SKETCH OF THE HISTORY OF THERMOMETRY.[1]

BY DR. ERNST MACH.

[CONCLUDED.]

THE rapid increase of the expansive force (pressure) and density of saturated vapors suggested to Cagniard de la Tour[2] the idea that at high pressures and temperatures vapors could be produced the density of which varied only slightly from that of their liquids. He filled a portion of a musket-barrel nearly half full of alcohol, and inserting in it a bullet of flint closed it. As the barrel was raised to higher and higher temperatures, the sound which the bullet produced when shaken against the sides of the barrel suddenly changed. In a glass tube from which the air had been expelled a quantity of liquid alcohol nearly half filling the tube was rendered entirely invisible by heating. When the tube was cooled, it again made its appearance as a dense shower. The experiments were then continued with the tube shown in Fig. 21. Ether was introduced at *a* and separated from the air in *b* by mercury. The compression of the air gave the pressure of the liquid, the thermometer of the bath in which the tube was immersed gave its temperature. Ether disappeared at 30 atmospheres and 160° C, alcohol at 119 atmospheres and 207° C, their vapors occupying something more than twice the space taken up by the liquid. Water disappeared at the temperature of melting zinc, and took up four times the space occupied by the liquid. Seeing that the tubes when too small for the expansion did not burst immediately, Latour correctly concluded that the liquids were extremely compressible in this state and had very large coefficients of expansion.

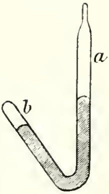

Fig. 21.

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

[2] *Ann. de chim.*, XXI., 1822, pp. 127, 178, XXII., 1823, p. 410.

Prompted by Davy, and perhaps also by the researches of Latour, Faraday[1] endeavored to liquefy chemically developed gases confined in closed spaces,—an undertaking in which he was in several instances successful. The idea of these experiments had, indeed, been clearly suggested by the proof which Gay-Lussac had furnished of the like deportment of *gases* and *non-saturated vapors*, as well as by Latour's experiment, showing that vapors at high pressures were liquefied by a slight diminution of temperature and revaporised by a slight increase of temperature. A simple example is that of the liquefaction of cyanogen, which occurs when mercuric cyanide is heated in one end *a* of a glass tube (Fig. 22), and the other end *b* of the tube is cooled in water. The generated gas is liquefied at *b*. These experiments were continued on a larger scale with carbonic acid gas by Thilorier and Natterer,[2] the latter of whom especially was successful in liquefying large quantities of carbonic acid gas by means of an appropriately constructed force-pump.

The experiments of Andrews[3] first indicated the mode of procedure by which finally Cailletet and Pictet (1877) were enabled to liquefy all gases. Andrews compressed dried, deaerated carbonic acid gas by means of mercury forced with a screw into a glass tube *G* ending in a capillary prolongation *g* (Fig. 23). The phenomena occurring in *g*, which was plunged in baths of varying temperatures, could thus be observed at leisure, whilst air confined in a similar tube and subjected to the same pressure served as a manometer. It was found that carbonic acid gas could not possibly be liquefied by any pressure at a temperature *above* + 30.92 C, whereas it was possible to liquefy it at temperatures *below* this point. Andrews called this temperature the *critical temperature*, and it was demonstrated that every vapor and every gas possessed such a critical point, the sole difference being that the point in question was *high* for the so-called vapors and easily condensable gases, and very low for the so-called permanent gases. Utilising the results of Andrews's researches and employing extreme degrees of cold, Cailletet and Pictet succeeded in liquefying all gases.

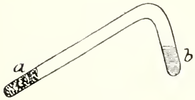

Fig. 22.

Aeriform bodies above the critical temperature are, accordingly, in Andrews's conception, *gases*, and those under the critical temperature *vapors*. The very rapidity of the augmentation of the

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[1] *Ann. de chim.*, XXII., 1823, p. 323, XXIV., 1823, pp. 297, 401, 403.

[2] *Pogg. Ann.*, Bd. 67, 1844.

[3] *Philosoph. Transact.*, 1869, p. 575.

curve of maximum pressures is suggestive of the idea that above a certain temperature this maximum pressure transcends all limits or becomes infinitely great. This limiting point actually exists; it is Andrews's critical temperature.

Fig. 23.

