A handbook of chemical manipulation

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Section IX. Specific Gravity

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SECTION IX.

SPECIFIC GRAVITY.

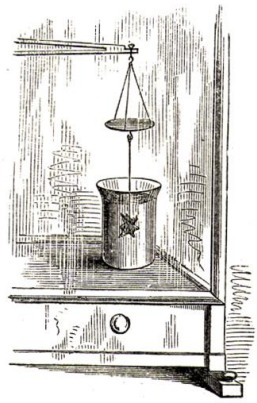
111. *Specific Gravity in general.*—The term specific gravity is understood to mean the relative weights of equal masses of matter. It will easily be seen that almost all the various natural and artificial objects which come under our cognizance, have densities peculiar to themselves, *i. e.* equal bulks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

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

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

to that of the volume of water displaced. The procedure therefore is as follows:—weigh the substance accurately, then suspend it by a fibre of silk or a fine hair to the hook beneath the short pan of the balance, and bring the latter to an equilibrium; now take a glass of pure distilled water, at as nearly as possible the standard temperature (60° Fahrenheit), and introduce it beneath the substance, so that the latter may be covered to a moderate depth; if any globules of air remain on it, they are to be removed. Immediately on the immersion of the substance in the water, the arm of the beam to which it was attached rises; and if we now place weights into the short pan until the equilibrium is restored, they will express the weight of a volume of water equal to that of the substance. For example:—

Fig. 68.



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

$$\frac{50{\cdot}00}{2{\cdot}59}=19{\cdot}3;$$

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

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

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

$$\frac{38{\cdot}95}{2{\cdot}00}=19{\cdot}475;$$

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

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

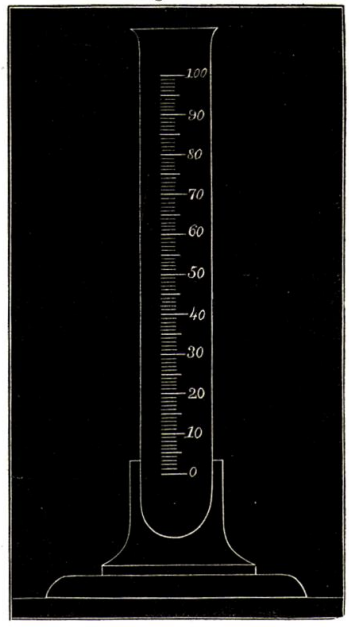
$$\frac{59{\cdot}25}{6{\cdot}78}=8{\cdot}739,$$

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

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

inspection. As an example:—17·93 grains of cadmium, which for the purpose of the experiment had been recently melted and made into a rod by casting in a glass tube, were dropped into the tube, which had previously been filled up to the zero of the scale with water; the fluid rose two divisions, indicating that a bulk of water equal to 17·93 grains of cadmium weighed 2 grains, and $\frac{17{\cdot}93}{2} = 8{\cdot}965$, the specific gravity required. Again, 26·61 grains on being dropped in raised the water three divisions, and $\frac{26{\cdot}61}{3} = 8{\cdot}87$. The density obtained before on the same specimen by a different process was 8·7. It will be seen therefore that the method is capable of yielding approximative results sufficient for many purposes; and when the great rapidity with which a result can be obtained is taken into consideration, it may not be going too far to assert that the instrument will, to many persons, more especially travelling mineralogists, be an acquisition. The points requiring care are, in the first place, to prevent bubbles of air from adhering to the specimen; also to allow the sides of the tube to thoroughly drain before ascertaining the zero point of the water, and to take great care in determining the exact part of the curve to be observed in each experiment. Without these precautions, the results obtained will be very far from the truth.

Fig. 69.



