

reservoirs communicates with the bottom of the boiler. The boiler, tubes, and reservoirs are all completely filled with water, with the

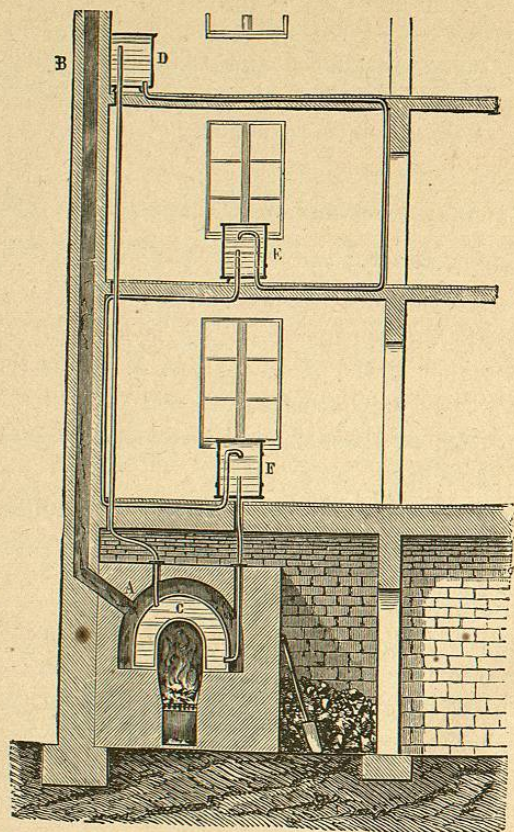


Fig. 36.—Heating by Hot Water.

exception of a small space left above in order to give room for the expansion of the liquid. An ascending current flows through the left-hand tube, and the circulation continues with great regularity, so long as the temperature of the water in the boiler remains constant.

CHAPTER V.

EXPANSION OF GASES.

44. Experiments of Gay-Lussac.—Gay-Lussac conducted a series of researches on the expansion of gases, the results of which were long regarded as classical. He employed a thermometer with a large reservoir A, containing the gas to be operated on; an index of mercury *mn* separated the gas from the external air, while leaving it full liberty to expand. The gas had previously been dried by pass-

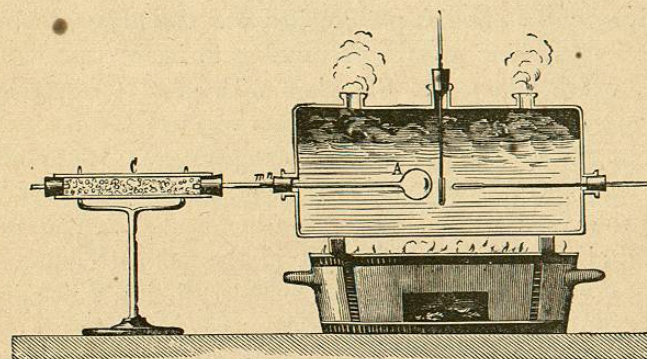


Fig. 37.—Gay-Lussac's Apparatus.

ing it through a tube containing chloride of calcium, or some other desiccating substance. The thermometer was first placed in a vessel filled with melting ice, and when the gas had thus been brought to 0° C., the tube was so adjusted that the index coincided with the opening through which the thermometer passed.

The tube and reservoir having been previously gauged, and the former divided into parts of equal capacity, the apparent volume of the gas (expressed in terms of these divisions) is indicated by the position of the index; let the apparent volume observed at 0° C. be called *n*, and let *H* denote the external pressure as indicated by a

barometer. The apparatus is then raised to a known temperature t by means of the furnace below the vessel, and the stem of the thermometer is moved until the index reaches the edge of the opening. Let n' be the apparent volume of the gas at this new temperature, and as the external pressure may have varied, let it be denoted by H' . The real volumes of the gas will be as n to $n' (1 + gt)$, where g denotes the mean coefficient of expansion of the glass; and the products of volume and pressure will be as nH to $n' (1 + gt) H'$. Hence if a denote the mean coefficient of expansion of the air, we have

$$nH(1 + at) = n'(1 + gt)H';$$

from which equation a can be determined.