Mendelejeff calls the critical temperature the "absolute boiling point." As the pressure increases, the temperature of boiling rises until the maximum expansive force of the liquid equals the pressure to which it is subjected. But at the critical temperature the pressure that could prevent the liquid from boiling is infinitely great; it boils under every pressure. Mendelejeff also showed that the superficial tension of the liquid, which decreases as the temperature rises, *disappears* at the critical temperature.

The deportment of carbonic acid gas as thus revealed by Andrews, and its deviations from the law of Boyle and Gay-Lussac, are graphically represented in Fig. 24. The curves correspond to those of Fig. 18. The abscissæ represent the volumes. The curves of the figure extend from the second to the fourteenth thousandth part of the volume of carbonic acid gas at 1 atmosphere of pressure and 0° C. The dotted line bounds the region within which the carbonic acid gas can exist partly in a liquid and partly in a gaseous form.

Fig. 16 may by a slight modification be made to visualise the deportment of gases and vapors. This modification is shown in Fig. 25. The pressure of the vapor at a given temperature ascends by the curve *mn*; but at *n* liquefaction begins. The pressure of the vapor at a higher temperature ascends by the curve *pg* to the greater maximum *g*; and so with the rest. To the right of the curve *ngrs*, the vapors behave as gases; to the left, liquefaction sets in. Conceiving a distant light with rays parallel to *VO* to cast a shadow of the curve *ngrs* on the plane *POT*, we should obtain Regnault's curve visualising the increase of the maximum pressure of the vapor with the temperature. The *lowest* temperature at which the curve *ut*, by which the rise of the pressure with diminishing volume is indicated, *no longer cuts the curve ngrs*, is the critical temperature. Accurately viewed, the sections of the surface of Fig. 25 parallel to *POV* are not exact hyperbolas for either gases or vapors. This is approximately true only of the sections to the right of *ngrs* at some distance from this curve. In the vicinity of the curve and to the left of it, the forms appear which the graphs of Andrews in Fig. 24 show.

Although the investigation of liquids furnished no such general results as that of gases, yet a few observations in connection with them must be mentioned. Even the Accademia del Cimento is said to have been familiar with the fact that water heated from the freezing-point contracted at first and only later expanded.[1] Deluc[2] observed that the peculiar behavior of water-thermometers was attributable to an anomaly of the water itself, and, taking no account of the expansion of the glass walls, fixed its point of greatest

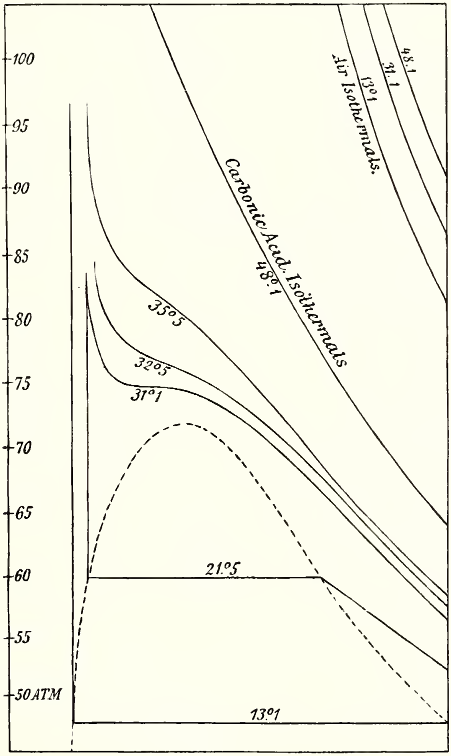

Fig. 24.

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[1] I have been unable to satisfy myself of the correctness of this report.

[2] *Sur les modifications de l'atmosphère*, Paris, 1772.

density at + 50° C. Hällstrom[1] was the first to examine more minutely into this phenomenon by determining the loss of weight of a glass body of known expansibility in water at different temperatures. Hagen and Matthiessen followed the same method. Despretz[2] observed the temperature of the different layers of water when cooled in a vessel. The water of least density formed the uppermost layer, and consequently when the water first began to cool had the highest temperature. On passing through the temperature of maximum density, this relation of things was reversed. F. Exner[3] augmented the delicacy of this method by using thermo-elements instead of thermometers. Plücker and Geissler used a thermometer-shaped vessel partly filled with water. The most accurate determination of the temperature of maximum density was in all probability that made by F. Exner, who found it to be + 3.945 C. The investigations just mentioned are important in point of principle, as they overthrew the very natural belief in the uniform and parallel behavior of all bodies expanding under the action of heat.

