering.—I have known some persons find a difficulty in soldering together very fine wires; such, for example, as are used for the secondary wires in induction-coils, &c. This may be done with perfect ease and neatness thus: clean, by filing, or by rubbing on sand, the end of the soldering-iron, then wet it with chloride of zinc, and take up a small piece of solder. The iron may be heated by a Bunsen's lamp. Untwist the silk from the two pieces of covered wire to the distance of an inch from the end, twist the two ends together, moisten with the chloride-of-zinc solution, and simply place the twist against the melted solder on the iron for a second and remove it; it will then be found that the two wires are perfectly connected: replace the silk, and wind fresh fine silk over the joint until no trace of the wire is visible, and fasten off with three "half-hitches," exactly as is done in tying a fishing-hook to gut; then dip in melted paraffin, and the joint will be perfect.

Weinhold* recommends sal-ammoniac to be mixed with the chloride of zinc, and in many cases it is doubtless preferable. Into a beaker of about 250 c. c. capacity put 50 grammes of crude commercial hydrochloric acid. To avoid weighing, 50 c. c. will do equally well. Add waste clippings of zinc by degrees until the first violent action becomes more tranquil; go on with the addition of zinc until some remains undissolved after a few hours. Then add 10 grammes of powdered sal-ammoniac, and stir until dissolved. Let the solution settle, and pour off the clear portion into a bottle for use.

The Aneroid Barometer.—The aneroid barometer may now be

* *Loc. cit.* 27

obtained of great accuracy and extreme sensitiveness. I have seen them able to detect the difference between the height of a table and the floor. They are also so cheap, that for vapour-densities and gas analyses the best kind may be substituted for a standard mercurial barometer where the difference in price is a consideration. It is always wise, however, to have them compared at intervals with a standard, as the mechanism is rather delicate.

Sprengel's Pump for producing Vacua.—It has passed into a proverb that the man who discovers a new method of working does more good to science than he who discovers a new object. This is obvious, because a new method of working will enable an unknown and unknowable number of new substances or objects to be discovered. The invention of the spectroscope has enlarged the field of work of the astronomer more than the discovery of a dozen planets, and it has equally strengthened the hands of the chemist. Dr. Sprengel's* discovery of a method of producing more perfect vacua than the best air-pumps, has enabled Crookes to obtain results with his radiometer and kindred instruments which could not have been effected without its aid. As it is in frequent use in the laboratory we shall give an account of it, but only in the form in which it is described in the author's now classic paper. For the more complex forms employed by Crookes in his researches, the student is referred to his papers in the 'Transactions of the Royal Society' (reference to which will be found further on), as even our sketch will to some, perhaps, appear too long. We have already stated that Bunsen's filter-pump, so invaluable in chemical researches, is an outcome from Sprengel's discovery.

The Sprengel pump has much affinity with the Trompe or Catalonian bellows, an ancient method of obtaining a blast in metallurgical operations. It is, in fact, the trompe reversed.

If a barometer had the top of the tube broken off air would enter, and the mercury would sink; and, of course, as the mercury fell, air would enter to supply its place. If, however, the experiment were so arranged that the supply of air was limited, but the mer-

* SPRENGEL, Chem. Soc. J. [2] iii. 9.

cury unlimited, a vacuum would result. This is the principle of the Sprengel pump.

Fig. 22 represents this instrument in its simplest form. A glass tube cd , longer than a barometer, and open at both ends, is the "fall-tube." It is supplied with mercury by the funnel A, the fall-tube being connected with it at c . The lower end d dips into a glass bulb B, and is secured by means of a cork. The bulb has a spout on one side, situated a few millimetres above the bottom of the tube cd . The first portions of the mercury which fall close the tube and prevent the entry of the air from below. The upper part of the fall-tube has a branch at x to which the receiver R is connected. The stopcock c being opened, the mercury falls and the exhaustion begins. At this point the fall-tube is filled with cylinders