By means of this method Gay-Lussac verified the law previously announced by Sir Humphry Davy for air, that the coefficient of expansion is independent of the pressure. He also arrived at the result that this coefficient is sensibly the same for all gases. He found its value for dry air to be .00375. This result, which was for a long time the accepted value, is now known to be in excess of the truth. Rudberg, a Swedish philosopher, was the first to point out the necessity for using greater precautions to insure the absence of moisture, which adheres to the glass with great tenacity at the lower temperature, and, by going off into vapour when heated, adds to the volume of the air at the higher temperature. He found that the last traces of vapour could only be removed by repeatedly exhausting the vessel with an air-pump when heated, and refilling it with dried air. Another weak point in the method employed by Gay-Lussac was the shortness of the mercurial index, which, in conjunction with the fact that mercury does not come into close contact with glass (as proved by the fact of its not wetting it), allowed a little leakage in both directions. These imperfections have been remedied in later investigations, of which the most elaborate are those of Regnault. He employed four distinct methods, of which we shall only describe one.

45. *Regnault's Apparatus.*—The glass vessel BC (Fig. 38) containing the air to be experimented on, is connected with the T-shaped piece EI, the branch I of which communicates, through desiccating tubes, with an air-pump, and is hermetically closed with a blow-pipe after the vessel has received its charge of dry air; while the branch ED communicates with the top of a mercurial manometer. A mark is made at a point b in the capillary portion of the tube, and in every

observation the mercury in the manometer is made to reach exactly to this point, either by pouring in more mercury at the top M' of the other tube of the manometer, or by allowing some of the liquid to escape through the cock R at the bottom. The air under experiment is thus always observed at the same apparent volume, and the observation gives its pressure. The vessel B is inclosed within a

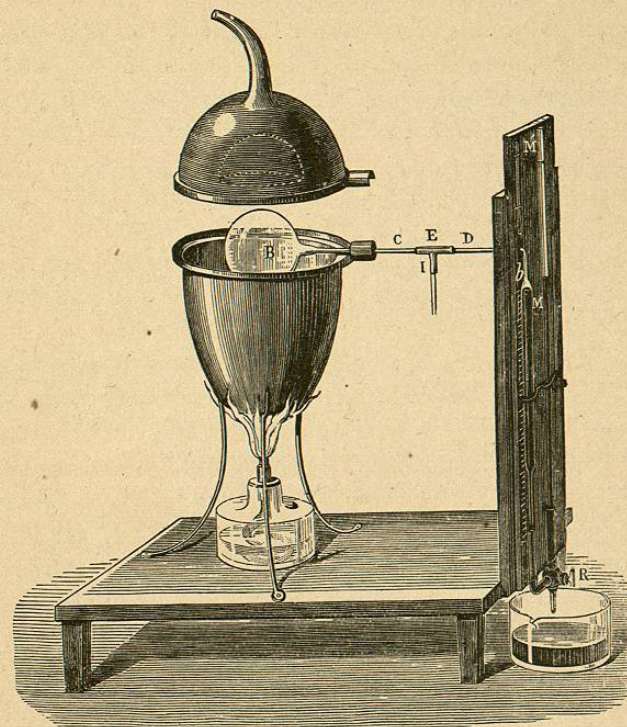


Fig. 38.—Regnault's Apparatus.

boiler, which consists of an inner and an outer shell, with a space between them, through which the steam circulates when the water boils.

In reducing the observations, the portion of the glass vessel within the boiler is regarded as having the temperature of the water in the boiler, while the portion of the tube external to the boiler is regarded as having the temperature of the surrounding air.

In this mode of operating, the volume, or at least the apparent volume, is constant, so that the coefficient a which is determined is substantially defined by the equation

$$P_t = P_0 (1 + at),$$

P_0 and P_t denoting the pressures at constant volume. The coefficient thus defined should be called the *coefficient of increase of pressure*. It is often called the "coefficient of expansion at constant volume," which is a contradiction in terms.