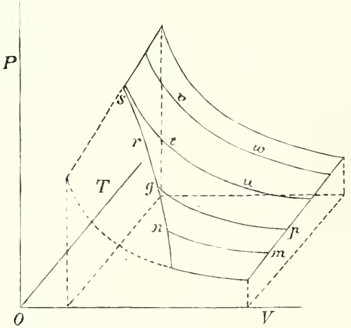

Fig. 25.

There still remain to be mentioned, for the methods involved, the measurements of the expansion of solids which Lavoisier and Laplace jointly conducted, and which Roy completed after the manner of Ramsden. Lavoisier and Laplace[4] added to the quadrant pyrometer of Musschenbroek, which was rotated by the expanding rod, a telescope set to a distant scale. The reading was considerably magnified, but every inaccuracy of the apparatus was also reproduced on an enlarged scale. Roy[5] employs three bars, all in ice (Fig. 26). The first carries two illuminated cross-threads, *F*, *F'*; the second, the one to be investigated, carries two microscopic objectives, *A*, *A'*; the third two oculars with cross-threads, *B* and *B'*. The images of the cross-threads *F*, *F'* are aligned with the cross-threads of the oculars. If the bar in the middle is now plunged in a bath of higher temperature, the distance between *A*

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[1] *Gilb. Ann.*, 1802.

[2] *Ann. de chim.*, LXX., 1839, LXXIII., 1840.

[3] *Wiener Academ.*, 1873.

[4] Biot, *Traité de physique*, 1816.

[5] *Philos. Transact.*, 1785.

and *A'* will be increased. By moving the bar in the direction *A*, *A'* the image of *F* can again be aligned with the cross-threads of the ocular *B*, and by a micrometric displacement of *A'* along the bar the image of *F'* can also be aligned with the cross-threads of ocular *B'*. This last displacement measures the linear dilatation of the middle bar.

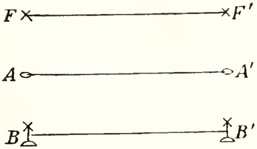

Fig. 26.

Dulong and Petit enriched the thermometric knowledge of their predecessors by a number of careful experiments, and set forth the entire thermometry of their time in a classical work honored with a prize by the Parisian Academy.[1] The labors of these physicists consist essentially in having made an *accurate* comparison of the different thermometric scales within *wide* ranges of temperature. The thermal conditions being the same, the comparative behavior of mercury-thermometers and air-thermometers corrected with regard to the expansion of the glass is as follows:

WHEN THE MERCURY-THERMOMETER INDICATES	THE AIR-THERMOMETER INDICATES
—36	—36
0	0
100	100
360	350

For reducing the indications of the mercury-thermometer to those of the air-thermometer, the foregoing table would be sufficient. But to compare the real dilatations of air and mercury, additional experiments must be made. A siphon tube *AB* (Fig. 27) was filled with mercury, and one of the arms *B* was plunged in a bath of melting ice, whilst the other *A* was immersed in a bath of oil at higher temperatures. The heights of the two columns of mercury, as measured by the cathetometer, were to each other directly as the volumes of the same mass of mercury at the two temperatures in question. The temperatures of the oil bath were determined by means of an air-thermometer and a mercurial weight-thermometer. This latter consisted of a vessel filled with mercury at 0° C and terminating in a bent capillary prolongation, from which quantities of mercury determinable by weight were expelled

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[1] *Sur la mesure des températures et sur les lois de la communication de la chaleur*, *Ann. de chim.*, VII., 1817, p. 113.

as the temperature rose. The amount of mercury expelled, like the *apparent* voluminal dilatation of the ordinary mercury-thermometer, was determined by the *difference of the dilatations* of the mercury and the glass. Column A of the following table gives the temperature derived from the absolute dilatation of the air, C that derived from the apparent dilatation of the mercury (as determined by the weight-thermometer), and B the mean absolute coefficient of dilatation of the mercury between 0° and the temperature recorded.

