CHAPTER XIX.

BOYLE'S (OR MARIOTTE'S) LAW.[1]

217. Boyle's Law.—All gases exhibit a continual tendency to expand, and thus exert pressure against the vessels in which they are confined. The intensity of this pressure depends upon the volume which they occupy, increasing as this volume diminishes. By a number of careful experiments upon this point, Boyle and Mariotte independently established the law that this pressure varies inversely as the volume, provided that the temperature remain constant. As the density also varies inversely as the volume, we may express the law in other words by saying that at the same temperature the density varies directly as the pressure.

If V and V′ be the volumes of the same quantity of gas, P and P′, D and D′, the corresponding pressures and densities, Boyle's law will be expressed by either of the equations

$$\frac{P}{P'} = \frac{V'}{V}, \quad \frac{P}{P'} = \frac{D}{D'}.$$

218. Boyle's Tube.—The correctness of this law may be verified by means of the following apparatus, which was employed by both the experimenters above named. It consists (Fig. 120) of a bent tube with branches of unequal length; the long branch is open, and the short branch closed. The tube is fastened to a board provided with two scales, one by the side of each branch. The

[1] Boyle, in his *Defence of the Doctrine touching the Spring and Weight of the Air against the Objections of Franciscus Linus*, appended to *New Experiments, Physico-mechanical*, &c. (second edition, 4to, Oxford, 1662), describes the two kinds of apparatus represented in Figs. 120, 121 as having been employed by him, and gives in tabular form the lengths of tube occupied by a body of air at various pressures. These observed lengths he compares with the theoretical lengths computed on the assumption that volume varies reciprocally as pressure, and points out that they agree within the limits of experimental error.

Mariotte's treatise, *De la Nature de l'Air*, is stated in the *Biographie Universelle* to have been published in 1679. (See Preface to Tait's *Thermodynamics*, p. iv.)

graduation of both scales begins from the same horizontal line through 0, 0. Mercury is first poured in at the extremity of the long branch, and by inclining the apparatus to either side, and cautiously adding more of the liquid if required, the mercury can be made to stand at the same level in both branches, and at the zero of both scales. Thus we have, in the short branch, a quantity of air separated from the external air, and at the same pressure. Mercury is then poured into the long branch, so as to reduce the volume of this inclosed air by one-half; it will then be found that the difference of level of the mercury in the two branches is equal to the height of the barometer at the time of the experiment; the compressed air therefore exerts a pressure equal to that of two atmospheres. If more mercury be poured in so as to reduce the volume of the air to one-third or one-fourth of the original volume, it will be found that the difference of level is respectively two or three times the height of the barometer; that is, that the compressed air exerts a pressure equal respectively to that of three or four atmospheres. This experiment therefore shows that if the volume of the gas becomes two, three, or four times as small, the pressure becomes two, three, or four times as great. This is the principle expressed in Boyle's law.

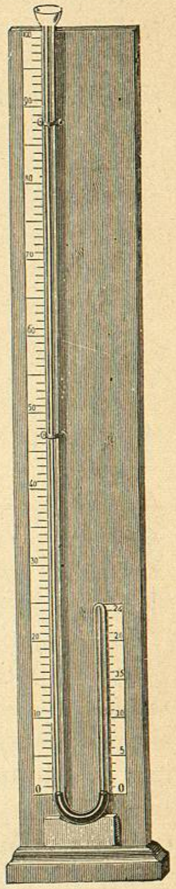

Fig. 120.
Boyle's Tube.

The law may also be verified in the case where the gas expands, and where its pressure consequently diminishes. For this purpose a barometric tube (Fig. 121), partially filled with mercury, is inverted in a tall vessel, containing mercury also, and is held in such a position that the level of the liquid is the same in the tube and in the vessel. The volume occupied by the gas is marked, and the tube is raised; the gas expands, its pressure diminishes, and, in virtue of the excess of the atmospheric pressure, a column of mercury *ab* rises in the tube, such that its height, added to the pressure of the expanded air, is equal to the atmospheric pressure. It will then be seen that if the volume of air becomes double what it was before, the height of the column raised is one-half that of the barometer; that is, the expanded air exerts a pressure equal to half that of the atmosphere. If the volume is trebled, the height of the column is two-thirds that of the barometer; that is, the pressure of the expanded air is one-third that of the atmosphere, a result in accordance with Boyle's law.

