SKETCH OF THE HISTORY OF THERMOMETRY.[1]

BY DR. ERNST MACH.

[CONTINUED.]

BOYLE, in 1661, and Mariotte, in 1676, enunciated the experimental law that the product of the volume of a given mass of gas at constant temperature by the pressure which it exerts on unit of surface is constant. If a mass of air of volume V be subjected to a pressure P, it will assume, on the pressure's increasing to $P' = nP$, the volume $V' = \frac{V}{n}$; whence $PV = nP\frac{V}{n} = P'V'$. If we represent the V's as abscissas and the corresponding P's as ordinates, the areas of the rectangles formed by the P's and Vs will in all cases be equal. The equation $PV = a\ constant$ gives as its graph an equilateral hyperbola, which is the visualisation of Boyle's Law. (See Fig. 9.)

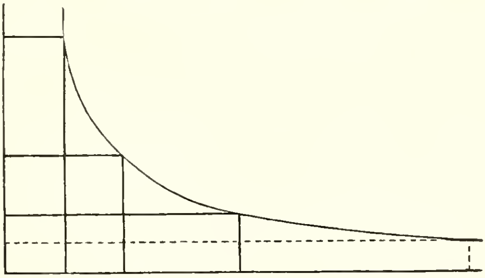

Fig. 9.

The experiments which led to this law are very simple. In a glass siphon-tube having a closed limb at *a* and an open limb at *b* (Fig. 10), a quantity of air *v* is introduced and shut off from the outside air by mercury. The pressure on the enclosed air is given

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[1] Translated from Mach's *Principien der Wärmelehre* by Thomas J. McCormack.

by the height of the mercury-barometer *plus* the difference of level *mn* of the two surfaces of the liquid, and can be altered at will by altering the height of the mercury column.

Fig. 10.

Experiments in verification of Boyle's law (which Boyle himself did not regard as absolutely accurate) were carried out through a wide range of pressures and for many different gases by Oerstedt and Schwendsen, Depretz, Pouillet, Arago and Dulong, and Mendelejeff,—but most accurately by Régnault,[1] and through the widest range of pressures by Amagat.[2]

If the pressure in the apparatus represented in Fig. 10 be doubled, the volume *v* of the gas will be diminished one half; if it be doubled again, it will be diminished one fourth. The errors in the readings increase greatly as the volume decreases, and to eliminate them Régnault resorted to an ingenious expedient. At *a* he attached a stop-cock through which air could be introduced under varying pressure; the volume of the enclosed air *v* could thus be always kept the same and subsequently compressed to $\frac{v}{2}$ by lengthening the column of mercury *mn*. With such an arrangement the measurements were always of like exactitude.

It appears that to reduce unit of volume under a pressure of one meter of mercury $\frac{1}{20}$, it is requisite in the case of air, carbonic acid gas, and hydrogen to increase the pressure to respectively 19.7198, 16.7054, and 20.2687 meters of mercury. The product PV, therefore, for high pressures, decreases for air and carbonic acid gas and increases for hydrogen. The two first-named gases are therefore more compressible and the last-named less compressible than Boyle's Law requires.

Amagat conducted his experiments in a shaft 400 meters deep and increased the pressure to 327 meters of mercury. He found that as the pressure increases the volume of PV first decreases, and after passing through a minimum again increases. With nitrogen, for $P=20.740$ meters of mercury, $PV=50989$; for $P=50$ meters, $PV=50800$, approximately a minimum; and for $P=327.388$ meters, $PV=65428$. Similar minima are furnished by other gases. Hydrogen showed no minimum, although Amagat suspected the existence of one at a slight pressure.

We shall not discuss here the attempts that have been made

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[1] *Mémoires de l'Académie*, Vol. XXI.

[2] *Annales de chimie et de physique*, Fifth Series, Vol. XIX. (1880).

by Van der Waals, E. and U. Dühring, and others to explain these phenomena by the molecular theory. It will be sufficient for us to remark that while Boyle's Law is not absolutely exact, it nevertheless holds very approximately through a wide range of pressures for many gases.

