

CHAPTER X.

QUANTITATIVE MEASUREMENTS RELATING TO VAPOURS.

122. Pressure of Aqueous Vapour.—The knowledge of the maximum pressure of the vapour of water at various temperatures is important, not only from a theoretical, but also from a practical point of view, inasmuch as this pressure is the motive force in the steam-engine. Experiments for determining it have accordingly been undertaken by several experimenters in different countries. The researches conducted by Regnault are especially remarkable for the range of temperature which they embrace, as well as for the number of observations which they include, and the extreme precision of the methods employed. Next to these in importance are the experiments of Magnus in Germany and of Fairbairn and Tate in England.

123. Dalton's Apparatus.—The first investigations in this subject which have any pretensions to accuracy were those of Dalton. The apparatus which he employed is represented in Fig. 80. Two barometric tubes A and B are inverted in the same cistern H; one is an ordinary barometer, the other a vapour-barometer; that is, a barometer in which a few drops of water have been passed up through the mercury. The two tubes, attached to the support CD, are surrounded by a cylindrical glass vessel containing water which can be raised to different temperatures by means of a fire. The first step is to fill the vessel with ice, and then read the difference of level of the mercury in the two tubes. This can be done by separating the fragments of ice. The difference thus observed is the pressure of aqueous vapour at zero Centigrade. The ice is then replaced by water, and the action of the fire is so regulated as to give different temperatures, ranging between 0° and 100° C., each of which is preserved constant for a few minutes, the water being at the same time well stirred by means of the agitator *pq*, so as to insure uniformity

of temperature throughout the whole mass. The difference of level in the two barometers is read off in each case; and we have thus the means of constructing, with the aid of graphical or numerical interpolation, a complete table of vapour-pressures from 0° to 100° C. At or about this latter temperature the mercury in the vapour-barometer falls to the level of the cistern; and the method is therefore inapplicable for higher temperatures. Such a table was constructed by Dalton.

124. Regnault's Modifications.—Dalton's method has several defects. In the first place, it is impossible to insure that the temperature shall be everywhere the same in a column as long as that which is formed by the vapour at 70°, 75°, and higher temperatures. In the second place, there is always a good deal of uncertainty in observing the difference of level through the sides of the cylindrical glass vessel. Regnault employed this method only up to the temperature of 50° C. At this temperature the pressure of the vapour is only about

9 centimetres (less than 4 inches) of mercury, and it is thus unnecessary to heat the barometers throughout their entire length. The improved apparatus is represented in Fig. 81. The two barometric tubes, of an interior diameter of 14 millimetres, traverse two holes in the bottom of a metal box. In one of the sides of the box is a large opening closed with plate-glass, through which the necessary observations can be made with great accuracy. On account of the shortness of the liquid column it was very easy, by bringing a spirit-lamp within different distances of the box, to maintain for a sufficient time any temperature between 0° and 50° C.

The difference of level between the two mercurial columns should be reduced to 0° C. by the ordinary correction. We should also take into consideration the short column of water which is above the

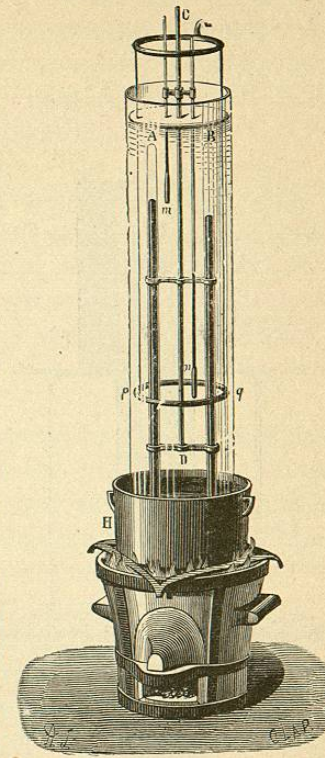


Fig. 80.—Dalton's Apparatus.

mercury in the vapour barometer, and which, by its weight, produces a depression that may evidently be expressed in mercury by dividing the height of the column by 13.59.