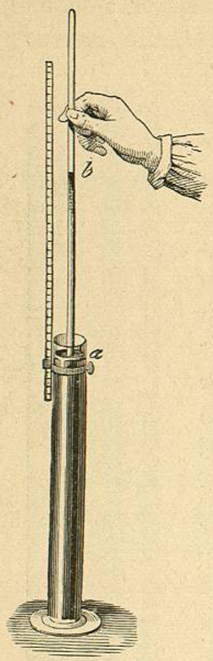

Fig. 121.—Proof of Boyle's Law for Expanding Air.

219. Despretz's Experiments.—The simplicity of Boyle's law, taken in conjunction with its apparent agreement with facts, led to its general acceptance as a rigorous truth of nature, until in 1825 Despretz published an account of experiments, showing that different gases are unequally compressible. He inverted in a cistern of mercury several cylindrical tubes of equal height, and filled them with different gases. The whole apparatus was then inclosed in a strong glass vessel filled with water, and having a screw piston as in Œrsted's piesometer (§ 130). On pressure being applied, the mercury rose to unequal heights in the different tubes, carbonic acid for example being more reduced in volume than air. These experiments proved that even supposing Boyle's law to be true for one of the gases employed, it could not be rigorously true for more than one.

In 1829 Dulong and Arago undertook a laborious series of experiments with the view of testing the accuracy of the law as applied to air; and the results which they obtained, even when the pressure was increased to twenty-seven atmospheres, agreed so nearly with it as to confirm them in the conviction that, for air at least, it was rigorously true. When re-examined, in the light of later researches, the results obtained by Dulong and Arago seem to point to a different conclusion.

220. Unequal Compressibility of Different Gases.—The unequal compressibility of different gases, which was first established by Despretz's experiments above described, is now usually exhibited by the aid of an apparatus designed by Pouillet (Fig. 122). A is a cast-iron reservoir, containing mercury surmounted by oil. In this latter liquid dips a bronze plunger P, the upper part of which has a thread cut upon it, and works in a nut, so that the plunger can be screwed up or down by means of the lever L. The reservoir A communicates

by an iron tube with another cast-iron vessel, into which are firmly fastened two tubes TT about six feet in length and $\frac{1}{10}$th of an inch in internal diameter, very carefully calibrated. Equal volumes of two gases, perfectly dry, are introduced into these tubes through their upper ends, which are then hermetically sealed. The plunger is then made to descend, and a gradually increasing pressure is exerted, the volumes occupied by the gases are measured, and it is ascertained that no two gases follow precisely the same law of compression. The difference, however, is almost insensible when the gases employed are those which are very difficult to liquefy, as air, oxygen, hydrogen, nitrogen, nitric oxide, and marsh-gas. But when we compare any one of these with one of the more liquefiable gases, such as carbonic acid, cyanogen, or ammonia, the difference is rapidly and distinctly manifested. Thus, under a pressure of twenty-five atmospheres, carbonic acid occupies a volume which is only $\frac{4}{5}$ths of that occupied by air.

221. Regnault's Experiments.—Boyle's law, therefore, is not to be considered as rigorously exact; but it is so nearly exact that to demonstrate its inaccuracy for one of the more permanent gases, and still more to determine the law of deviation for each gas, very precise methods of measurement are necessary. In ordinary experiments on compression, and even in the elaborate investigations of Dulong and Arago, a definite portion of gas is taken and successively diminished in volume by the application of continually increasing pressure. In experiments of this kind, as the pressure increases, the volume under measurement becomes smaller, and the precision with which it can be measured consequently diminishes.