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

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

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

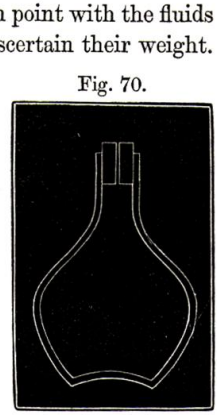
116. If the solid is soluble in water, one of two courses must be adopted: either it may be varnished very thinly, so as to prevent the water from touching it, or its specific gravity may be taken by the first method given, substituting a fluid in which the body is insoluble, and making a correction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

$$\cdot 850 : 87 : 1000 : 102{\cdot}3, \text{ and}$$
$$102{\cdot}3 : 1 : 100 : \cdot 978, \text{ the value required.}$$

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

be obtained in several ways. The difficulty which is found in obtaining equal bulks of solids, is not found in this instance; it only being necessary to fill a vessel to a given point with the fluids the density of which is to be compared, and ascertain their weight. We have said that water is used as a standard of comparison for liquids and solids, the usual method being to construct a bottle capable, when the stopper is put in its place, of holding exactly 1000 grains of water. By merely, therefore, counterpoising the empty bottle, and, after filling with the liquid whose specific gravity is to be ascertained, adding weights to restore the equilibrium, we obtain the result sought without any calculation. For example:—A bottle which holds exactly 1000 grains of water is counterpoised, and then filled with pure concentrated oil of vitriol, and the stopper, which is perforated, is then put in its place; the excess escapes by the aperture, and is carefully wiped off; on replacing the bottle, 1845 grains were required to balance it; this number represents the specific gravity sought, which is more correctly written 1·845. If a liquid lighter than water be used, the result is still the specific gravity, but the decimal point is of course placed in front of the number found. For instance, some spirits of wine digested for some time over excess of dry carbonate of potash and slowly distilled, was put, under the circumstances previously mentioned, into the bottle, when 810 grains were required to equipoise it: ·810 is therefore the specific gravity sought.

Fig. 70.



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

freezing-point, it is true that as expansion takes place, the fluid merely rises in the neck, and if the latter be sufficiently capacious and the fluid is not very volatile, the experiment will succeed. But if the fluid evaporates rapidly at moderate temperatures, it is impossible to obtain accurate results. M. Regnault, to avoid this difficulty, uses a flask of the form shown in fig. 71. The fluid is filled to the mark on the neck, and the stopper is inserted in its place. By this means evaporation becomes impossible, and, if expansion takes place during the weighing, the fluid cannot escape in consequence of the enlargement in the neck.

Fig. 71.

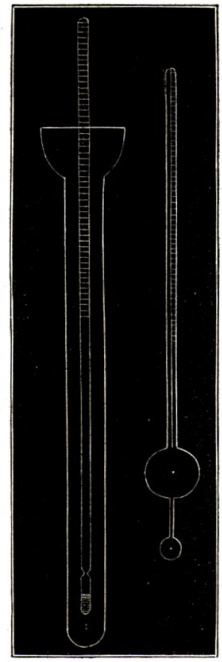
118. It is of the greatest importance, when accuracy is required, that the temperature of the liquid should be at or very near the normal point 60°, otherwise considerable errors will result. It is necessary, therefore, to be careful when taking the densities of recently-made mixtures, the temperature of the ingredients before mixing not necessarily being the same afterwards; in fact, it is very seldom that substances dissolve in water without either elevation or depression of temperature: if fused chloride of zinc is dissolved in water, the temperature rises considerably; when, on the contrary, iodide of potassium or nitrate of ammonia is dissolved, the temperature falls to a great extent; and although few of the salts in use in the laboratory present such distinctly marked phenomena, it becomes essential to be alive to the possibility of alterations of temperature.

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

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

119. We have alluded above to the hydrometer (fig. 73), which is an instrument in constant use in the laboratory to obtain densities without the necessity of weighing: it may be constructed to give results of any degree of accuracy, but this involves the use of several instruments; in general laboratory practice two only are employed: one with a range from the density of pure ether to that of water, and the other from water to oil of vitriol; one of the chief objections to their use, is the quantity of liquid required to fill the glass in which the hydrometer is floated, but, by employing the modification represented in fig. 72, this difficulty is to a great extent removed, a result being obtainable with only an ounce or two of fluid.

Fig. 72. Fig. 73.