It was necessary to adduce the foregoing facts for the reason that the behavior of gases with respect to pressure is of importance in the consideration of their behavior with respect to heat,—a subject which was first minutely investigated by Gay-Lussac.[1] This inquirer makes mention of the researches of Amontons, and also employs the observations of Lahire (1708) and Stancari, from which the necessity of thoroughly drying the gases clearly appeared. Gay-Lussac's procedure was as follows. A perfectly dry cylinder closed by a stop-cock is filled with gas and plunged into a bath of boiling water. After the superfluous gas has been expelled, the cock is closed and the cylinder cooled in melting ice. On opening the cock under water, a part of the cylinder fills with water. By weighing the cylinder thus partly filled with water, afterwards completely filled with water, and again when empty, we obtain the coefficient of expansion of the gas from the melting-point of ice to the boiling-point of water. At 0° C. temperature 100 volumes of air, hydrogen, and nitrogen give respectively 137.5, 137.48, 137.49 volumes at 100° C. Also for other gases, and even for vapor of ether, Gay-Lussac obtained approximately the same coefficient of expansion, viz., 0.375. He states that, fifteen years before, Charles (1787) knew of the equality of the thermal dilatation of gases; but Charles had published nothing on the subject. Dalton[2] likewise had occupied himself with this question earlier than Gay-Lussac, and had both remarked the equality of the thermal dilatation of gases and given 0.376 as the coefficient of expansion.

For the comparison of different gases, Gay-Lussac also used two perfectly similar graduated glass receivers dipped a slight distance apart in mercury (Fig. 11). When like volumes of different gases were introduced into these receivers under like pressures and at like temperatures, both always appeared to be filled to the same marks of division.

In another investigation, Gay-Lussac[3] employed a vessel shaped somewhat like a thermometer and having a horizontal tube in which the air was shut off from the atmosphere by a drop of

[1] *Annales de chimie*, first series, Vol. XLIII. (1802).

[2] *Nicholson's Journal*, Vol. V. (1801).

[3] Biot, *Traité de physique*, Vol. I., p. 182, Paris, 1816.

mercury, the vessel being heated simultaneously with mercury-thermometers. Between the melting-point of ice and the boiling-point of water the dilatation of the air is very nearly proportional to the indications of the mercury-thermometer.

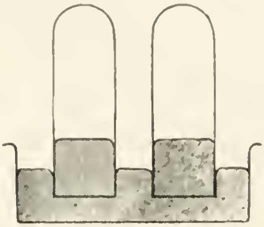

Fig. 11.

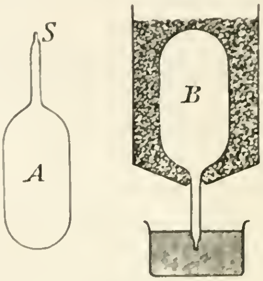

Fig. 12.

The experiments above described were subsequently performed on a larger scale and with closer attention to sources of error, by Rudberg,[1] Magnus,[2] Régnault,[3] Jolly,[4] and others. Two methods are principally employed. The first consists (Fig. 12) in heating a glass vessel *A* to the temperature of boiling, repeatedly exhausting it, and then filling it with air that has passed over chloride of calcium. While still at boiling temperature, the tip *S* is hermetically sealed, the barometer noted, the vessel inverted and encased (*B*) in melting ice, with the tip under mercury. When cool, the tip is broken off, and the mercury rises into the vessel; the difference of level of the mercury within and without the tube is then noted, and the apparatus weighed the required number of times. It is the method of Gay-Lussac with the requisite refinements.

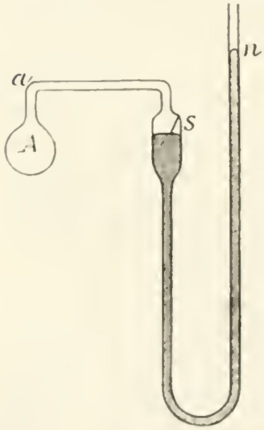

Fig. 13.