In another mode of operating Regnault observed the expansion at constant pressure, and thus determined the *coefficient of expansion* properly so called. A small but steady difference was found between the two. If Boyle's law were exact they would be identical. As a matter of fact, the coefficient of increase of pressure was found, in the case of air and all gases except hydrogen, to be rather less than the coefficient of expansion. In other words, the product of volume and pressure at one and the same temperature t° was found to be least when the volume was least; a result which accords with Regnault's direct observations on Boyle's law.

46. Results.—The following table contains the final results for the various gases which were submitted to experiment:—

	Coefficient of increase of pressure at con- stant volume.		Coefficient of increase of volume at con- stant pressure.
Air.....	0·003665	0·003670
Nitrogen.....	0·003668	
Hydrogen.....	0·003667	0·003661
Carbonic oxide.....	0·003667	0·003669
Carbonic acid.....	0·003688	0·003710
Nitrous oxide.....	0·003676	0·003720
Cyanogen.....	0·003829	0·003877
Sulphurous acid.....	0·003845	0·003903

It will be observed that the largest values of the coefficients belong to those gases which are most easily liquefied.

We may add that the coefficients increase very sensibly with the pressure; thus between the pressures of one and of three atmospheres the coefficient of expansion of air increases from 0·00367 to 0·00369. This increase is still more marked in the case of the more liquefiable gases.

47. Reduction to the Fahrenheit Scale.—The coefficient of expansion of any substance per degree Fahrenheit is $\frac{5}{9}$ of the coefficient per degree Centigrade; the volume at 32° F. being made the standard from which expansions are reckoned, so that if V_0 denote the volume at this temperature and V the volume at t° F., the coefficient of expansion α is defined by the equation

$$V = V_0 \{1 + \alpha (t - 32)\}.$$

48. Air-thermometer.—The close agreement between the expansions of different gases, and between the expansions of the same gas at different pressures, is a strong reason for adopting one of these bodies as the standard substance for the measurement of temperature by expansion, rather than any particular liquid.

Moreover, the expansion of gases being nearly twenty times as great as that of mercury, the expansion of the containing vessel will be less important; the apparent expansion will be nearly the same as the real expansion, and differences of quality in the glass will not sensibly affect the comparability of different thermometers.

Air-thermometers have accordingly been often used in delicate investigations. They consist, like other thermometers, of a reservoir and tube; but the latter, instead of being sealed, is left open. This open end, in one form of the instrument, is pointed downwards, and immersed in a liquid, usually mercury, which rises to a greater or less distance up the tube as the air in the thermometer contracts or expands. As variations of pressure in the surrounding air will also affect the height of this column of liquid, it is necessary to take readings of the barometer, and to make use of them in reducing the indications of the air-thermometer. Even if the barometer continues steady, it is still necessary to apply a correction for changes of pressure; since the difference between the pressure in the air-thermometer and that of the external air is not constant, but is proportional to the height of the column of liquid.

In the form of air-thermometer finally adopted by Regnault, the air in the instrument was kept at constant (apparent) volume, and its variations of pressure were measured, the apparatus employed being precisely that which we have described in § 45.

49. Perfect Gas.—In discussions relating to the molecular constitution of gases, the name *perfect gas* is used to denote a gas which would exactly fulfil Boyle's law; and molecular theories lead to the conclusion that for all such gases the coefficients of expansion would be equal. Actual gases depart further from these conditions as they are more compressed below the volumes which they occupy at atmospheric pressure; and it is probable that when very highly rarefied they approach the state of "perfect gases" very closely indeed.

50. Absolute Temperature by Air-thermometer.—*Absolute temperature by the air-thermometer* is usually defined by the condition that the temperature of a given mass of air at constant pressure is to be regarded as *proportional to its volume*. If the difference of

temperature between the two ordinary fixed points be divided into a hundred degrees, as in the ordinary Centigrade thermometer, the two fixed points themselves will be called respectively 273° and 373° ; since air expands by $\frac{1}{273}$ of its volume at the lower fixed point for each degree, and therefore by $\frac{100}{273}$ of this volume for a hundred degrees.