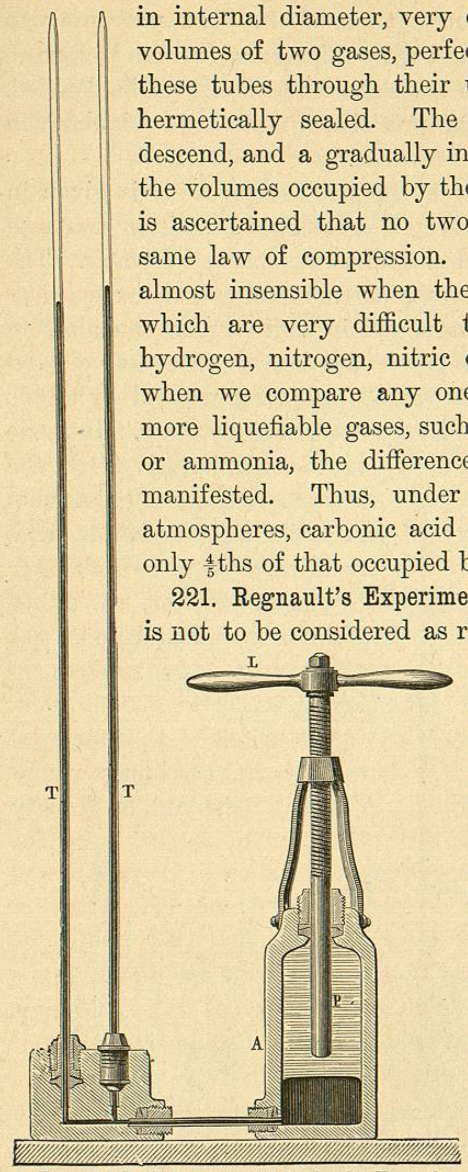

Fig. 122.—Pouillet's Apparatus for showing Unequal Compressibility of Different Gases.

Regnault adopted the plan of operating in all cases upon the same volume of gas, which being initially at different pressures, was always reduced to one-half. The pressure was observed before and after this operation, and, if Boyle's law were true, its value should be found to be doubled. In this way the same precision of measurement is obtained at high as at low pressures.

A general view of Regnault's apparatus is given in Fig. 123. There is an iron reservoir containing mercury, furnished at the top with a force-pump for water. The lower part of this reservoir communicates with a cylinder which is also of iron, and in which are two openings to admit tubes. Communication between the reservoir and the cylinder can be established or interrupted by means of a stop-cock R, of very exact workmanship. Into one of the openings is fitted the lowest of a series of glass tubes A, which are placed end to end, and firmly joined to each other by metal fittings, so as to form a vertical column of about twenty-five metres in height.