The second method (Fig. 13) consists in plunging a vessel *A* full of dry air as far as the bend of the tube *a*, first in a bath of melting ice and then in steam from boiling water, while simultaneously so regulating the height of the mercury column at *n* that the inside surface of the mercury constantly grazes the glass spicule *s*. The volume of the air is thus kept constant, and what is really

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[1] *Poggendorfs Annalen*, 41, 44.

[2] *Poggendorfs Annalen*, 45.

[3] *Mémoires de l'Acad.*, Vol. XXI.

[4] *Poggendorfs Annalen*, *Jubelband.*

measured is the *increment of the expansive force* of the gas when heated.

If a volume of gas v under a constant pressure p be raised from 0° to 100° C., it will expand to the volume $v(1+\alpha)$, where α is called the *coefficient of expansion*. If the gas as it now is at 100° C. were compressed back to its original volume, it would exert, according to Boyle's Law, a pressure p', where $vp' = v(1+\alpha)p$. Whence it follows that $p' = p(1+\alpha)$. If Boyle's Law held *exactly*, α would likewise be the *coefficient of the increment of expansive force*, or, more briefly, *the coefficient of expansive force*. But as the law in question is not absolutely exact, the two coefficients are not identical. Calling the coefficient of expansion α and the coefficient of expansive force β, the values of these coefficients for the interval from 0° to 100° C. for a pressure of about one atmosphere are, according to Régnault:

	α	β
Hydrogen............	0.36613	0.36678
Air..................	0.36706	0.36645
Carbonic Acid Gas.....	0.37099	0.36871

The coefficients of expansion increase slightly, according to Régnault, with the increase of the density of the gas. It further appears that the coefficients of expansion of gases which deviate widely from Boyle's Law decrease slightly as the temperature measured by the air-thermometer rises.

Gay-Lussac has shown that between 0° and 100° C. the *expansion* of gases is *proportional* to the indications of the mercury-thermometer. Designating the degrees of the mercury-thermometer by t and the $\frac{1}{100}$ part of the coefficient of expansion as above determined by α, we shall have, at constant pressure, $v = v_0(1+\alpha t)$, and at constant volume $p = p_0(1+\alpha t)$, where v_0, p_0, v, p, respectively represent the volume and pressure of the gases at 0° and t°, and where the coefficients of expansion and expansive force are assumed to be the same. Each of these equations expresses Gay-Lussac's Law.[1]

Boyle's Law and Gay-Lussac's Law are usually combined. For a given mass of gas the product p_0v_0 at the definite temperature 0° has a constant value. If the temperature be increased to t° C. and the volume kept constant, the pressure will increase to $p' = p_0(1+\alpha t)$; wherefore $p'v_0 = p_0v_0(1+\alpha t)$. And if the pressure p and the volume v at t° be altered at will, the product will be $pv = p'v_0$.

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[1] In this country and in England, Gay-Lussac's Law is usually called Charles's Law.—*Tr.*

Whence $pv = p_0 v_0 (1 + \alpha t)$. This last law is called the combined Law of Boyle and Gay-Lussac.

Boyle's Law was visualised by an equilateral hyperbola. The proportional increase of the volume or the pressure of a gas with its temperature may be represented, conformably to Gay-Lussac's Law, by a straight line (Fig. 14). Remembering that α is very approximately equal to $\frac{1}{273}$, we may say that for every increase of 1° Celsius the volume or pressure increases $\frac{1}{273}$ of its value at 0°, and that there is likewise a corresponding decrease for every degree Celsius. This increase may be conceived *without limit*. By taking away $\frac{1}{273}$ 273 times, we reach the pressure 0 or the volume 0. If therefore the gas acted in strict conformity with the Law of Boyle and Gay-Lussac *without limit*, then at —273° Celsius of the mercury-thermometer it would exert *no* pressure whatever and would present Amontons's "degree of greatest cold." The temperature —273° C. has accordingly been called the *absolute zero*, and the temperature reckoned from this point in degrees Celsius (viz., $T = 273 + t$) the *absolute temperature*.