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

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

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

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

Fig. 74.

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

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

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

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

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

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

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

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

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

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

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

Specific Gravities of Vapours and Gases.

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

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

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

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

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

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

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

which are not much heavier than air, require balloons of considerable size. Fig. 75 shows the shape usually adopted. It is necessary that they should be of light glass free from lead, and of a kind that will allow the point to be readily sealed by a brush of flame directed on it with the blowpipe. The flask must be perfectly freed from aqueous vapour by connecting it with the air-pump, a long chloride-of-calcium tube intervening; after covering it with hot sand and alternately exhausting and admitting air several times, the balloon will be thoroughly dried. The tube of the flask is now (unless it has been done previously) to be drawn out and cut off with a file, so as to leave an aperture of the size and shape of the upper part of fig. 76. The edges are to be slightly rounded in the lamp-flame, to prevent the danger of small pieces of glass being broken off.

Fig. 75.

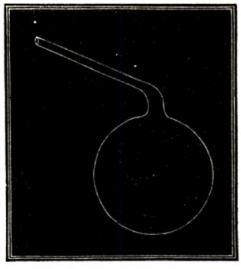


Fig. 76.

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

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

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

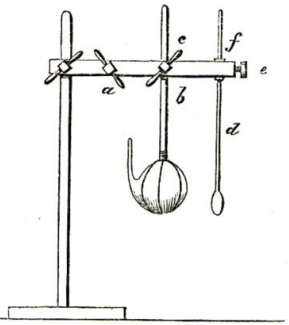
the point of the globe is to be inserted, and the latter being warmed to expel some of the air, the lamp is removed, and, as the balloon cools, the fluid enters. If the substance the density of which in the state of vapour is to be determined, happens to be in the solid form at ordinary temperatures,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

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

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

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

Fig. 77.

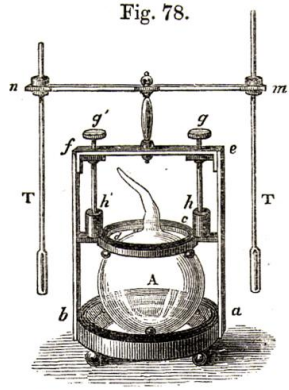


The balloon is supported by means of a rod, *b*, sliding through an aperture in the arm; it may be arrested at any height by means of a screw, *c*. The thermometer, *d*, is kept at any required height by the screw, *e*, which acts on pieces of cork placed at *f* to prevent fracture arising from too great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

Another method of supporting the balloon is represented in fig. 78. It is placed between two

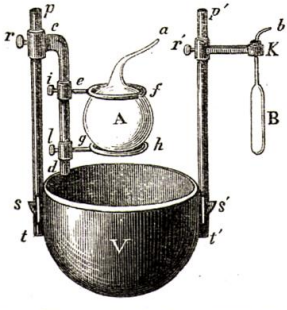
rings, $a\,b$ and $c\,d$; the latter is moveable up and down, and is fixed on the balloon by means of screws, $g'\,g$, which press on two corks, $h\,h$. The screws work in the cross piece, $e\,f$, which also serves to support a rod, the latter in its turn carrying an arm, $n\,m$, having two pierced corks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

Fig. 78.



132. But the most convenient method of supporting the balloon and thermometer is represented in fig. 79, where an iron pot, V, has two rods ($t\,p$ and $t'\,p'$) attached to its ears by means of screws, $s\,s'$; on one of these rods slides the bent bar, $c\,d$; it may be arrested at any height by means of the screw, r. Two rings, $e\,f$ and $g\,h$, move on the bar, $c\,d$; they are precisely similar to the rings of retort-stands, and may be secured in the desired position by the screws, $i\,l$. The flask, A, may therefore be steadily held in the bath, and the point, a, moved in any direction with ease, a very necessary thing in many cases. The rod, $t'\,p'$, supports an arm, r' K, having a pierced cork at its extremity, serving to hold the air-thermometer, B, or a mercurial one, according as the temperature to which the bath is to be raised is more or less elevated.