The height of the mercurial column in this long manometric tube could be exactly

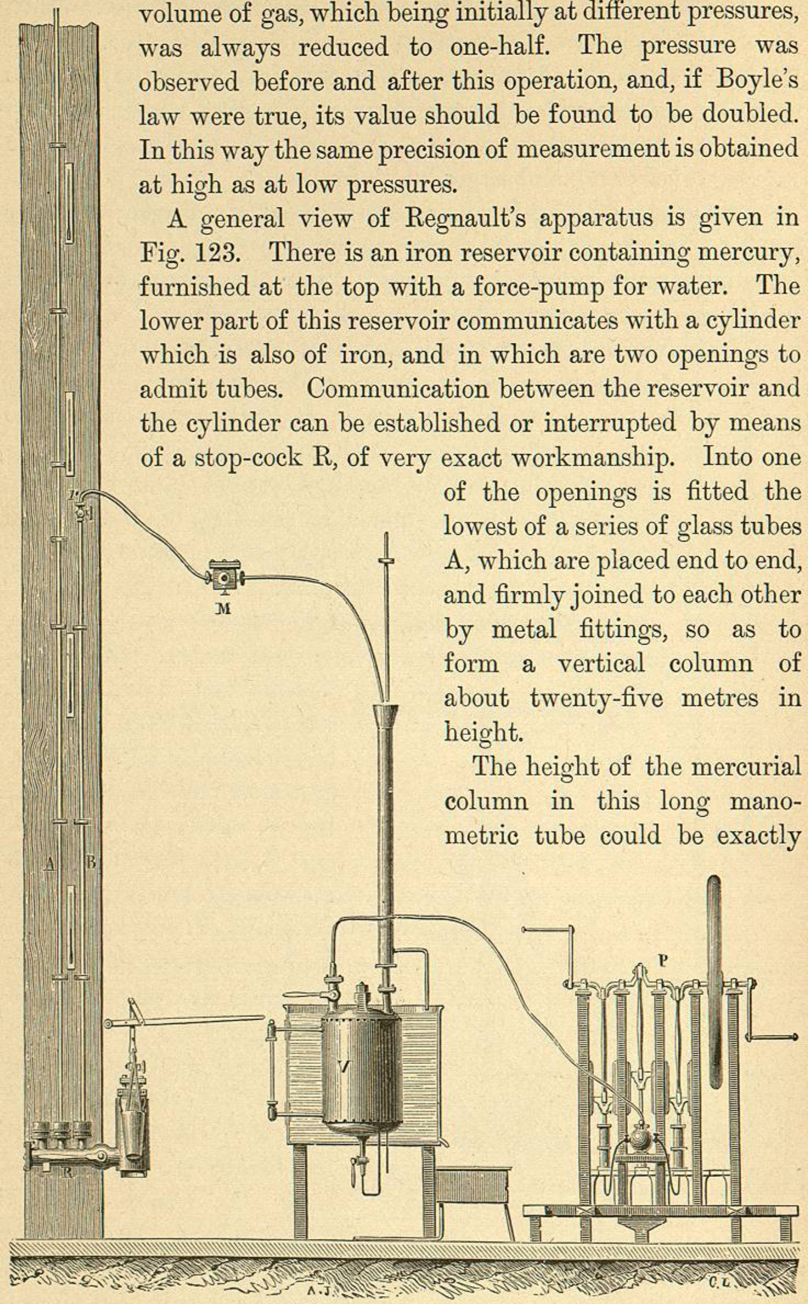

Fig. 123.—Regnault's Apparatus for Testing Boyle's Law.

determined by means of reference marks placed at distances of about ·95 of a metre, and by the graduation on the tubes forming the upper part of the column. The mean temperature of the mercurial column was given by thermometers placed at different heights. Into the second opening in the cylinder fits the lower extremity of the tube B, which is divided into millimetres, and also gauged with great accuracy. This tube has at its upper end a stop-cock *r* which can open communication with the reservoir V, into which the gas to be operated on is forced and compressed by means of the pump P.

An outer tube, which is not shown in the figure, envelops the tube B, and, being kept full of water, which is continually renewed, enables the operator to maintain the tube at a temperature sensibly constant, which is indicated by a very delicate thermometer. Before fixing the tube in its place, the point corresponding to the middle of its volume is carefully ascertained, and after the tube has been permanently fixed, the distance of this point from the nearest of the reference marks is observed.[1]

After these explanatory remarks we may describe the mode of conducting the experiments. The gas to be operated on, after being first thoroughly dried, was introduced at the upper part of the tube B, the stop-cock of the pump being kept open, so as to enable the gas to expel the mercury and occupy the entire length of the tube. The force-pump was then brought into play, and the gas was reduced to about half of its former volume; the pressure in both cases being ascertained by observing the height of the mercury in the long tube above the nearest mark. It is important to remark that it is not at all necessary to operate always upon exactly the same initial volume, and reduce it exactly to one-half, which would be a very tedious operation; these two conditions are approximately fulfilled, and the graduation of the tube enables the observer always to ascertain the actual volumes.

222. Results.—The general result of the investigations of Regnault

[1] Regnault's apparatus was fixed in a small square tower of about fifteen metres in height, forming part of the buildings of the Collége de France, and which had formerly been built by Savart for experiments in hydraulics. The tower could therefore contain only the lower part of the manometric column; the upper part rose above the platform at the top of the tower, resting against a sort of mast which could be ascended by the observer. The readings inside the tower could be made by means of a cathetometer, but this was impossible in the upper portion of the column, and for this reason the tubes forming this portion were graduated.—*D.*

is, that Boyle's law does not exactly represent the compressibility even of air, hydrogen, or nitrogen, which, with carbonic acid, were the gases operated on by him. He found that for all the gases on which he operated, except hydrogen, the product VP of the volume and pressure, instead of remaining constant, as it would if Boyle's law were exact, diminished as the compression was increased. This diminution is particularly rapid in the cases of the more liquefiable gases, such as carbonic acid, at least when the experiments are conducted at ordinary atmospheric temperatures. The lower the temperature, the greater is the departure from Boyle's law in the case of these gases. For hydrogen, he found the departure from Boyle's law to be in the opposite direction;—the product VP increased as the gas was more compressed.