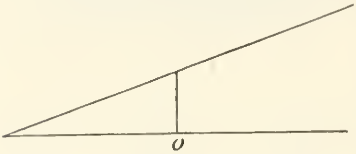


Fig. 14.

Even if this view of the matter be not taken seriously,—and we shall see later that there are grave objections to it,—still the presentation of the facts is simplified by it. Writing the Law of Boyle and Gay-Lussac

$$pv = p_0 v_0 \,(1 + \alpha t) = p_0 v_0 \alpha \left(\frac{1}{\alpha} + t\right) = p_0 v_0 \alpha T,$$

and considering that $p_0 v_0 \alpha$ is a constant, we have

$$\frac{pv}{T} = const.,$$

the simplified expression of the law.

The Law of Boyle and Gay-Lussac likewise admits of geometric representation. Conceive laid (Fig. 15) in the plane of the paper, a large number of long, similar, slender tubes filled with equal quantities of the same kind of gas. These tubes are made fast at one extremity to OT and closed at the other by moveable pistons. The first tube, at OV, has a temperature 0° C., the next a temperature of 1° C., the next 2° C., etc., so that the temperature increases uniformly from O to T. We now conceive the pistons to be all gradually pushed inwards, mercury columns measuring the pressure p erected over each position of the pistons at right angles to the plane of their action, and through the upper extremities of these columns a surface laid. The surface so obtained is imaged in Fig. 16, and is merely a synthesis of the graphs of Fig. 9 and Fig. 14. Every section of the surface parallel to the plane TOP is a straight line, conforming to Gay-Lussac's Law. Every section parallel to POV is an equilateral hyperbola, conforming to Boyle's Law. The surface as an aggregate furnishes a complete synoptic view of the pressures exerted by the *same* gaseous mass at any volume and at any temperature whatsoever.

The laws in question are in part also fulfilled for vapors. According to Biot,[1] J. A. Deluc[2] appears to have been the first to frame anything like a correct view of the deportment of vapors.

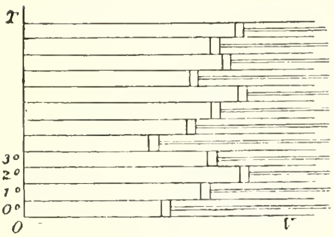


Fig. 15.

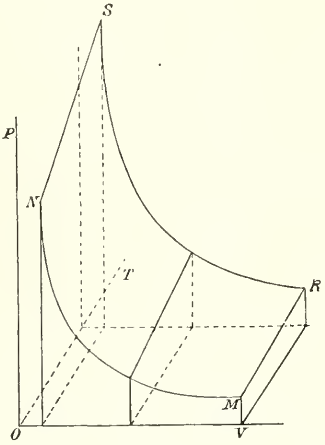


Fig. 16.

H. B. Saussure[3] knew from observation that the maximum quantity of vapor which a given space can contain depends not on the nature or density of the gas filling the space, but solely on the temperature. Doubtless this suggested to Dalton[4] the idea of inquiring whether water really was *absorbed* by gases, as was then generally supposed. He caused the liquid to be vaporised in the Torricellian vacuum, and obtained for a given temperature the *same* pressure as in air. *Air*, therefore, played no part in vaporisation. Priestley's discovery, that gases of widely differing specific gravities diffused into one another uniformly, combined with that just men-

[1] Biot, *Traité de physique*, Paris, 1816.