To adapt this apparatus to low temperatures, it is modified in the following way. The upper extre-

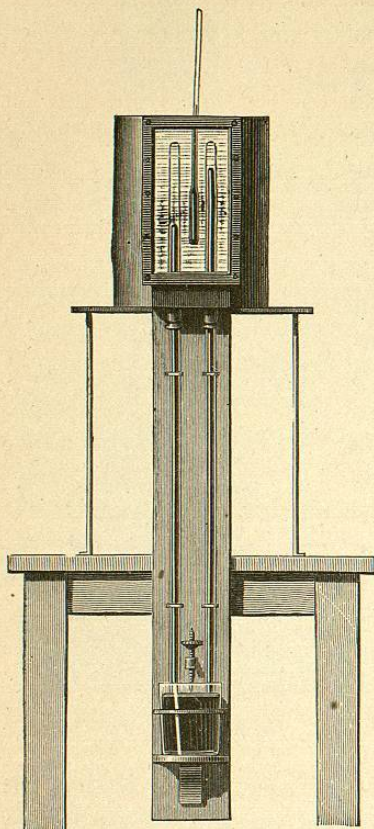


Fig. 81.—Modified Form of Dalton's Apparatus.

above the mercury, is filled with vapour. This form of apparatus can also be employed for temperatures up to 50° , the only difference being that the ice is replaced by water at different temperatures, allowance being made, in each case, for the elastic force of the unexhausted air.

In the case of temperatures below zero, the box is no longer required, and the globe alone is placed in a vessel containing a freezing-mixture. The barometric tubes are surrounded by the air of the apartment.

mity of the vapour barometer tube is drawn out and connected with a small copper tube of three branches, one of which communicates with an air-pump, and another with a glass globe of the capacity of about 500 cubic centimetres. In the interior of this globe is a small bulb of thin glass containing water, from which all the air has been expelled by boiling. The globe is several times exhausted of air, and after each exhaustion is refilled with air which has been passed over desiccating substances. After the last exhaustion, the tube which establishes communication with the air-pump is hermetically sealed, the box is filled with ice, and the pressure at zero of the dry air left behind in the globe by the air-pump is measured; it is of course exceedingly small. Heat is then applied to the globe, the little bulb bursts, and the globe, together with the space

In this case the space occupied by the vapour is at two different temperatures in different parts, but it is evident that equilibrium can exist only when the pressure is the same throughout. But the pressure of the vapour in the globe can never exceed the maximum pressure for the actual temperature; this must therefore be the pressure throughout the entire space, and is consequently that which corresponds to the difference of level observed.

In reality what happens is as follows:—The low temperature of the globe causes some of the vapour to condense; equilibrium is consequently destroyed, a fresh quantity of vapour is produced, enters the globe, and is there condensed, and so on, until the pressure is everywhere the same as the maximum pressure due to the temperature of the globe. This condensation of vapour in the cold part of the space was utilized by Watt in the steam-engine; it is the *principle of the condenser*.

Before Regnault, Gay-Lussac had already turned this principle to account in a similar manner for the measurement of low temperatures.

By using chloride of calcium mixed with successively increasing quantities of snow or ice, the temperature can be brought as low as -32° C. (-25.6° F.), and it can be shown that the pressure of the vapour of water is quite appreciable even at this point.

125. Measurement of Pressures for Temperatures above 50° .—In investigating the maximum pressure of the vapour of water at temperatures above 50° , Regnault made use of the fact that the pressure of the steam of boiling water is equal to the external pressure.

His apparatus consists (Fig. 82) of a copper boiler containing water which can be raised to different temperatures indicated by very delicate thermometers. The vapour produced passes through a tube inclined upwards, which is kept cool by a constant current of water; in this way the experiment can be continued for any length of time, as the vapour formed by ebullition is condensed in the tube, and flows back into the boiler. The tube leads to the lower part of a large reservoir, in which the air can be either rarefied or compressed at will. This reservoir is in communication with a manometer. The apparatus shown in the figure is that employed for pressures not exceeding 5 atmospheres. Much greater pressures, extending to 28 atmospheres, can be attained by simply altering the dimensions of the apparatus without any change in its principle. The manometer employed in this case was the same as that used in testing Boyle's law, consisting of a long column of mercury.