Fig. 79.



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

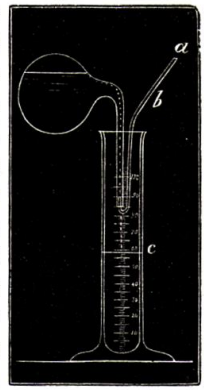
of sheet iron, the latter serving as a gas-furnace and support for the kettle.

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

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

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

Fig. 80.



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

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

D = the required density of the vapour;

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

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

V = capacity of balloon in cubic centimetres;

v = residual air;

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

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

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

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

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

FUSIBLE METAL.

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

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

257° . 3·180	338° . 2·480	464° . 2·090
266 . 3·105	356 . 2·438	518 . 2·088
284 . 2·907	374 . 2·378	590 . 2·085
302 . 2·727	392 . 2·248	608 . 2·083
320 . 2·604	428 . 2·132	637 . 2·083

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

following arrangement:—A capillary tube, *a b*, fig. 81, ending in an enlarged portion, *c d*, is attached to the balloon with the aid of the blowpipe; the balloon being immersed in the bath, it is, by means of the tube *c d*, made to communicate with a large bottle placed in a water-bath, kept at a constant temperature, not greatly differing from that of the atmosphere. A second tubulature in the bottle communicates with a mercurial manometer, which constantly shows the internal pressure, and also with an air-pump, by means of which the air in the bottle and balloon is reduced to the required degree of elasticity. The experiment is then conducted in the same manner as usual, it being only necessary to substitute in the formula the elastic force of the air observed on the manometer for the barometric pressure*.

Fig. 81.

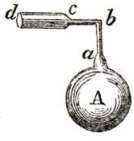
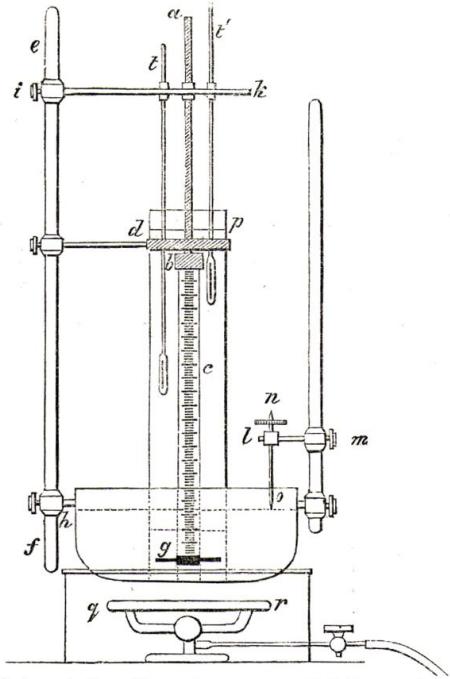


Fig. 82.



137. It now remains to describe the second process (devised by M. Gay-Lussac) for determining the volume occupied by a given weight of substance at a known temperature and pressure.

* Where extreme accuracy is desired, or where the above modification becomes necessary, the reader is referred to M. Regnault's work, which contains a very convenient formula, including all the corrections.

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

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

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

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

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

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

$$W = 0{\cdot}0012932 \text{ grm. } V. \frac{1}{1+0{\cdot}00367\,T} \cdot \frac{P}{760}.$$

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

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

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

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

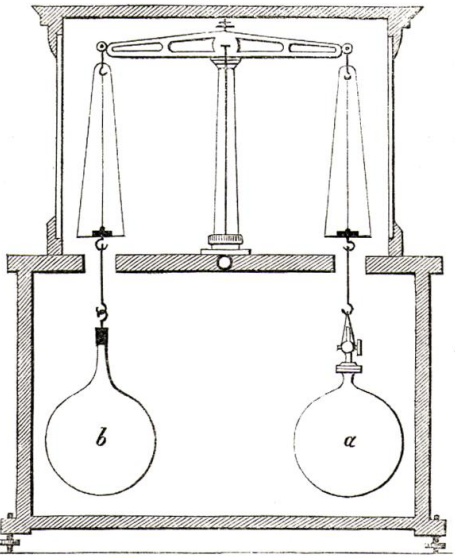
In order to lessen the influence of small but unavoidable errors of weighing, &c., large balloons, capable of containing 10 litres, are used. The balance also is large, but of great delicacy; for when charged with one kilogramme in each pan, it permits with certainty an appreciation of half a milligramme.