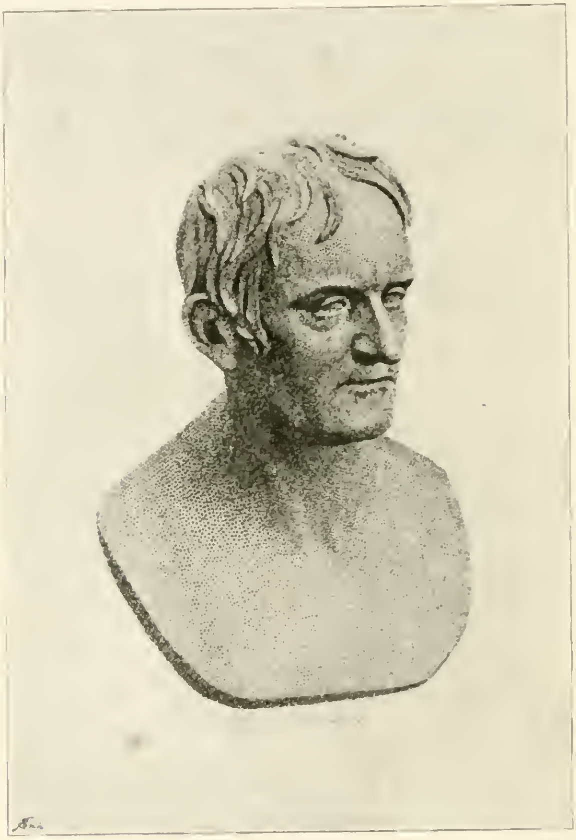
[2] *Idées sur la météorologie*, Paris, 1787.

[3] *Essai sur l'hygrometrie*, Neuchatel, 1783.

[4] *On the Constitution of Mixed Gases, etc.*, *Mem. Manchest. Soc.*, V., 1801.

tioned, led Dalton to the conception that in a mixture of gases and vapors occupying a given space *every portion behaved as if it alone were present.* Dalton's way of expressing this fact was by saying that the particles of a gas or vapor could exert pressure only on particles of its own kind.

The discovery that gases behave toward one another precisely as *void spaces*,[1] is one of the most important and fruitful that Dalton ever made. The way to it had been prepared by the observations above mentioned, and in reality it furnishes nothing but a lucid conceptual expression of the facts, such as science in the Newtonian sense requires. But the preponderance of the speculative



John Dalton (1766–1844).

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[1] *Manchester Memoirs*, Vol. V., 1801, p. 535. Compare Henry, *Life of Dalton*, p. 32. Dalton says: "and consequently (the particles) arrange themselves just the same as in a void space."

element and of a bent for capricious theorising in Dalton, which becomes so fateful in the researches to be discussed further on, makes its appearance here also. Dalton cannot refrain from introducing along with his statement of the facts an entirely redundant conception, which impairs the clearness of his ideas and diverts attention from the main point. This is the "pressure of the particles of different gases on one another."[1] This hypothetical conception, which can never be made the subject of experimental verification, certainly does not impart clearness to the *directly observable* fact; on the contrary, it involved its author in unnecessary controversies.

Gay-Lussac[2] showed, by the experiment represented in Fig. 11, that vapor of ether at a temperature *above the boiling-point* of ether behaved exactly as air did on changes of temperature. The observations of Saussure and Dalton adduced in the preceding paragraphs, together with that just mentioned, indicate that vapors may occur in two states, viz., as *saturated* and as *non-saturated* or *superheated* vapors.

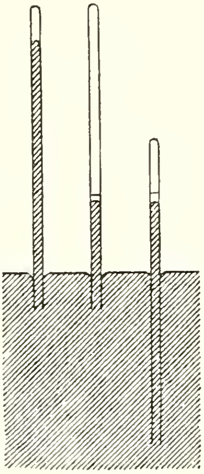

Fig. 17.