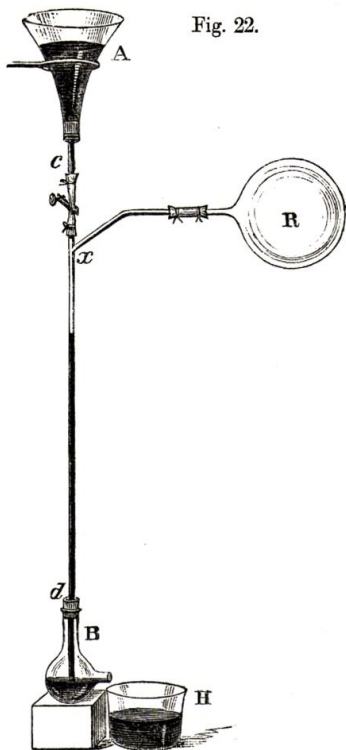


Fig. 22.

of mercury separated by spaces filled with air; they continue to descend as long as the cock c is kept open and the funnel A supplied with mercury. Air and mercury escape from the spout of the bulb B; the latter falls into the vessel H, and it is returned into A until the globe R is exhausted. The state of exhaustion of R may be judged of by the smallness of the spaces between the cylinders of mercury. As the exhaustion becomes greater, the lower part of the fall-tube appears like a continuous column of mercury, nearly the height of the barometer at the time. At

this point a noise is heard, common to all liquids shaken in a vacuum. The operation may be known to be complete when the falling column of mercury encloses no air, and when a drop of mercury falls upon the top of the column without enclosing any air-bubble. The height of the column now corresponds with the barometer, whose Torricellian vacuum is the globe R.

Fig. 23.

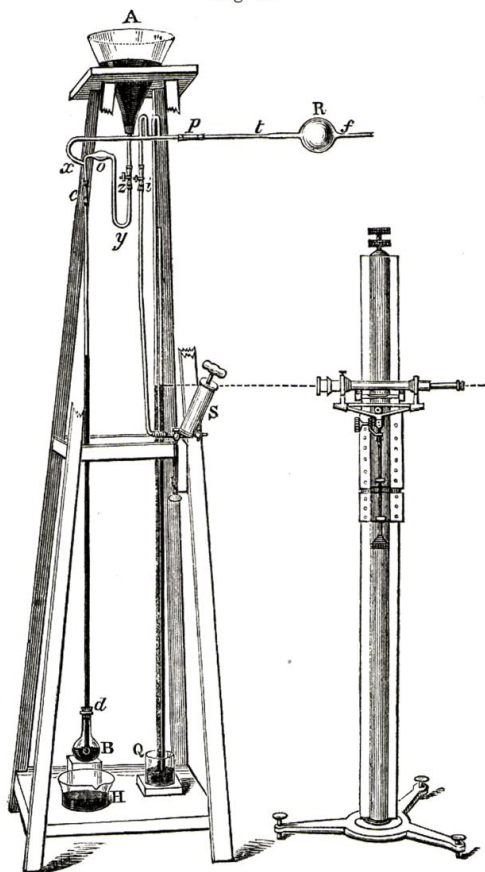


Fig. 23 represents a modification adapted to laboratory purposes. The funnel A, supported on a wooden stand, contains the supply of mercury. The tube xyz connects it with the fall-tube cd , and on opening the clamp z , the mercury begins to run. The tube xp leads to the vessel to be exhausted, and is also in connexion with two tubes: one passes to the exhausting-syringe S, while the other, serving as a gauge, dips into a glass of mercury containing a barometer. When the Sprengel pump is in action, the rise of the mercury in the gauge will indicate the amount of exhaustion. The object of the exhausting-syringe is to facilitate the production of the vacuum, because the fall-tube must necessarily be of small internal diameter. The greater portion of the air is to be removed by the exhausting-syringe, and then the connexion between the receiver and the syringe is closed by means of the clamp i . The remainder of the air is removed by the Sprengel pump. The bulb B and the basin H are arranged exactly as in the previous engraving. The instrument is not made more than six feet high, in order that the mercury in H, and which has passed through the fall-tube, can be readily returned to the funnel A. To prevent any admixture of air with the mercury in the act of pouring it into A, a glass plate is allowed to float on the surface of the metal, and the latter is poured gently upon it. The connexions between the various parts are made of well-fitting black vulcanized caoutchouc tubing, known as "French tubing." This is the same kind that has been recommended, at page 68, for the connexions in the apparatus for organic analysis; and, as in the latter case, copper wire is used for binding the joints.

