

the bath consists simply of boiling water. When higher temperatures are required, a saline solution, oil, or a fusible alloy is employed. In all cases, the liquid should be agitated, that its temperature may be the same in all parts. This temperature is indicated by the thermometer t .

When the substance in the globe has attained its boiling-point, evaporation proceeds rapidly, and the vapour escapes, carrying out the air along with it. When the vapour ceases to issue, we may assume, if the quantity of matter originally taken has been sufficiently large, that all the air has been expelled, and that the globe is full of vapour at the temperature given by the thermometer, and at the external pressure H . The globe is then hermetically sealed at the extremity p of the neck, which has been previously drawn out into a fine tube.

133. Calculation of the Experiment.—As already remarked, the densities of vapours given in treatises on chemistry express *the ratio of the weight of a given volume of the vapour to that of the same volume of air at the same temperature and pressure*. In order to deduce this ratio from the preceding experiment, we must first find the weight of the vapour. This is done by weighing the globe with its contents, after allowing it to cool. Suppose the weight thus found to be W . Before the experiment the globe had been weighed full of dry air at a known temperature t and pressure h . Suppose this weight to be W' ; the difference $W - W'$ evidently represents the excess of the weight of the vapour above that of the air. If, then, we add $W - W'$ to the weight of the air, we shall evidently have the weight of the vapour. Now the weight of the air is easily deduced from the known volume of the globe. If V denote this volume at zero expressed in litres, the weight in grammes of the air contained in the globe at the time of weighing is

$$V(1 + Kt) \cdot 1.293 \times \frac{1}{1 + at} \cdot \frac{h}{760}$$

K denoting the coefficient of cubical expansion of glass, and a the coefficient of expansion of air. The weight of the vapour contained in the globe is consequently

$$A = W - W' + V(1 + Kt) \times 1.293 \times \frac{1}{1 + at} \cdot \frac{h}{760}$$

Let H be the pressure and T the temperature at the time of sealing the globe. The volume occupied by the vapour under these circumstances was $V(1 + KT)$. The density of the vapour will therefore

be obtained by dividing A by the weight of this volume of air at the same temperature and pressure. But this weight is

$$A' = V(1 + KT) \cdot 1.293 \cdot \frac{1}{1 + aT} \cdot \frac{H}{760};$$

hence, finally, the required relative density is

$$D = \frac{A}{A'} = \frac{W - W' + V(1 + Kt) \cdot 1.293 \cdot \frac{1}{1 + at} \cdot \frac{h}{760}}{V(1 + KT) \cdot 1.293 \cdot \frac{1}{1 + aT} \cdot \frac{H}{760}}$$

The correctness of this formula depends upon the assumption that no air is left in the globe. In order to make sure that this condition is fulfilled, the point p of the neck of the globe is broken off under mercury; the liquid then rushes in, and, together with the condensed vapour, fills the globe completely, if no air has been left behind.

This last operation also affords a means of calculating the volume V ; for we have only to weigh the mercury contained in the globe, or to measure it in a graduated tube, in order to ascertain its volume at the actual temperature, whence the volume at zero can easily be deduced.

134. Example.—In order better to illustrate the method, we shall take the following numerical results obtained in an investigation of the vapour-density of sulphide of carbon:—

Excess of weight of vapour above weight of air, $W - W' = .3$ gramme; temperature of the vapour $T = 59^\circ$; external pressure $H = 752.5$ millimetres; volume of the globe at a temperature of 12° , 190 cubic centimetres; temperature of the dry air which filled the globe at the time of weighing, $t = 15^\circ$; pressure $h = 765$; $K = \frac{1}{38700}$.