The phenomena involved may be clearly illustrated by an experiment which presents in rapid and lucid succession the different cases, before considered separately. We perform (Fig. 17) the Torricellian experiment, and introduce into the vacuum of the Torricellian tube a small quantity of ether. A portion of the ether vaporises immediately, and the mercury column is depressed by the pressure of the vapor, say, at 20° C., a distance of 435 *mm*. If the temperature in the barometer tube be raised by a water bath, say to 30° C., the column will show a depression of 637 *mm*; whilst in a bath of melting ice it will show only 182 *mm*. The pressure of vapors, therefore, increases with the temperature. If the tube containing the ether be plunged deeper into the mercury, so as to diminish the space occupied by the vapor, the height of the surface of the mercury in the tube will still not be altered. The pressure of the vapor, therefore, remains the same. But it will be noticed that the quantity of liquid ether has slightly increased and that

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[1] The passage reads: "When two elastic fluids, denoted by A and B, are mixed together, there is no mutual repulsion amongst their particles; that is, the particles of A do not repel those of B, as they do one another. Consequently, the pressure or whole weight upon any one particle arises solely from those of its own kind."

[2] *Ann. de chim. et de phys.*, XLIII (1802), p. 172.

therefore a portion of the vapor has been liquefied. As the tube is withdrawn the quantity of liquid ether diminishes and the pressure again is the same.

A small quantity of air introduced into the Torricellian vacuum also causes a depression of the barometer column,—say 200 *mm.* If the tube be now plunged in until the air space is reduced one half, the depression according to Boyle's Law will be 400 *mm.* In precisely the same manner vapor of ether behaves, conformably to Gay-Lussac's observation, provided the quantity of ether introduced into the tube is so small that *all* the ether vaporises and a still greater quantity *could* vaporise. For example, when at 20° C. a depression of only 200 *mm* is generated by the inclosed ether, the tube contains no liquid ether. Diminishing the Torricellian vacuum one half doubles the depression. The depression may be increased by further immersion to 435 *mm.* But still further immersion of the tube no longer augments the depression, and liquid ether now makes its appearance.

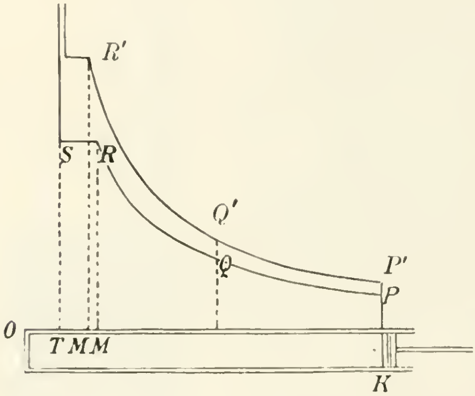

Fig. 18.

The preceding observations relative to vapors may be epitomised by a simple illustration. A long tube closed at *O* contains an adequate quantity of rarefied vapor. If the piston *K* be gradually pushed in and mercury columns measuring the pressures be erected at every point over which the piston passes, the extremities of these columns will all lie in the hyperbola *PQR.* But from a definite position *M* of the piston on, the increase of pressure ceases, and liquefaction takes place. If at the position *T* of the piston nothing but liquid remains in the tube, then a very great increase of pressure follows on the slightest further movement of the piston. Repeating this experiment at a higher temperature, we obtain increases of pressure corresponding to Gay-Lussac's Law and the coefficient of expansive force (0.00367), as the curve *P′Q′R* indicates. The liquefaction of vapors begins only at higher pressures and greater densities.

Vapors of sufficiently small density approximately fulfil, accordingly, the Law of Boyle and Gay-Lussac. Such vapors are called *non-saturated* or *superheated* vapors. If the concentration of the vapors is continued, they reach a *maximum* of *pressure and density* which cannot be exceeded for any given temperature, as every further diminution of the vapor space causes a partial liquefaction of the vapor. Vapors at the maximum of pressure are called *saturated* vapors. Given enough liquid and sufficient time and this maximum of pressure will always establish itself in a closed space.