There is some advantage in altering the definition so as to make the temperature of a given mass of air at constant volume *proportional to its pressure*. The two fixed points will then be 273° and 373° as above, and the zero of the scale will be that temperature at which the pressure vanishes.

The advantage of the second form of definition is that it enables us to continue our scale down to this point—called absolute zero—without encountering any physical impossibility, such as the conception of reducing a finite quantity of air to a mathematical point, which would be required according to the first form of definition.

Practically, "absolute temperatures by air-thermometer" are computed by adding 273 to ordinary "temperatures by air-thermometer," these latter being expressed on the Centigrade scale. We shall employ the capital letter T to denote absolute temperature, and the small letter t to denote ordinary temperature. We have

$$T = 273 + t,$$

and the general law connecting the volume, pressure, and temperature of a gas is

$$\frac{VP}{T} = \text{constant};$$

or, introducing the density D instead of the volume V ,

$$\frac{P}{DT} = \text{constant}.$$

As above explained, these laws, though closely approximate in ordinary cases, are not absolutely exact.

51. **Pyrometers.**—The measurement of high temperatures such as those of furnaces is very difficult. Instruments for this purpose are called pyrometers. One of the best is the air-thermometer employed by Deville and Troost, having a bulb of hard porcelain.

52. **Density of Gases.**—The *absolute density* of a gas—that is, its mass per unit volume—which is denoted by D in the above formula, is proportional, as the formula shows, to $\frac{P}{T}$, and may therefore

undergo enormous variation. In stating the *relative density* of a gas as compared with air, the air and the gas are supposed to be at the same pressure and temperature. For purposes of great accuracy this pressure and temperature must be specified, since, as we have seen, there are slight differences in the changes produced in different gases by the same changes of pressure and temperature. The comparison is generally supposed to be made at the temperature 0°C. , and at the pressure of one standard atmosphere.

53. **Measurement of the Relative Density of a Gas.**—The densities of gases have been the subject of numerous investigations; we shall describe only the method employed by Regnault.

The gas is inclosed in a globe, of about 12 litres capacity (Fig. 39), furnished with a stop-cock leading to a three-way tube, one of whose branches is in communication with a manometer, and the other with an air-pump. The globe is exhausted several times, and each time the gas is dried on its way to the globe by passing through a number of tubes containing pieces of pumice-stone moistened with sulphuric acid. When all moisture has been removed, the globe is surrounded with melting ice, and is kept full of gas at the pressure of the atmosphere till sufficient time has been given for its contents to assume the temperature of the melting ice. The stop-cock is then closed, the globe is taken out, carefully dried, and allowed to take the temperature of the atmosphere. It is then weighed with a delicate balance.

The experiment is repeated, with no change except that by means of the air-pump the gas in the globe is reduced to as small a pressure as possible. Let this pressure be denoted by h , and the atmospheric pressure in the previous experiment by H . Then the difference of the two weights is the weight of as much gas at temperature 0° and pressure $H - h$ as would fill the globe. Let w denote this difference, and let w' be the difference between two weighings made in the same

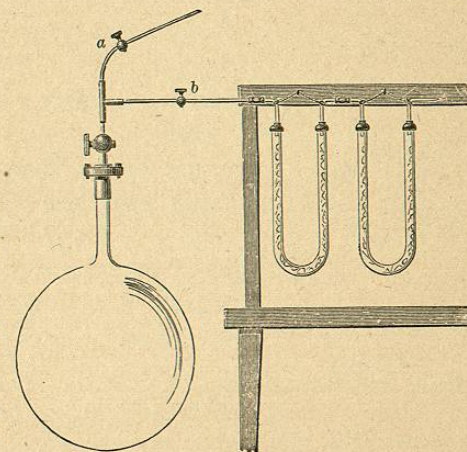


Fig. 39.—Measurement of Density of Gases.