The volume V of the globe at zero is

$$\frac{190}{1 + \frac{12}{38700}} = 189.94 \text{ cubic centimetres} = .18994 \text{ litre.}$$

The weight of the air contained in the globe is

$$.18994 \times 1.293 \cdot \left(1 + \frac{15}{38700}\right) \cdot \frac{1}{1 + 15 \times .00366} \cdot \frac{765}{760} = .23442 \text{ gramme.}$$

Weight of the vapour,

$$.23442 + W - W' = .53442 \text{ gramme.}$$

The weight of the same volume of air at the same temperature and pressure is

$$.18994 \times 1.293 \cdot \left(1 + \frac{59}{38700}\right) \cdot \frac{1}{1 + .00366 \times 59} \cdot \frac{752.5}{760} = .20019 \text{ gramme.}$$

The density is therefore

$$\frac{53442}{20019} = 2.67.$$

Deville and Troost have effected several improvements in the application of Dumas' method to vapours at high temperatures. These temperatures are obtained by boiling various substances, such as chloride of zinc, cadmium, which boils at 860°C ., or zinc, which boils at 1040°C . For temperatures above 800° , the glass globe is replaced by a globe of porcelain, which is hermetically sealed with the oxygen-hydrogen blowpipe. The globe itself serves as a pyrometer to determine the temperature; and since the weight of air becomes very inconsiderable at high temperatures, some heavier vapour, such as that of iodine, is substituted in its place. If we suppose, as we may fairly do, that at these high temperatures the coefficient of expansion of the vapour of iodine is the same as that of air, the temperature may easily be deduced from the weight of iodine contained in the globe. We subjoin a table of some relative densities of vapours obtained by this method:—

Water,	0.622	Phosphorus,	4.5
Alcohol,	1.6138	Cadmium,	3.94
Ether,	2.586	Chloride of aluminium,	9.347
Spirit of turpentine,	5.0130	Bromide of aluminium,	18.62
Iodine,	8.716	Chloride of zirconium,	8.1
Sulphur,	2.23	Sesquichloride of iron,	11.39

135. Limiting Values of Relative Densities.—In investigating the relative density of acetic acid vapour, Cahours found that it went on decreasing as the temperature increased, up to a certain point, beyond which there was no sensible change. A similar circumstance is observed in the case of all substances, only in different degrees. The vapour of sulphur, for instance, has a relative density of 6.65 at 500°C ., while at about 1000°C . it is only 2.23. This indicates that the vapours in question are more expansible by heat than air until the limiting temperatures are attained. It is probable that the nearer a vapour is to its critical point (§ 105) the greater is the change produced in its absolute density by a given change whether of temperature or pressure. The limiting density-ratio is always that which it is most important to determine, and we should consequently take care that the temperature of the vapour is sufficiently high to enable us to obtain it.

136. Gay-Lussac's Method.—Gay-Lussac determined the density of the vapour of water and of some other liquids by a method a little

more complicated than that described above, and which for that reason has not been generally adopted in the laboratory. We proceed to describe it, however, on account both of its historical interest and of the importance of the question which it has assisted in solving.

A graduated tube divided into cubic centimetres, suppose, is filled with mercury, and inverted in a cast-iron vessel containing the same liquid. The inverted tube is surrounded by a glass envelope containing water, as in Dalton's apparatus. A small glass bulb containing a given weight w (expressed in grammes) of distilled water is passed into the tube, and rises to the surface of the mercury. The temperature of the apparatus is then raised by means of a fire below, the bulb bursts, and the water which it contained is converted into vapour. If the quantity of water be not too great, it is all converted into vapour; this is known to be the case when, at the temperature of about 100° , the mercury stands higher in the tube than in the vessel, for if there were any liquid water present, the space would be saturated, and the pressure of the vapour would be equal to the external pressure.

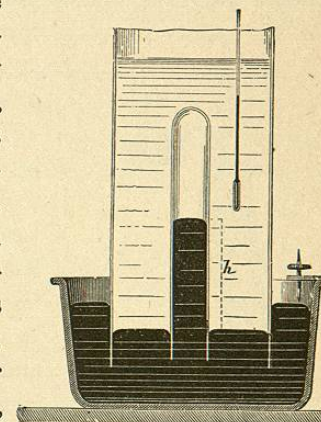


Fig. 85.—Gay-Lussac's Apparatus.