The space between the inside of the caoutchouc tubing and the outside of the glass tubing is filled with a cement of fused caoutchouc. To prevent the latter soiling the interior of the glass tubes, Sprengel first puts the apparatus together, then ties the caoutchouc joint with wire, and turns back the end of the tubing over the coil, coats the inside of the end with the cement, and turns it back again into its proper position. The connexion of the funnel with the tube zyc is made by means of a perforated caoutchouc cork. We have already (p. 46) described the method

of perforating caoutchouc corks, but Sprengel uses oil instead of caustic soda for moistening the cork-borers. These caoutchouc corks can now be procured at the instrument-makers. When the apparatus has been put together, the mercury is allowed to enter the fall-tube in such quantities as to raise the mercury of the gauge as quickly as possible. When the rattling noise is heard, which indicates that the exhaustion is approaching completeness, it is better to lessen the supply of mercury and to let it fall drop by drop until the exhaustion is completed. From 10 to 15 lbs. of mercury are found to be a convenient quantity to work with.

Dr. Sprengel has endeavoured to increase the rapidity of action of his instrument by increasing the internal diameter of the fall-tube. For the instrument to act, the supply of mercury must be sufficient to close the fall-tube; but if too rapid it closes the aperture at *x*. It is evident that volume may be increased in height or breadth. By lengthening the fall-tube, the bulk of the enclosed air will be increased, and the operation shortened without increasing the weight of mercury used; but as it is inconvenient to have the instrument taller than the operator, he endeavoured to employ tubes of larger diameter. But as he was unable to form, in a vacuum, drops of mercury of more than 3 millimetres in diameter, the limit was at once found.

When time is no object, it is better to use the instrument in its simplest form (fig. 22). By its use a receiver of about 500 c. c. can be exhausted in half an hour. He has always found that fall-tubes with a bore of 2.5 to 2.75 mm. gave better vacua than any other sizes. Before proceeding to test the efficiency of his instruments, Dr. Sprengel gave his whole attention to the construction of air-tight joints: in this he did not succeed. It is well known that barometers become gradually inaccurate as air finds its way between the glass and the mercury into the Torricellian vacuum. To offer a greater resistance to the air which might enter from the funnel, he gave the tube *zyo* the form of a U-tube. It was, however, from the caoutchouc tubes that the greatest leakage occurred; but the cement before described answered so well, that the gauge did not fall more than 0.5 mm. in 24 hours.

When the mercury is heated, and allowed to run down quickly, the instrument becomes a kind of electric machine. In the dark, flashes of electric discharge illuminate the exhausted tubes, and sparks may be drawn at intervals from the basin in which the mercury collects. The fall-tube becomes soiled after some time, especially after using heated mercury. Dr. Sprengel attributes this to ozone formed by the electric action. To attain high vacua the fall-tube must be clean as well as the mercury.

Dr. Sprengel then shows that it is not difficult to exhaust receivers until they retain only $\frac{1}{1300000}$ of their volume of air.

Crookes *, in his important researches on repulsion arising from radiation, has made two important improvements in the Sprengel pump. Instead of trusting to the comparison between the barometric gauge and the barometer to give the internal rarefaction, he joined a mercurial siphon-gauge to one arm of the pump. This was useful in measuring very high rarefactions in experiments where a difference of pressure equal to a tenth of a millimetre was important. By its side is an indicator for still higher rarefactions; it is simply a small tube having platinum wires sealed in, and intended to be attached to an induction-coil. At exhaustions too high to be shown by the siphon-gauge, valuable information can be obtained of the nearness to a perfect vacuum by the electrical indications of this tube. He frequently carried exhaustions to such a point that an induction-spark preferred to strike its full distance in air rather than pass the quarter of an inch separating the points of the wires in the vacuum-tube.

REMARKS ON A FEW OF THE PROCESSES AND REACTIONS EMPLOYED IN SOME RESEARCHES.

