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John Dalton

Excerpt

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NEW SYSTEM
OF
CHEMICAL PHILOSOPHY.



CHAP. I.

ON HEAT OR CALORIC.

THE most probable opinion concerning the nature of caloric, is, that of its being an elastic fluid of great subtilty, the particles of which repel one another, but are attracted by all other bodies.

When all surrounding bodies are of one temperature, then the heat attached to them is in a quiescent state ; the absolute quantities of heat in any two bodies in this case are not equal, whether we take the bodies of equal weights or of equal bulks. Each kind of matter has its peculiar affinity for heat, by which it requires a certain portion of the fluid, in order to be in equilibrium with other bodies at a certain temperature. Were the *whole*

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quantities of heat in bodies of equal weight or bulk, or even the *relative quantities*, accurately ascertained, for any temperature, the numbers expressing those quantities would constitute a table of *specific heats*, analogous to a table of *specific gravities*, and would be an important acquisition to science. Attempts of this kind have been made with very considerable success.

Whether the specific heats, could they be thus obtained for one temperature, would express the relation at every other temperature, whilst the bodies retained their form, is an enquiry of some moment. From the experiments hitherto made there seems little doubt of its being nearly so ; but it is perhaps more correct to deduce the specific heat of bodies from equal *bulks* than from equal *weights*. It is very certain that the two methods will not give precisely the same results, because the expansions of different bodies by equal increments of temperature are not the same. But before this subject can well be considered, we should first settle what is intended to be meant by the word temperature.

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SECTION 1.

ON TEMPERATURE,

And the Instruments for measuring it.

The notion of the specific heat of bodies and of temperature, may be well conceived from a system of cylindrical vessels of different diameters connected with each other by pipes at the bottom, and a small cylindrical tube attached to the system, all capable of holding water or any other liquid, and placed perpendicular to the horizon. (See Plate 1. Fig. 1.) The cylinders are to represent the different specific heats of bodies; and the small tube, being divided into equal parts, is to represent the thermometer or measure of temperature. If water be poured into one vessel it rises to the same level in them all, and in the thermometer; if equal portions be successively poured in, there will be equal rises in the vessels and in the tube; the water is obviously intended to represent heat or caloric. According to this notion, then, it is evident that equal increments of heat in any body correspond to equal increments of temperature.

This view of the subject necessarily requires, that if two bodies be taken of any one tempe-

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rature, and then be raised to any other temperature, the additional quantities of heat received by each will be exactly proportioned to the whole quantities of that fluid previously contained in them. This conclusion, though it may be nearly consistent with facts in general, is certainly not strictly true. For, in elastic fluids, it is well known, an increase of *bulk* occasions an increase of specific heat, though the weight and temperature continue the same. It is probable then that solids and liquids too, as they increase in bulk by heat, increase in their capacity or capability of receiving more. This circumstance, however, might not affect the conclusion above, provided all bodies increased in one and the same proportion by heat; but as this is not the case, the objection to the conclusion appears of validity. Suppose it were allowed that a thermometer ought to indicate the accession of *equal* increments of the fluid denominated caloric, to the body of which it was to shew the temperature;—suppose too that a measure of air or elastic fluid was to be the body; query, whether ought the air to be suffered to expand by the temperature, or to be confined to the same space of one measure? It appears to me the most likely in theory to procure a standard capacity for heat by subjecting a body to heat,

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whilst its bulk is kept constantly the same. Let m = the quantity of heat necessary to raise the elastic fluid 10° in temperature in this case; then $m + d$ = the quantity necessary to raise the same 10° , when suffered to expand, d being the difference of the absolute quantities of heat contained by the body in the two cases. Now, $\frac{1}{10} m$ = the quantity of heat necessary to raise the temperature 1° in the first case; but $\frac{1}{10} (m + d)$ can not be the quantity necessary in the second case; it will be a less quantity in the lower degrees, and a greater in the higher. If these principles be admitted, they may be applied to liquids and solids; a liquid, as water, cannot be raised in temperature equally by equal increments of heat, unless it is confined within the same space by an extraordinary and perhaps incalculable force; if we suffer it to take its ordinary course of expansion, then, not equal, but increasing increments of heat will raise its temperature uniformly. If sufficient force were applied to condense a liquid or solid, there can be no doubt but heat would be given out, as with elastic fluids.