This arrangement accordingly gives the weight of a known volume of the vapour of water. This volume, in cubic centimetres, is $V(1+KT)$, where V denotes the number of divisions of the tube occupied by the vapour, each of which when at the temperature zero represents a cubic centimetre. The temperature T is marked by a thermometer immersed in the water contained in the envelope. The pressure of the vapour is evidently equal to the external pressure *minus* the height of the mercury in the tube.

In order to find the relative density, we must divide w by the weight of a volume $V(1+KT)$ of air at the temperature T and pressure $H-h$, giving

$$\frac{w}{V(1+KT) \times 0.01293 \times \frac{1}{1+\alpha T} \cdot \frac{H-h}{760}}.$$

It may be remarked that the vapour in this experiment is superheated; but superheated vapour of water obeys Boyle's law, and has

therefore the same relative density as saturated vapour at the same temperature.

The relative density of the vapour of water, as thus determined by Gay-Lussac, is about $\frac{1}{3}$, or .625. Several recent investigations have given as a mean result .622, which agrees with the theoretical density deduced from the composition of water.¹

137. **Meyer's Method.**—Victor Meyer has invented a method of determining vapour densities, which is illustrated by Fig. 86. His apparatus consists of a flask B with a long narrow neck, from which a fine tube branches off near the top, and bends down under the surface of mercury. A graduated glass jar D filled with mercury can be inverted over the end of the branch tube.

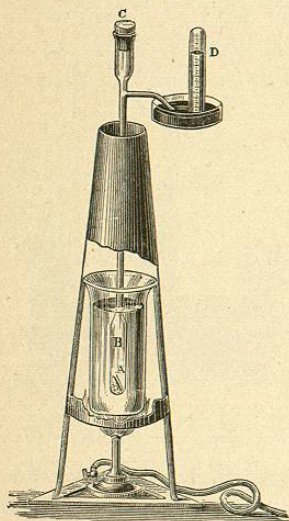


Fig. 86.—Meyer's Apparatus.

The first operation is to heat the flask by means of a surrounding bath to the temperature at which it is intended to form the vapour. This operation expands the air and expels a portion in bubbles through the mercury. This portion may be allowed to escape into the atmosphere, and when no more bubbles issue, but equilibrium of pressure has been established, the graduated jar is to be inverted over the end of the tube ready for the second operation, which consists in introducing the substance to be vaporized into the flask, the indian-rubber plug C at the top of the neck being removed for this purpose and quickly replaced. The formation of the vapour expels more air through the mercury, and this air must be collected in the graduated jar.

Comparing the contents of the flask when this operation has been completed with its contents before the plug was drawn, it is obvious that the vapour has taken the place of air at the same temperature and pressure. The relative vapour density will therefore be the quotient of the mass of the vapour by the mass of the air displaced. The mass of the vapour is, known, being the same as that of the

¹ Water is composed of 2 volumes of hydrogen, and 1 volume of oxygen, forming 2 volumes of vapour of water. The sum of the density of oxygen and twice the density of hydrogen is 1.244, and the half of this is exactly .622.—D.

substance introduced into the flask; and the mass of the air displaced is known, being the same as that of the air collected in the graduated jar. In the figure, A represents a small tube containing the substance to be vaporized, and asbestos is placed at the bottom of the flask to prevent the latter from being broken when this tube is dropped in.

138. **Volume of Vapour formed by a given Weight of Water.**—When the density of the vapour of water is known, the increase of volume which occurs when a given quantity of water passes into the state of vapour may easily be calculated. Suppose, for instance, that we wish to find the volume which a cubic centimetre of water at 4° will occupy in the state of vapour at 100°. At this temperature the pressure of the vapour is equal to one atmosphere, and its weight is equal to .622 times the weight of the same volume of air at the same temperature and pressure. If then V be the volume in litres, we have (in grammes)

$$V \times 1.293 \times \frac{1}{1+100\alpha} \times .622 = 1.$$

whence

$$V = \frac{1+100\alpha}{1.293 \times .622} = \frac{1.366}{.804246} = 1.698 \text{ lit.} = 1698 \text{ cubic centimetres.}$$

Hence we see that water at 4° gives about 1700 times its volume of vapour at 100° C.