As the nomenclature and atomic weights as now received are very different from those employed when this work was written, it would be impossible, without rewriting the whole of this

* CROOKES, Phil. Trans. clxiii. 295, clxiv. 509, 516; Phil. Mag., Aug. 1874.

chapter, to adapt it completely to modern views. But it is not necessary; every student of chemistry who is sufficiently advanced to pursue original researches will, without difficulty, be able to make the simple calculations required. When an important point strikes the author as necessary to be elucidated, further details will be given. It must be distinctly understood that it is only a *few* of the reactions and processes that are attempted to be given. The references will be to the paragraphs.

It was said, § 757, in considering the action of nitric acid upon carbon, that Hatchett had, by treatment of carbon with nitric acid, formed a curious substance or series of substances which he called artificial tannin; and, in a note, it was remarked that it was greatly to be desired that this subject should be reinvestigated by modern methods. Since that time, this has been done, with signal success, by Sir Benjamin Brodie*. By treating purified graphite repeatedly with nitric acid and chlorate of potassium, he has produced a most singular substance, which he calls graphitic acid. He assumes from his researches that the carbon in this new substance has a different atomic weight from ordinary carbon. When a piece of graphitic acid the size of a hemp-seed is heated in a test-tube over the lamp it explodes, nearly filling the test-tube with a fine variety of carbon.

Sulphides of Carbon.—It was said in § 765 that no sulphide of carbon corresponding to oxalic acid had at that time been formed. Since then Loew †, by treating carbon sesquisulphide with dilute nitric acid, has produced a substance which is possibly analogous to oxalic acid.

Ozone.—A great number of researches have been made since this work was written on the preparation and properties of this singular substance. It is also evident that several substances which liberate iodine from iodide of potassium, and bleach sulphide of lead, have been mistaken for it. The writer found that isoprene, a hydrocarbon existing among the products of the destructive distillation of caoutchouc, when left in a partly filled

* BRODIE, Ann. Ch. Pharm. cxiv. 6.

† LOEW, Zeitschr. f. Chem. [2] i. 722, ii. 172, iv. 623.

bottle for some months, became what, in 1860, was considered as ozonized. It readily decolorizes sulphate of indigo, and, under certain circumstances, converts sulphide of lead into sulphate. When this fluid was submitted to distillation, and the temperature of the oil was kept as low as was compatible with the progress of the distillation of the unaltered isoprene, nothing specially occurred until the fluid thickened, causing the temperature to rise. The oxidizing substance then began to act with energy, a cloudy vapour rose accompanied by an intensely sharp odour, and the contents of the retort instantly solidified into a pure white spongy mass. The formula of isoprene is C_5H_8 ($C=12$), and the solid substance gave on analysis numbers agreeing with $C_{10}H_{16}O$. But Kingzett* maintains that the substance which gives turpentine and other essential oils their oxidating properties cannot be ozone or peroxide of hydrogen, for reasons given, *antè* p. 40.

Although Andrews has maintained that the Rühmkorff spark is ill adapted for the preparation of ozone, and that even the ordinary machine spark is much less effective than the silent discharge, yet Houzeau† has devoted himself to the Rühmkorff coil as a source of ozone. He finds that the formation is more rapid in renewed than in confined air, and that it is formed more abundantly at the negative than at the positive pole. He also finds that it increases with the intensity of the spark, and diminishes as the distance between the electrodes is increased. A low temperature favours the formation of ozone, and oxygen yields ten times as much ozone as air. Houzeau's "ozonizer" is formed as follows:—A glass tube has a platinum wire about 6 decimetres long placed in it, and one end passes through the side of the upper end; a coil of platinum wire is wound round the tube. The two wires are attached to a Rühmkorff coil capable of yielding a 2 or 3 centimetre spark. A slow stream of oxygen being passed through the tube, it will become strongly charged with ozone. Houzeau has, by this means, prepared oxygen containing as much as 188 milligrammes of ozone per litre.

* KINGZETT, Chem. Soc. J. [2] xii. 511.

† HOUZEAU, Compt. Rend. lxx. 1286.