In using this apparatus, the air in the reservoir is first rarefied until the water boils at about 50° C.; the occurrence of ebullition being recognized by its characteristic sound, and by the temperature

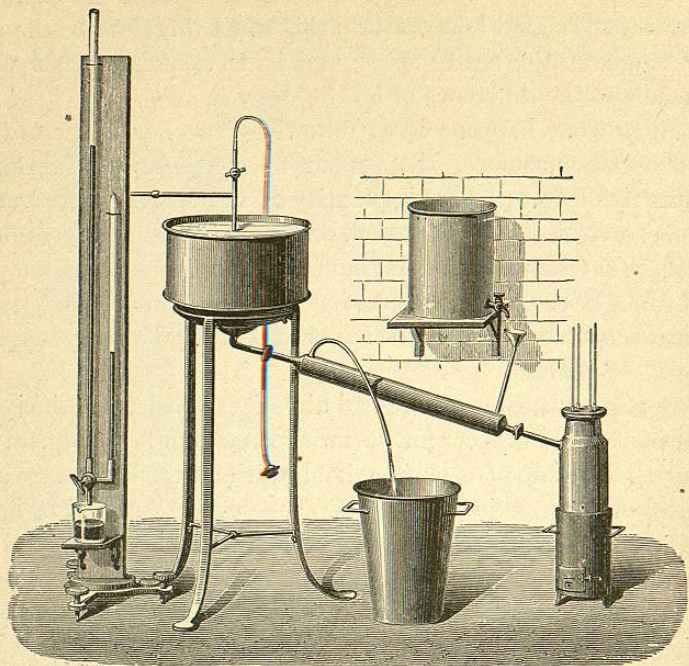


Fig. 82.—Regnault's Apparatus for High Temperatures.

remaining invariable. This steadiness of temperature is of great advantage in making the observations, inasmuch as it enables the thermometers to come into perfect equilibrium of temperature with the water. The pressure indicated by the manometer during ebullition is exactly that of the vapour produced. By admitting air into the reservoir, the boiling-point is raised by successive steps until it reaches 100°. After this, air must be forced into the reservoir by a compression-pump.

The following is an abstract of the results thus obtained:—

Temperatures Centigrade.	Pressures in Millimetres of Mercury.	Temperatures Centigrade.	Pressures in Millimetres of Mercury.
-32°	0·32	5°	6·53
-20	0·93	10	9·17
-10	2·09	15	12·70
- 5	3·11	20	17·39
0	4·60	25	23·55

Temperatures Centigrade.	Pressures in Millimetres of Mercury.	Temperatures Centigrade.	Pressures in Millimetres of Mercury.
30°	31·55	70°	233·09
35	41·82	75	288·61
40	54·91	80	354·64
45	71·39	85	433·04
50	91·98	90	525·45
55	117·47	95	633·77
60	148·70	100	760·00
65	186·94		

	Pressures in Atmospheres.		Pressures in Atmospheres.
100°	1	180°	9·929
121	2·025	189	12·125
134	3·008	199	15·062
144	4·000	213	19·997
152	4·971	225	25·125
159	5·966	230	27·534
171	8·036		

126. Curve of Steam-pressure.—The comparison of these pressures with their corresponding temperatures affords no clue to any simple relation between them which might be taken as the physical law of the phenomena. It would appear that the law of variation of maximum pressures is incapable of being thrown into any simple expression—judging at least from the failure of all efforts hitherto made. An attentive examination of the above table will enable us to assert only that the maximum pressure varies more rapidly than the temperature. Thus between 0° and 100° the variation is only 1 atmosphere, but between 100° and 200° it is about 15, and between 200° and 230° about 13 atmospheres.

The clearest way of representing to the mind the law according to which steam-pressure varies with temperature, is by means of a curve whose ordinates represent steam-pressures, while the abscissæ represent the corresponding temperatures. Such a curve is exhibited in Fig. 83. Lengths proportional to the temperatures, reckoned from 0° C., are laid off on the base-line (called the line of abscissæ), and perpendiculars (called ordi-

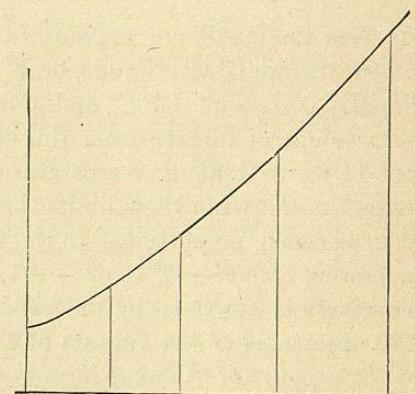


Fig. 83.