The latent heat of evaporation is doubtless connected with this increase of volume; and it may be remarked that both these elements appear to be greater for water than for any other substance.

139. **Heat of Evaporation.**—The latent heat of evaporation of water, and of some other liquids, can be determined by means of Despretz's apparatus, which is shown in Fig. 87.

The liquid is boiled in a retort C, which is connected with a worm S surrounded by cold water, and terminating in the reservoir R. The vapour is condensed in the worm, and collects in the reservoir, whence it can be drawn by means of the stop-cock *r*. The tube T, which is fitted with a stop-cock *r'*, serves to establish communication between the reservoir and the atmosphere, or between the reservoir and a space where a fixed pressure is maintained, so as to produce ebullition at any temperature required, as indicated by the thermometer *t*. A is an agitator for keeping the water at a uniform temperature, indicated by the thermometer *t'*.

In using the apparatus, the first step is to boil the liquid in the

retort, and when it is in active ebullition, it is put in communication with the worm. The temperature of the calorimeter has previously been lowered a certain number of degrees below that of the surrounding air, and the experiment ceases when it has risen to the same number of degrees above. The compensation may thus be considered as complete, since the rate of heating is nearly uniform.

If W be the equivalent of the calorimeter in water, t its initial temperature, θ its final temperature; then the quantity of heat gained by it is $W(\theta - t)$. This heat comes partly from the latent heat disengaged at the moment of condensation of the vapour, partly from the loss of temperature of the condensed water, which sinks from T , the boiling-point of the liquid, to the temperature of the calorimeter. If, then, x denote the latent heat of evaporation, w the weight of the

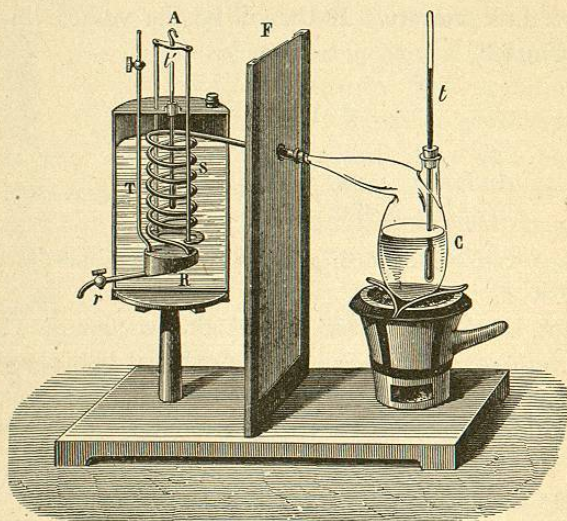


Fig. 87.—Despretz's Apparatus.

liquid collected in the box R , and c its specific heat, we have the equation

$$W(\theta - t) = wx + wc(T - \theta).$$

This experiment is exposed to some serious causes of error. The calorimeter may be heated by radiation from the screen F which protects it from the direct radiation of the furnace. Heat may also be propagated by means of the neck of the retort. Again, the vapour is not *dry* when it passes into the worm, but carries with it small

drops of liquid. Finally, some of the vapour may be condensed at the top of the retort, and so pass into the worm in a liquid state. This last objection is partly removed by sloping the neck of the retort upwards from the fire, but it sometimes happens that this precaution is not sufficient.

140. *Regnault's Experiments.*—The labours of Regnault in connection with the subject of latent heat are of the greatest importance, and have resulted in the elaboration of a method in which all these sources of error are entirely removed. The results obtained by him are the following:—

The quantity of heat required to convert a gramme of water at 100° into vapour, without change of temperature, is 537 gramme-degrees.

If the water were originally at zero, the total amount of heat required to raise it to 100° and then convert it into vapour would evidently be 637 gramme-degrees; and it is this total amount which is most important to know in the application of heat in the arts.