223. Manometers or Pressure-gauges.—Manometers or pressure-gauges are instruments for measuring the elastic force of a gas or vapour contained in the interior of a closed space. This elastic force is generally expressed in units called atmospheres (§ 198), and is often measured by means of a column of mercury.

When one end of the column of mercury is open to the air, as in Regnault's experiments above described, the gauge is called an open mercurial gauge.

The open mercurial pressure-gauge is often used in the arts to measure pressures which are not very considerable. Fig. 124 represents one of its simplest forms. The apparatus consists of a box, generally of iron, at the top of which is an opening closed by a screw stopper, which is traversed by the tube *b*, open at both ends, and dipping into the mercury in the box. The air or vapour whose elastic force is to be measured enters by the tube *a*, and presses upon the mercury. It is evident that if the level of the liquid in the box is the same as in the tube, the pressure in the box must be exactly equal to that of the atmosphere. If the mercury in the tube rises above that in the box, the pressure of the air in the box must exceed that of the atmosphere by a pressure corresponding to the height of the column raised. The pressures are generally marked in atmospheres upon a scale beside the tube.

224. Multiple Branch Manometer.—When the pressures to be measured are considerable, as in the boiler of a high-pressure steam-engine, the above instrument, if employed at all, must be of a length corresponding to the pressure. If, for instance, the pressure in question is eight atmospheres, the length of the tube must be at least

8×30 inches$=20$ feet. Such an arrangement is inconvenient even for stationary machines, and is entirely inapplicable to movable machines.

Without departing from the principle of the open mercurial pressure-gauge, namely, the balancing of the pressure to be observed against the weight of a liquid increased by one atmosphere, we may reduce the length of the instrument by an artifice already employed by Fahrenheit in his barometer (§ 207).

The apparatus for this purpose consists of an iron tube ABCD

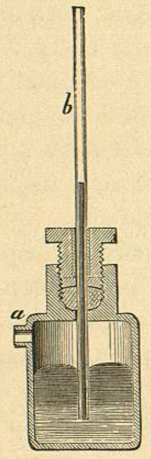

Fig. 124.—Open Mercurial Manometer.

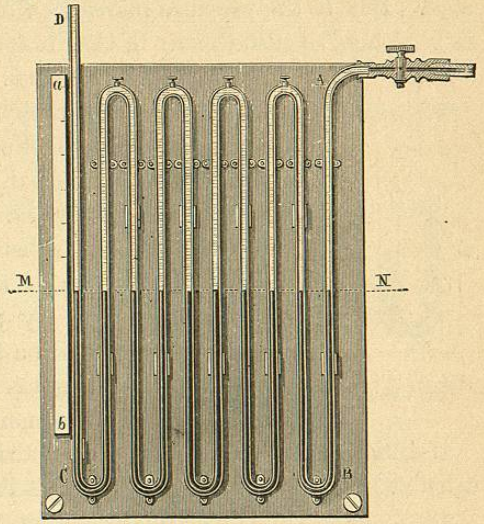

Fig. 125.—Multiple Branch Manometer.

(Fig. 125) bent back upon itself several times. The extremity A communicates with the boiler by a stop-cock, and the last branch CD is of glass, with a scale by its side.

The first step is to fill the tube with mercury as far as the level MN. At this height are holes by which the mercury escapes when it reaches them, and which are afterwards hermetically sealed. The upper portions are filled with water through openings which are also stopped after the tube has been filled. If the mercury in the first tube, which is in communication with the reservoir of gas, falls through a distance h, it will alternately rise and fall through the same distance in the other tubes. The difference of pressure between the two ends of the gauge is represented by the weight of a column of mercury of height $10h$ diminished by the weight of a column of water of height $8h$. Reduced to mercury, the difference of pressure is therefore $10h - \frac{8h}{13 \cdot 5} = 9 \cdot 4h$.