It is impossible to spare more space to describe the other forms of ozonizers that have been devised. The student desirous of pursuing the subject more fully must consult the scientific journals. Numerous valuable papers will be found by:—

Andrews,	Hollmann,	Siemens,
Andrews and Tait,	Joulet,	Soret,
Baumert,	Kingzett,	Than,
Boillot,	Loew,	Von Babo and Clausius,
Carius,	Marignac and De la Rive,	Weltzein,
Frémy and Becquerel,	Meissen,	Williamson,
C. Hofmann,	Schönbein,	Wright.

On Processes and Reactions connected with the Metals.—We have said, § 769, that “The rarity of a metal depends upon two circumstances, either of which may cease to exist.” We also remarked that “vanadium is a metal the reactions of which are so marked, that undoubtedly, if obtainable in quantity at a reasonable price, it might be made available in the arts.” This prediction, which did not require much power of prevision, has been fully verified. It has been found that the presence of even mere traces causes a remarkable improvement in the quality of aniline black.

Classification of the Elements.—This subject, which, at the period this work was written, had hardly been seriously attacked, has now been studied with great care and success by Mendeljeff * and Newlands. The subject is excessively interesting, but would require far more space than could be spared in this sketch. The papers of the latter chemist will be found on reference to the back volumes of the ‘Chemical News.’

Chemical properties of Metals.—The mistakes which have been made by the greatest analysts in the study of the various columbites and tantalites have led to an amount of work and controversy which only great care and patience would enable a student to master. The subject is, however, so important and so instructive, that we strongly recommend any student really attached to chemical mineralogy to study it. He will find numerous references in Watts’s Dict. Chem. vol. iv. p. 49 (first edit.).

* MENDELJEFF, Ann. Ch. Pharm. Sup. viii. 133–229.

Action of Non-metallic Elements on Metallic Oxides.—This subject has been studied elaborately as regards the action of the halogens by C. F. Cross and S. Sugira*.

On the Determination of the Atomic Weights of Metals.—It has been said, at the commencement of this chapter, that the atomic weights and nomenclature of chemistry have been so much changed since the work was written, that it would be impossible, without rewriting the whole, to bring it into harmony with modern ideas. It may, however, be not entirely useless to show how simple and easy a task it is to convert the old system into the new. For example, in the equation in § 812 oxygen is taken as 8 and tin as 58. Oxygen being taken as 16 and tin as 118, we say:—

$$27\cdot2 : 100 :: 32 : 117\cdot64$$

$\underbrace{\hspace{1.5cm}}_{2 \text{ eq.}} \quad \underbrace{\hspace{1.5cm}}_{\text{At. wt. of tin.}}$

If we assume that 100 parts of tin give 127·1 of peroxide we have

$$27\cdot1 : 100 :: 32 : 118\cdot08,$$

which is very near indeed to 118, the value assigned to tin by Dumas. Mulder's experiments give as low a value for the atomic weight of tin as 116.

We have said, § 814, that silver appears to be one of those metals the equivalents of which are multiples by a whole number of that of hydrogen. It must be remembered, however, that the most elaborate researches ever made upon atomic weights, those of M. J. S. Stas †, have led him to the conclusion that the law of Prout is either not true, or only approximately so. But there is the remarkable fact remaining, that, for many of the elements tried, the differences, from being absolute multiples of unity, are very small. Chlorine, amongst others, is a glaring exception, because even if its atomic weight were 35·5 instead of 35·46 which Stas found, it would be a multiple of half the atomic weight of

* CROSS and SUGIRA, Chem. Soc. J., Sept. 1878, p. 405.

† STAS, 'Nouvelles Recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels.' Bruxelles, 1865. I have to thank M. Stas for a copy of this great work.

hydrogen. Some chemists have gone so far as to advocate halving the atomic weight of hydrogen to get over what they term "this difficulty." It will, I think, be evident that it would be most unwise to do so in the present state of our knowledge.