In general, if Q denote the total quantity of heat¹ required to raise water from zero to the temperature T , and then convert it into vapour at this temperature, the value of Q may be deduced with great exactness from the formula

$$Q = 606.5 + .305T. \quad (a)$$

From what we have said above, it will be seen that if λ denote the latent heat of evaporation at temperature T , we must have

$$Q = \lambda + T,$$

whence, by substituting for Q in (a), we have

$$\lambda = 606.5 - .695T. \quad (b)$$

Hence it appears that latent heat varies in the opposite direction to temperature. This fact had been previously discovered by Watt; but he went too far, and maintained that the increase of the one was *equal* to the diminution of the other, or, in his own words, that "the sum of the sensible and latent heats" (that is $T + \lambda$) "is constant." From (a) we can find the total heat for any given temperature, and from (b) the latent heat of evaporation at any given tem-

¹ Called by Regnault the total heat of saturated vapour at T° , or the total heat of vaporization at T° .

perature. The results for every tenth degree between 0° and 230° are given in the following table:—

Temperatures Centigrade.	Latent Heat.	Total Heat.	Temperatures Centigrade.	Latent Heat.	Total Heat.
0°	606	606	120°	522	642
10	600	610	130	515	645
20	593	613	140	508	648
30	586	616	150	501	651
40	579	619	160	494	654
50	572	622	170	486	656
60	565	625	180	479	659
70	558	628	190	472	662
80	551	631	200	464	664
90	544	634	210	457	667
100	537	637	220	449	669
110	529	639	230	442	672

To reduce latent heat and total heat from the Centigrade to the Fahrenheit scale, we must multiply by $\frac{9}{5}$. Thus the latent and total heat of steam at 212° F. are 966.6 and 1146.6. Total heat is here reckoned from 32° F. If we reckon it from 0° F., 32 must be added.

The following table taken from the researches of Favre and Silbermann, gives the latent heat of evaporation of a number of liquids at the temperature of their boiling-point, referred to the Centigrade scale:—

	Boiling- point.	Latent Heat.		Boiling- point.	Latent Heat.
Wood-spirit,	66.5°	264	Acetic acid,	120°	102
Absolute alcohol, . .	78	208	Butyric acid,	164	115
Valeric alcohol, . . .	78	121	Valeric acid,	175	104
Ether,	38	91	Acetic ether,	74	100
Ethyl,	38	58	Oil of turpentine, . .	156	69
Valeric ether,	113.5	113.5	Essence of citron, . .	165	70
Formic acid,	100	169			

CHAPTER XI.

HYGROMETRY.

141. *Humidity*.—The condition of the air as regards moisture involves two elements:—(1) the amount of vapour present in the air, and (2) the ratio of this to the amount which would saturate the air at the actual temperature. It is upon the second of these elements that our sensations of dryness and moisture chiefly depend, and it is this element which meteorologists have agreed to denote by the term *humidity*; or, as it is sometimes called, *relative humidity*. It is usually expressed as a percentage.

The words *humid* and *moist*, as applied to air in ordinary language, nearly correspond to this technical use of the word *humidity*; and air is usually said to be dry when its *humidity* is considerably below the average. In treatises on physics, “dry air” usually denotes air whose humidity is zero.

The air in a room heated by a hot stove contains as much vapour weight for weight as the open air outside; but it is drier, because its capacity for vapour is greater. In like manner the air is drier at noon than at midnight, though the amount of vapour present is about the same; and it is for the most part drier in summer than in winter, though the amount of vapour present is much greater.

It is to be borne in mind that a cubic foot of air is able to take up the same amount of vapour as a cubic foot of empty space; and “relative humidity” may be defined as *the ratio of the mass of vapour actually present in a given space, to the mass which would saturate the space at the actual temperature*.

Since aqueous vapour fulfils Boyle’s law, these masses are proportional to the vapour-pressures which they produce, and relative humidity may accordingly be defined as *the ratio of the actual*