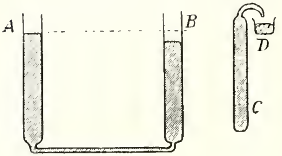

Fig. 27.

A	B	C
0	0	0
100	$\frac{1}{5550}$	100
200	$\frac{1}{5425}$	204.61
300	$\frac{1}{5300}$	313.15

Designating the absolute voluminal dilatation of the mercury by α, that of the glass by β, and the apparent dilatation of the mercury in the glass vessel by γ, we have $\gamma=\alpha-\beta$. Accordingly, the dilatation of glass also is given by the table. Calling the temperature derived from the dilatation of air A, that derived from the dilatation of glass at the same thermal state D, and supposing the scales to be coincident at 0° and 100°, we obtain:

A	D
100	100
200	213.2
300	352.0

Knowing the dilatation of mercury and glass, there is nothing to prevent our inserting a small rod of iron in a glass-thermometer and filling the remainder of the tube with mercury. Treating this arrangement as a weight thermometer and rendering the surfaces of the enclosed substances proof against amalgamation by oxidising, we obtain in a perfectly obvious manner the voluminal dilatation of iron or of any other metal. If v is the volume of the glass tube and v_1 the volume of the metallic rod at 0° C, and if α, β, γ be the coefficients of dilatation respectively of mercury, glass, and the metal between 0° and t, then the total volume of the mercury expelled at the temperature t will be $\omega = v\alpha - v\beta + v_1\gamma$, from which γ is determinable.

From experiments like the foregoing, Dulong and Petit reached the following conclusions:

1. Deriving the temperatures from the indications of the air-thermometers, the coefficients of dilatation of all other bodies are found to increase with the temperature.
2. Determining the temperatures by the indications of an iron thermometer, the coefficients of dilatation of all other bodies are found to diminish as the temperature increases.
3. Measuring the temperatures by the absolute voluminal dilatation of mercury, the coefficients of dilatation of iron and copper increase, while those of platinum and air decrease, as the temperature increases.

The dilatations of air, iron, copper, and platinum corresponding to the same thermal states are given by the following table:

AIR	IRON	COPPER	PLATINUM
100	100	100	100
300	372.6	328.8	311.6

Hence, if several different solids are subjected to the same thermal changes, their variations of volume are by no means proportional to *one another*, but each body exhibits an *individual* behavior peculiar to itself. The gases only, as Gay-Lussac showed, obey the same law of dilatation. This result of the labors of Dulong and Petit is, *in point of principle*, of great importance for the theory of thermometry.

Deluc and Crawford early sought for a body the *dilatations* of which should be proportional to the *quantities of heat*[1] it absorbed. Dulong and Petit likewise granted the rationality of a scale of temperature the degrees of which should coincidently measure the quantities of heat absorbed by the thermometric substance; and the same idea occurred, as we have seen, in a slightly different form, to Renaldini.[2] But these inquirers very correctly remarked that such a scale would be of value only provided the same independent relationship as subsisted between capacity for heat and

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[1] We are obliged by the context to anticipate here the definitions of quantity of heat, specific heat, and capacity of heat, which will be critically discussed in a later chapter.

[2] Cp. *The Open Court* for November, 1902, p. 650.

the scale of temperature here in question likewise obtained for all other bodies; or, what is tantamount to the same thing, only provided the variations of the thermal capacities of all bodies for the same variations of thermal state were *proportional to one another.* This question, accordingly, was attacked experimentally.

The capacities of bodies for heat were now investigated with greater accuracy and throughout wider ranges of temperature than ever before. *Boiling water* and *boiling mercury* were employed to raise the bodies to the required temperatures. Accurately weighed quantities of the different substances were then immersed in a like accurately determined large body of water, the ascent of the temperature of which determined the quantities of heat given off by the bodies. The following table gives the results of this experiment:

	MEAN CAPACITY BETWEEN 0° AND 100°	MEAN CAPACITY BETWEEN 0° AND 300°
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0549
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0355	0.0355
Iron	0.1098	0.1218
Glass	0.177	0.190

As will be seen, not only do the capacities for heat increase with the temperature as recorded by the air-thermometer, but they also increase in different proportions with different substances, and would also increase in like manner were the temperature recorded by the mercury-thermometer. The law of the variation of capacity for heat is therefore *peculiar to each substance.*

Dalton imagined himself justified by the state of research of his time in formulating the following singular laws of temperature:

> "All pure homogeneous liquids, as water and mercury, expand from the point of their congelation, or greatest density, a quantity always as the square of the temperature from that point.
>
> "The force of steam from pure liquids, as water, ether, etc., constitutes a geometrical progression to increments of temperature in arithmetical progression.
>
> "The expansion of permanent elastic fluids is in geometrical progression to equal increments of temperature.