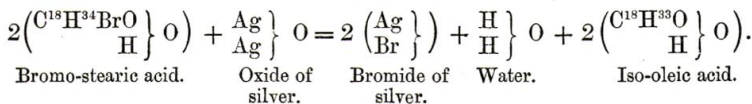
General considerations on the Elements.—At the time of publication of this work, the observations of M. Dumas on the manner in which the elements in many cases fell into groups of three attracted great attention. The numerical relations in the triad containing chlorine, bromine, and iodine remain unchanged; and when we come to the next group, where the atomic weights have *all* been doubled, the relation remains the same; for if we add the present equivalent of sulphur 32 to that of tellurium 129 we have 161 as the result; and if we divide this number by 2 we have 80·5; and as the new atomic weight of selenium is 79·5, the result is as before. If we take the next triad with the new atomic weight of lithium 7 instead of 6·43, the result is numerically perfect, for $39 + 7 = 46$ and $\frac{46}{2} = 23$, exactly the atomic weight of sodium as at present received. The calcium, barium, and strontium group having all been doubled, the result, will, of course, be as before.

With regard to the group of the platinum metals, they have all of necessity been doubled, and the remark in § 822 as to their relation to the equivalent of rhodium obviously requires modification. The whole subject of the proper grouping and classification of the elements is much too long to be discussed here, and the student is again referred to the important papers of Mendeljeff and Newlands.

In § 837 we have described a method of preparing malic acid. Since that time Kekulé and Perkin and Duppa have prepared it artificially by acting on bromo-succinic acid with moist oxide of silver. The literature on this subject alone is voluminous. A good account of it will be found in Naquet's 'Modern Chemistry,' 1868, pp. 613 and 826; also in Watts's Chem. Dict.

In § 843 it has been said that the formula of stearic acid was not perfectly established. Since that time it has been shown in

various ways to be $C^{18} H^{36} O^2$. Iso-oleic acid has been prepared from it, by treating bromo-stearic acid with oxide of silver :



In the above reaction, $C=12$, $O=16$, &c.

It has been said, § 846, in discussing some animal acids, that they may be isolated from fluids in which they are contained by first concentrating the liquid by evaporation, and then adding a metallic salt, the base of which forms a comparatively insoluble precipitate with the acid present; and hippuric acid has been given as an example. A better method in this case is to add to cows' urine 2 or 3 per cent. of hydrochloric acid. The mixture should then be left for 24 hours in enamelled or earthenware pans. This crude acid is to be mixed with milk of lime and boiled. Filter the liquid off and precipitate the solution with carbonate of sodium, boil, filter again and precipitate with chloride of calcium; this will carry down much of the colouring-matter with the carbonate of calcium derived from the excess of carbonate of sodium. The solution is to be filtered and precipitated with hydrochloric acid. The hippuric acid thus obtained should be colourless.

In a note to § 847 it has been remarked that the preparation of uric acid from guano promised to become of great value in the arts, owing to the valuable colouring properties discovered in murexide. I have seen calico-printing with this substance done on an immense scale; but it has fallen into disuse for several reasons, among others the discovery of the aniline colours. Beilstein's process for preparing it involved the use of mercury, rendering it dangerous to the workpeople.

In alluding, in § 854, to the substitution of the hydrogen in phenol by hyponitric acid, it must be remembered that the latter is now regarded as a radical (nitryl) and, in combination, has the formula NO^2 , $O=16$.

Treatment with Peroxides &c., § 856.—Professor Dewar has made an important research upon picoline*. This substance has been vainly worked upon with nitric and chromic acids in the hope of getting decomposition products, but without success. But by treatment with potassium permanganate he has succeeded in obtaining a fine crystallizable derivative. He mixed 150 grammes of potassium permanganate, 25 grammes of picoline, and a litre and a half of water in a glass flask with a vertical condenser or cohobating tube. Heat was then applied, and, when the liquid nearly came to the boil, the action became so violent that the lamp had to be removed. In 30 minutes the permanganate was reduced. In addition to nitric, acetic, oxalic, and carbonic acids, he obtained a new acid, to which he has given the name of dicarbo-pyridenic acid— $C^5 H^3 N \begin{cases} CO^2 H \\ CO^2 H \end{cases}$. It is a fine substance crystallizing from water in plates resembling naphthalene.