nates) are erected at their extremities, the lengths of these perpendiculars being made proportional to the steam-pressures. The scales employed for the two sets of lengths are of course quite independent of one another, their selection being merely a question of convenience. The curve itself is obtained by joining the extremities of the perpendiculars, taking care to avoid sudden changes of direction; and it not only serves to convey to the mind an idea of the amounts of pressure and their rates of variation at different temperatures, but also furnishes the readiest means of determining the pressures at temperatures intermediate between those of observation

It will be noticed that the curve becomes steeper as the temperature increases, indicating that the pressure increases faster at high than at low temperatures.

127. Empirical Formulæ.—Though all attempts at finding a rational formula for steam-pressure in terms of temperature have hitherto failed, it is easy to devise empirical formulæ which yield tolerably accurate results within a limited range of temperature; and by altering the values of the constants in such a formula by successive steps, it may be adapted to represent in succession the different portions of the curve above described.

The simplest of these approximate formulæ¹ is that of Dulong and Arago, which may be written—

$$\left(\frac{40+C}{140}\right)^5 \quad \text{or} \quad \left(\frac{40+F}{252}\right)^5,$$

and gives the maximum pressure *in atmospheres*, corresponding to the temperature C° Centigrade, or F° Fahrenheit. This formula is rigorously correct at 100° C., and gives increasing errors as the temperature departs further from this centre, the errors amounting to about 1½ per cent. at the temperatures 80° C. and 225° C. Hence it appears that between these limits the maximum pressure of aqueous vapour is nearly proportional to the fifth power of the excess of the temperature above -40° C. or -40° F. (for it so happens that this temperature is expressed by the same number on both scales).

128. Pressures of the Vapours of Different Liquids.—Dalton held that *the vapours of different liquids have equal pressures at temperatures equally removed from their boiling-points*. Thus the boiling-point of alcohol being 78°, the pressure of alcohol vapour at 70° should be equal to that of the vapour of water at 92°. If this law were correct, it would only be necessary to know the boiling-point

¹ For a general formula, see *Rankine on Steam-engine*, p. 237.

of any liquid in order to estimate the pressure of its vapour at any given temperature; but subsequent experiment has shown that the law is far from being rigorously exact, though it is approximately correct for temperatures differing by only a few degrees from the boiling-points.

Regnault has performed numerous experiments on the vapour-pressures of some of the more volatile liquids, employing for this purpose the same form of apparatus which had served for determining the pressures of aqueous vapour. The following are some of his results:—

VAPOUR OF ALCOHOL.			
Temperatures Centigrade.	Pressures in Millimetres.	Temperatures Centigrade.	Pressures in Millimetres.
-20°	3.24	+ 30°	78.52
0	12.70	100	1697.55
+10	24.23	155	6259.19

VAPOUR OF ETHER.			
Temperatures Centigrade.	Pressures in Millimetres.	Temperatures Centigrade.	Pressures in Millimetres.
-20°	68.90	+ 30°	634.80
0	184.39	100	4953.30
+10	286.83	120	7719.20

VAPOUR OF SULPHIDE OF CARBON.			
Temperatures Centigrade.	Pressures in Millimetres.	Temperatures Centigrade.	Pressures in Millimetres.
-20°	47.30	+ 30°	434.62
0	127.91	100	3325.15
+10°	198.46	150	9095.94

129. Expression of Vapour-pressure in Absolute Measure.—The maximum pressure of a given vapour at a given temperature is, from its very nature, independent of geographical position, and should therefore, properly speaking, be denoted by one and the same number at all places. This numerical uniformity will not exist if the pressure be expressed, as in the preceding sections, in terms of the length of a column of mercury which balances it. For example, in order to adapt Regnault's determinations to London, we must multiply them by the fraction $\frac{34.56}{34.57}$, inasmuch as 3456 millimetres of mercury exert the same pressure at London as 3457 at Paris. In general, to adapt determinations of pressure made at a place A, to another place B, we must multiply them by the fraction

$$\frac{\text{gravity at A}}{\text{gravity at B}}$$

For if *h* denote the height (in centimetres) of a column of mercury at 0°, which produces a pressure *p* (dynes per sq. cm.), and *d* be the density of mercury at 0°, we have (see *Hydrostatics* in Part I.)

$$p = gh d.$$

Hence, in order that p may be the same at different places, the values of gh must be the same; in other words, h must vary inversely as g .