The relationship between temperature and the pressure of saturated vapors has been investigated for different vapors by many inquirers. The methods they employed are reducible to two fundamental types. The first consists in introducing the liquid to be investigated into the Torricellian vacuum and in placing the latter in a bath of definite temperature. The amount of depression with respect to the height of the barometer column gives the pressure of the vapor. If the open end of a siphon barometer, which has been exhausted and charged with the liquid, be hermetically sealed and placed in a bath of given temperature, the mercury column will indicate the pressure of the vapor independently of that of the atmosphere. This procedure is only a modification of the preceding one. The method here employed is commonly called the *static* method.

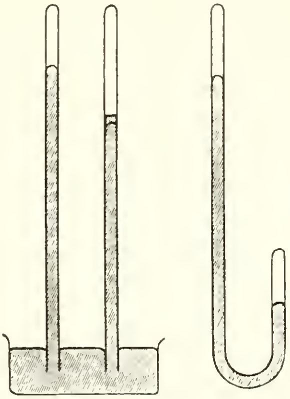

Fig. 19.

Vapors are being constantly generated at the free surface of liquids. For a liquid to *boil*, that is, for bubbles of the vapor to form in its interior, expand, rise to the surface and *burst*, it is necessary that the pressure of the hot vapor in these bubbles should at least be in equilibrium with that of the atmosphere. The *temperature of boiling* is therefore that temperature at which the pressure of the saturated vapor (the maximum pressure) is equal to the pressure of the atmosphere. If a liquid, therefore, be *boiled* under the receiver of an air-pump, by means of which the air-pressure can be raised or lowered at will, (being kept constant by the cooling and re-liquefaction of the generated vapors,) the temperature at which the liquid boils will give the temperature for which the air-pressure produced is the maximum pressure of the vapor. Thus, in Figure 20, *B* is a large glass balloon connected with an air-pump, by which the air-pressures are regulated. In *G* the liquid is boiled and the vapors generated, while in the bent tube *R*, which can be cooled, they are re-liquefied. This method is commonly called the *dynamical* method.

Experiments were conducted according to these methods by Ziegler (1759), Bétancourt (1792), G. G. Schmidt (1797), Watt,[1] Dalton[2] (1801), Noe (1818), Gay-Lussac[3] (1816), Dulong and Arago (1830), Magnus[4] (1844), Regnault[5] (1847), and others.

For the same temperature the maximum pressure varies greatly with the liquid, and it also increases rapidly with the temperature. Even Dalton *sought* a universal law for the dependence of maximum pressures on temperature, and his investigations were continued in recent times by E. and U. Dühring and others. The purpose and scope of our work preclude our discussing these researches.

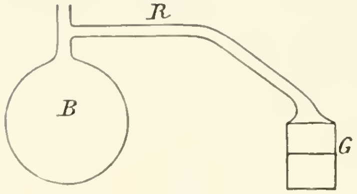

Fig. 20.

The most extensive investigations, owing to their practical importance for the operation of steam engines, were conducted with *water-vapor*. Régnault found the following relationship between temperatures and maximum pressures, expressed in millimeters of mercury:

°C.	*mm.*	°C.	*mm.*
0.00	4.54	111.74	1131.60
52.16	102.82	131.35	2094.69
100.74	777.09	148.26	3359.54

It will be seen from this extract from Regnault's table that the pressure of water-vapor from 0° to 100° C. increases by about one atmosphere; while from 100° to 150° it increases by more than three atmospheres. The rapid rise of the curve of pressures on increase of temperature, as represented in the graphed illustrations which Regnault furnished, renders this relationship even more striking.

A more extended extract from this table in the vicinity of the vaporous pressure of 760 *mm* is of value in ascertaining the influence of atmospheric pressure in the determination of the boiling-point on thermometers.

[TO BE CONTINUED.]

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[1] Brewster's *Encyclopädie*, (1810–1830).

[2] *Mem. Manchest. Soc.*, V., 1801.

[3] Biot, *Traité de physique*, Paris, 1816.

[4] *Poggendorfs Annalen*, LXI.

[5] *Mémoires de l'Acad.*, Vol. XXI.