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

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

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

Fig. 83.



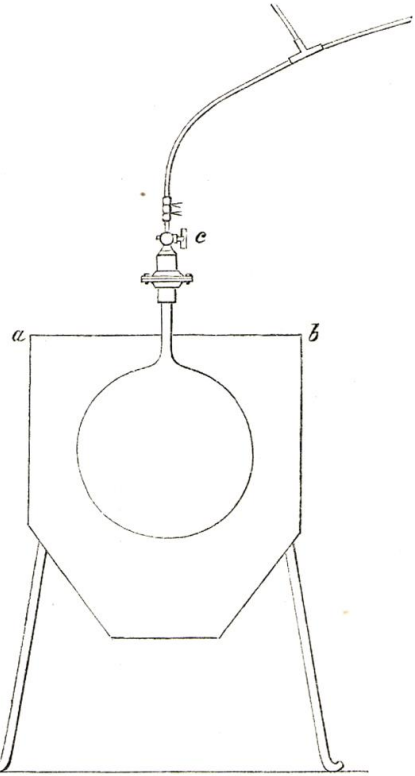
cemented to it a brass mounting, terminating in a hook, to enable it to be suspended from the balance-pan. If the united weight of the water displaced by the balloon, *b*, and its mounting is less by *n* grammes than the weight of the water displaced by the balloon, *a*, we must attach to *b* a glass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

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

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

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

Fig. 84.

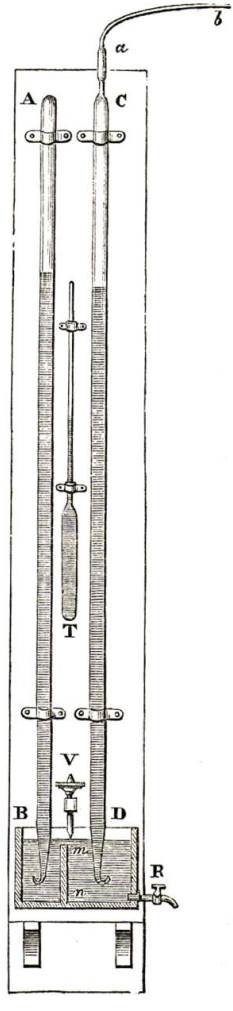


the gas-holder*, or with the air-pump. The air having been removed as completely as possible, the gas is allowed to enter,

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

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

Fig. 85.



into two parts, the smaller of which serves for the cistern of the barometer. Into the second compartment is plunged the tube, C D, which has the same diameter as A B. C D is capable, by means of a leaden tube, *a b*, of being placed in communication with the balloon.

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

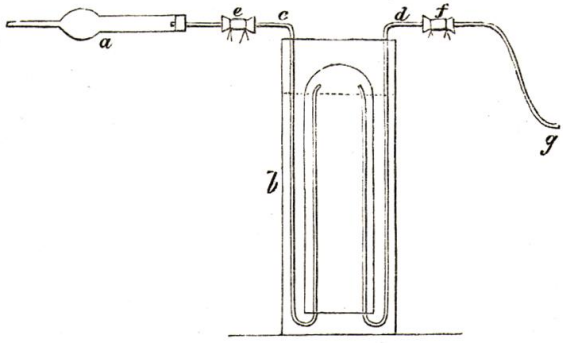
The division, *m n*, in the cistern is necessary, in order to prevent air reaching the barometer in consequence of the great oscillations in the level of the mercury during experiments. The balloon, thus again exhausted, and having the elasticity of its residual gas known, is to be closed, removed, wiped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

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

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

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

Fig. 86.



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

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