130. **Laws of Combination by Volume.**—It was discovered by Gay-Lussac, that when two or more gaseous elements at the same temperature and pressure enter into chemical combination with each other, the two following laws apply:—

1. The volumes of the components bear a very simple ratio to each other, such as 2 to 3, 1 to 2, or 1 to 1.

2. The volume of the compound has a simple ratio to the sum of the volumes of the components.

Ammonia, for example, is formed by nitrogen and hydrogen uniting in the proportion of one volume of the former to three of the latter, and the volume of the ammonia, if reduced to the same pressure as each of its constituents, is just half the sum of their volumes. Further investigation has led to the conclusion (which is now generally received, though hampered by some apparent exceptions), that these laws apply to all cases of chemical combination, the volumes compared being those which would be occupied respectively by the combining elements and the compound which they form, *when reduced to the state of vapour*, at such a temperature and pressure as to be very far removed from liquefaction, and consequently to possess the properties of what we are accustomed to call permanent gases.

It is obvious that if all gases and vapours were equally expansible by heat, the volume-ratios referred to in this law would be the same at all temperatures; and that, in like manner, if they were all equally compressible (whether obeying Boyle's law, or departing equally from it at equal pressures), the volume-ratios would be independent of the pressure at which the comparison was made.

In reality great differences exist between different vapours in both respects, and these inequalities are greater as the vapours are nearer to saturation. It is accordingly found that the above laws of volume-ratio often fail to apply to vapours when under atmospheric pressure and within a few degrees of their boiling-points, and that, in such cases, a much nearer fulfilment of the law is obtained by employing very high temperatures, or operating in inclosures at very low pressures.

131. **Relation of Vapour-densities to Chemical Equivalents.**—Chemists have determined with great accuracy the combining proportions by weight of most of the elements. Hence the preceding laws can

be readily tested for bodies which usually exist in the solid or liquid form, if we are able to compare the densities of their vapours. In fact, if two such elements combine in the ratio, by weight, of w_1 to w_2 , we have

$$v_1 = \frac{w_1}{d_1}, \quad v_2 = \frac{w_2}{d_2},$$

$v_1 v_2 d_1 d_2$ denoting the volumes and densities of the vapours of weights $w_1 w_2$ of the two substances.

Hence we have the equation—

$$\frac{v_1}{v_2} = \frac{w_1}{w_2} \cdot \frac{d_2}{d_1},$$

which gives the required volume-ratio of the vapours, if the ratio of their densities be known.

The densities themselves will differ enormously according to the pressure and temperature at which they are taken, but their ratio will only vary by comparatively small amounts, and would not differ at all if they were equally expansible by heat, and equally compressible. Hence comparison will be facilitated by tabulating the ratios of the densities to that of some standard gas, namely air, under the same conditions of pressure and temperature, rather than the absolute densities. This is accordingly the course which is generally pursued, so generally indeed, that by the *vapour-density of a substance* is commonly understood the relative density as measured by this ratio.

The process most frequently employed for the determination of this element is that invented by Dumas.

132. **Dumas' Method.**—The apparatus consists of a glass globe B, containing the substance which is to be converted into vapour.

The globe is placed in a vessel C, containing some liquid which can be raised to a suitable temperature. If the substance to be operated on is one which can be vaporized at 100°C .

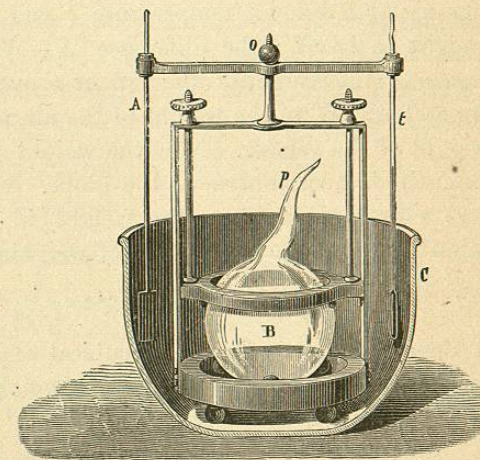


Fig. 84.—Dumas' Apparatus.