> "The refrigeration of bodies is in geometrical progression in equal increments of time."[1]

Consonantly with these views, Dalton proposed a new scale of temperature, the degrees of which increased in length with the temperature. The mean between freezing and boiling water, or 122° on the new scale, corresponds about to 110° on the Fahrenheit scale. If a quantity of air expands on being heated, in the ratio of 1 to 1.0179, Dalton adds 10° on his new scale; and when its volume diminishes in the ratio of 1.0179 to 1, he subtracts 10°. The points 32 and 212 are identical on Dalton's and Fahrenheit's scale.

Studying unbiassedly the portion of Dalton's treatise with which we are here concerned, one is struck with the wilful caprice with which he frames his assumptions and theories. The clearness and precision of his exposition has suffered so much by the introduction of superfluous hypothetical elements, that it is by no means easy at times to grasp clearly his meaning. He compares the heated body to a vessel, the heat it contains to the liquid the vessel holds, the temperature to the height at which the fluid stands. It is an indisputable fact for him that equal increments of heat in any body correspond to equal increments of temperature. Since, however, according to his conception, the capacity increases with the volume, this conception is again untenable. No precise definition of what he understands by temperature is found in the text. The properties of his new scale are determinable from his table alone.

The following is an illustration of the temerity with which Dalton embraced the most hazardous theories. The higher and more rarefied layers of the atmosphere are *colder*. On rarefaction, the air cools, and consequently gains, according to Dalton's conception, in capacity for heat. Dalton, in explanation of the coldness of the higher regions of the atmosphere, then calmly assumes that layers of air in contact tend, not towards equality of temperature, but towards equality of heat.[2]

As a matter of fact, Dulong and Petit,[3] in consequence of their investigations, which showed the behavior of bodies to be in each case *peculiar to themselves*, and so subject to no general law, found themselves obliged to repudiate utterly the thermometric laws of Dalton. Even Dalton himself subsequently became convinced of the untenability of his laws.[4]

[1] *A New System of Chemical Philosophy*, London, 1808, p. 13. Compare also Henry, *Memoirs of the Life and Scientific Researches of Dalton*, London, 1854, p. 66.

[2] *A New System of Chemical Philosophy*, Part I., London, 1808, p. 126.

[3] *Ann. de chim.*, VII., 1817, pp. 150 et seq.

[4] Henry, *Life of Dalton*, p. 67.

The researches of Dulong and Petit thus indisputably demonstrated, as their authors in their conclusion claimed, that all thermometric scales were dependent on the particular thermometric substance selected. Universal comparability was, they found, the property of gas-thermometers only, and, without condemning all others, they recommended these thermometers as the best. We have now substantially reached the point of view which we shall assume in the following discussion. It is unnecessary for our purpose, which is entirely one of principle, nay, it would be quite inadmissible, to consider here in detail the recent and more refined investigations in thermometry which Pernet and others have conducted.

The development of thermometry from the employment of the first air-thermometer (probably in 1592) to the attainment of lucidity in points of principle in this domain (1817) covered an interval of some 225 years. Manifold were the paths entered upon, and again and again were they forsaken and re-trodden before the fragments of our knowledge were all gathered and united into a comprehensive view of the whole. The air-thermometer was invented. Its defects led to the employment of liquid thermometers, the insufficient comparability of which provoked new efforts and thus ultimately threw into full consciousness and light the quest for a *rational* scale of temperature. The determination of fixed points and the search for a rational scale required much time and experimentation, the upshot of which was the reinstatement of the air-thermometer as a normal instrument in its proper rights. We are now in a position to consider critically the results of our historical survey, which we shall next proceed to do.