Picoline, treated in this manner, also yields another new acid of higher atomic weight; it does not fuse at $220^\circ C$.

In § 863 *for* Picric acid *read* Sulphacetic acid.

In paragraph 872 the formulæ of cholic acid and cholate of sodium were shown side by side. Since that was written, the name of glycocholic acid has been given to this substance.

The results obtained during many years of research, devoted to the products of the destructive distillation of cinchonine, compel me to modify the note to § 886. I have there stated that cinchonine, instead of only affording chinoline as had been supposed, yields pyrrol, pyridine, picoline, lutidine, collidine, chinoline, and lepidine. I have now to add that there are distinct differences between the lutidine from cinchonine † and that from bone-oil ‡. It is therefore highly probable that the other homologues of the lutidine from cinchonine (the latter of which I have called β lutidine) are also different from the bodies of the same formula found in bone-oil. In addition to this I find that chinoline and its homologues from cinchonine are very different in their properties from

* DEWAR, Chem. News, xxiii. 38.

† GREV. WILLIAMS, Proc. Roy. Soc. xiii. 305.

‡ ANDERSON, Trans. Roy. Soc. Edinb. xx. part ii.

the bases having the same formula found in coal-oils, &c. The distillate from cinchonine contains at least eight homologues of chinoline. The characteristics which distinguish chinoline made from cinchonine from the metamerie leucoleine from coal-oil are :—

1. That the former yields by treatment with iodide of amyl followed by an alkali a superb blue, cyanine, which leucoleine does not do.
2. That chinoline from cinchonine yields readily a finely crystallized acid chromate, which leucoleine does not do.

But, on the other hand, Professor Dewar and M. Ballo both have found chinoline in certain coal-oils. I have discussed the whole question, as regards M. Ballo's results, in a paper published in the *Journal of the Chemical Society* *. Although I have not myself ever found chinoline in coal-oils, I can quite believe that its formation may take place under certain conditions.

I should have preferred to enlarge, and, in some respects, modify § 876; but the literature on the subject of malic acid and its derivatives has become so bulky that the student must, as has been said (p. 79), be referred to Watts's 'Chemical Dictionary' and Naquet's 'Modern Chemistry' for further details.

Definition of an Alcohol, § 919.—Another definition, which expresses more modern views, is that an alcohol is a substance derived from a fundamental hydrocarbide by the substitution of hydroxyl for hydrogen.

Caprylic Alcohol, § 925.—For the extensive literature on this substance, now known as octylic alcohol, see Watts's *Chem. Dict.*

Definition of an Ether, § 929.—The most modern definition of an ether is, perhaps, a substance produced from an alcohol by the substitution of an alcoholic or acid radical for the hydroxylic hydrogen, or of a halogen for hydroxyl.

Definition of an Aldehyde, § 934.—At the time of writing this work the literature on the subject of aldehydes was somewhat scanty. The definition I gave was, perhaps, the best at the time; but now that these bodies have been more thoroughly studied, a better one can be given; it is as follows :—An aldehyde is the first product of oxidation of a primary n hydric alcohol, from

* GREY. WILLIAMS, *Chem. Soc. J.* 1863, p. 375.

which it is obtained by the removal of $2n$ atoms of hydrogen. It is intermediate between the alcohol and the corresponding acid, from which latter it differs by containing n atoms of oxygen less.

The Benzole series, § 945.—It must be remembered that the word benzole is now almost universally employed to designate the commercial product containing other homologues, and that pure benzole, C^6H^6 , is now called *benzene*. The literature connected with benzene is now so enormous, that even a sketch of it would require more space than can be afforded to it here.

Chloride of Capryl, § 962.—Capryl in combination, C^8H^{17} , and in the free state, $C^{16}H^{34}$, is now known as octyl. The above formulæ assume $C=12$.

The Spectroscope.—I had intended to add an account of the use of the spectroscope; but the ‘Supplement’ has already so far outgrown the limits originally intended, that it would be impossible to do so, more especially as even a brief notice would require more space than the Supplement itself. I cannot, therefore, do better than refer the student to Roscoe’s ‘Spectrum Analysis’*.

* Macmillan and Co., London.

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