It may perhaps be urged by some that the difference of heat in condensed and rarefied air, and by analogy probably in the supposed cases of liquids and solids, is too small to have sensible influence on the capacities or affinities

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of bodies for heat ; that the effects are such, as only to raise or depress the temperature a few degrees ; when perhaps the whole mass of heat is equivalent to two or three thousand such degrees ; and that a volume of air supposed to contain 2005° of temperature being rarefied till it become 2000° , or lost 5° of temperature, may still be considered as having its capacity invariable. This may be granted if the data are admissible ; but the true changes of temperature consequent to the condensation and rarefaction of air have never been determined. I have shewn, (Manchester Mem. Vol. 5, Pt. 2.) that in the process of admitting air into a vacuum, and of liberating condensed air, the inclosed thermometer is affected as if in a medium of 50° higher or lower temperature ; but the effects of instantaneously doubling the density of air, or replenishing a vacuum, cannot easily be derived from those or any other facts I am acquainted with ; they may perhaps raise the temperature one hundred degrees or more. The great heat produced in charging an air-gun is a proof of a great change of capacity in the inclosed air.— Upon the whole then it may be concluded, that the change of bulk in the same body by change of temperature, is productive of considerable effect on its capacity for heat, but

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that we are not yet in possession of data to determine its effect on elastic fluids, and still less on liquids, and solids. M. De Luc found, that in mixing *equal weights* of water at the freezing and boiling temperatures, 32° and 212° , the mixture indicated nearly 119° of Fahrenheit's mercurial thermometer; but the numerical mean is 122° ; if he had mixed *equal bulks* of water at 32° and 212° , he would have found a mean of 115° . Now the means determined by experiment in both these ways are probably too high; for, water of these two temperatures being mixed, loses about 1-90th of its bulk; this condensation of volume (whether arising from an increased affinity of aggregation, or the effect of external mechanical compression, is all one) must expel a quantity of heat, and raise the temperature above the true mean. It is not improbable that the true mean temperature between 32° and 212° may be as low as 110° of Fahrenheit.

It has been generally admitted that if two portions of any liquid, of equal weight but of different temperatures, be mixed together, the mixture must indicate the true mean temperature; and that instrument which corresponds with it is an accurate measure of temperature. But if the preceding observations be correct, it may be questioned whether any

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two liquids will agree in giving the same mean temperature upon being mixed as above.

In the present imperfect mode of estimating temperature, the equable expansion of mercury is adopted as a scale for its measure. This cannot be correct for two reasons; 1st. the mixture of water of different temperatures is always *below* the mean by the mercurial thermometer; for instance, water of 32° and 212° being mixed, gives 119° by the thermometer; whereas it appears from the preceding remarks, that the temperature of such mixture ought to be found above the mean 122° ; 2d. mercury appears by the most recent experiments to expand by the same law as water; namely, as the square of the temperature from the point of greatest density.—The apparently equal expansion of mercury arises from our taking a small portion of the scale of expansion, and that at some distance from the freezing point of the liquid.

From what has been remarked it appears that we have not yet any mode easily practicable for ascertaining what is the true mean between any two temperatures, as those of freezing and boiling water; nor any thermometer which can be considered as approximating nearly to accuracy.

Heat is a very important agent in nature; it

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cannot be doubted that so active a principle must be subject to general laws. If the phenomena indicate otherwise, it is because we do not take a sufficiently comprehensive view of them. Philosophers have sought, but in vain, for a body that should expand uniformly, or in arithmetical progression, by equal increments of heat; liquids have been tried, and found to expand unequally, all of them expanding more in the higher temperatures than in the lower, but no two exactly alike. Mercury has appeared to have the least variation, or approach nearest to uniform expansion, and on that and other accounts has been generally preferred in the construction of thermometers. Water has been rejected, as the most unequally expanding liquid yet known. Since the publication of my experiments on the expansion of elastic fluids by heat, and those of Gay Lussac, immediately succeeding them, both demonstrating the perfect sameness in all permanently elastic fluids in this respect; it has been imagined by some that gases expand equally; but this is not corroborated by experience from other sources.

Some time ago it occurred to me as probable, that water and mercury, notwithstanding their apparent diversity, actually expand by the same law, and that the quantity of expansion

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is as the square of the temperature from their respective freezing points. Water very nearly accords with this law according to the present scale of temperature, and the little deviation observable is exactly of the sort that ought to exist, from the known error of the equal division of the mercurial scale. By prosecuting this enquiry I found that the mercurial and water scales divided according to the principle just mentioned, would perfectly accord, as far as they were comparable; and that the law will probably extend to all other pure liquids; but not to heterogeneous compounds, as liquid solutions of salts.

If the law of the expansion of liquids be such as just mentioned, it is natural to expect that other phenomena of heat will be characteristic of the same law. It may be seen in my Essay on the Force of Steam (Man. Mem. Vol. 5, Part 2.) that the elastic force or tension of steam in contact with water, increases *nearly* in a geometrical progression to equal increments of temperature, *as measured by the common mercurial scale*; it was not a little surprising to me at the time to find such an approach to a regular progression, and I was then inclined to think, that the want of perfect coincidence was owing to inaccuracy in the division of the received thermometer; but