



XLIV. Researches on some important points of the theory of heat

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for the more numerous are the objects to which the attention must be directed, the more likely is the chance of error arising and increasing from the intricacy of combination. In short, the principles here set forth, if unacknowledged in the usual directions, must nevertheless be latent in any mode of approximating to the true answer of this great problem in navigation; it only then remains to be desired, that the most compendious way of so far solving it as is possible, may be adopted.

In what was said, the meridian of the place was supposed to have been already determined by one of the commonly practised methods: as, however, there are times when no other heavenly bodies but the stars are visible, it may not be deemed inapplicable, to show how that spangled canopy alone affords sufficient clue for finding the mid-heaven arch above any diameter of the compass.

The subjoined rules depend upon the zenith point being correctly distinguished; which is always the postulate of marine observations.

1st. It being known that two (or more) stars have the same longitude, *i. e.* lie south and north of one another, when they are in a line with the zenith the meridian coincides therewith; and when they are not in a line with the zenith, yet a line drawn through the zenith parallel to the line in which they are is identical with the meridian. When sufficiently elevated and clear to view, either pole and the zenith give the meridian line.

2d. It being known that two (or more) stars have the same latitude, *i. e.* lie west and east of one another, when they are equally above the horizon, the line that joins them is to be equally bisected by a perpendicular to the same,—the bisecting line is in the plane of the true meridian.

1819.

W. W.

XLIV. *Researches on some important Points of the Theory of Heat.* By MM. PETIT and DULONG*.

CONVINCED that certain properties of matter would exhibit themselves under simpler forms, and might be expressed by more regular and less complex laws, could we but refer them to the elements on which they immediately depend, we have endeavoured to introduce into the study of some of the properties which appear more intimately connected with the individual action of the material molecules, the most certain results of the atomic theory. We are led to hope, from the success we have already met with, that the atomic theory will receive from our investigation a new

* From *Annales de Chimie et Phys.* tome x.

degree of probability, and sure methods of determining the truth among different, equally probable, hypotheses.

By directing our observations in a suitable manner we have discovered simple relations between phenomena, the connexion of which had not been previously attended to. The many points of view under which these phenomena may be considered, preclude our embracing the whole at one time; but we have thought that it might be useful, in the interim, to make known the results we have obtained.

These first results relate to specific heats. The determination of this has been the object of the labours of many philosophers. The attempts hitherto made to discover some laws in the specific heats of bodies have all been unsuccessful. It is not uncommon, for example, to meet with numbers, in the best tables, three or four times as great as they ought to be.

Our first care was directed to what could render the measurements that we were to use as accurate as possible. Among the methods of determining the capacities of bodies, those in which the melting of ice, or the mixing of bodies with water, are employed, may doubtless, if properly conducted, lead to very exact results; but most of the substances on which it is indispensable to operate, can seldom be obtained in sufficient volume to enable us to apply these methods; and it was therefore necessary that we should have recourse to a different one. That which we have chosen appears to unite all the requisite conditions. It is founded upon the law of cooling.

It is well known that there exist between the times of cooling of different bodies placed in the same circumstances, and the specific heats of the same bodies, relations in consequence of which the ratio of the capacities may be deduced from that of the times of cooling. Mayer first applied this principle, and satisfied himself that the capacities determined in this way differ little from those obtained for the same bodies by the method of mixture. Leslie, who adopted this method, pointed out an additional precaution, of which Mayer did not suspect the necessity; viz. to inclose the body operated on in an envelope, which must always be the same, to prevent the error which would result from inequality in the radiating power of the surfaces. The most important, however, of all the causes of uncertainty, and to which neither of these philosophers paid any attention, is that which results from the unequal conductivity of the substances that are compared. This cause has the less influence the smaller the volume of the bodies on which we operate, and the slower the heat is permitted to make its escape. The aim then should be to fulfil both of these conditions; but it is difficult to reconcile them, because, when we diminish the volume of the body, we augment the velocity

city with which the heat is dissipated. However, by uniting the different causes which contribute to retard the cooling of a given mass, we are enabled, as our experiments have proved, to place it in such circumstances that the differences in the conductivity of the substances operated upon, have no sensible influence on the measure of the capacities.

To attain this end, the most obvious method is not to begin the observation till the temperature of the body is only a few degrees higher than that of the surrounding bodies. All our experiments, therefore, were made in temperatures between 10° and 15° (centigrade) above the surrounding medium. The changes of temperature should be measured with the greatest care; for even a slight error in the estimate might occasion a great one in the result. By operating, as we have stated, at the same temperature for all the bodies, we avoid errors resulting from the graduation of the thermometer; and by observing this instrument through a lens, we can increase the size of the degrees so much as not to commit an error exceeding the 50th of a degree,—a quantity so minute that it may be disregarded. To obtain uniformity of temperature in the ambient medium during the whole time of every experiment, the body was always placed in a vessel whose sides were blackened interiorly, and covered on all parts with a thick coating of melting ice.

To this first means for diminishing the rate of cooling we added another, the influence of which we could calculate from our knowledge of the laws of the communication of heat. From these laws it results that the velocity of cooling of a body may, *cæteris paribus*, be considerably diminished when its surface possesses but a very weak radiating power, and is immersed in an air very much dilated. To accomplish this, we determined to operate on solid bodies only in a state of very fine powder. In this state they were strongly pressed into a cylindrical vessel of silver, very thin, very small, and the axis of which was occupied by the bulb of the thermometer. This silver cylinder was then placed in the centre of the vessel, the air contained in which was rarefied till its tension did not exceed two millimetres; and care was taken to reproduce the same rarefaction in each experiment.

We thus succeeded in making the cooling of very small bodies go on very slowly, and consequently easy to be observed with precision. It is sufficient to say, that when measuring the capacities of the densest bodies, as gold and platinum, the quantities on which we operated did not exceed 30 grammes; and that the time of cooling was never less than 15 minutes.

We ought now to give the formula which served for the calculation, but the details would lead us into a discussion which we reserve for the publication of the definitive results of all the direct

direct experiments which we have made on the subject. We add only a single remark ; that having compared the specific heats thus obtained for the worst conductors with those given by the method of mixture, or by the calorimeter, their agreement has afforded the most convincing proof of the accuracy of our process. We shall now present in a table the specific heat of several simple bodies, restricting ourselves to those results concerning which we entertain no doubt.

	Specific Heats, that of Water being 1.	Weight of the Atoms, that of Oxygen being 1.	Product of the Weight of each Atom by the corresponding Ca- pacity.
Bismuth ..	0.0288	13.300	0.3830
Lead	0.0293	12.950	0.3794
Gold	0.0298	12.430	0.3704
Platinum .	0.0314	11.160	0.3740
Tin	0.0514	7.350	0.3779
Silver	0.0557	6.750	0.3759
Zinc	0.0927	4.030	0.3736
Tellurium .	0.0912	4.030	0.3675
Copper ..	0.0949	3.957	0.3755
Nickel ...	0.1035	3.690	0.3819
Iron	0.1100	3.392	0.3731
Cobalt . . .	0.1498	2.460	0.3685
Sulphur ..	0.1880	2.011	0.3780

To render the law which we propose to make known intelligible, we have, in the preceding table, joined to the specific heats of the different bodies the relative weights of their atoms. These, as is known, are deduced from the ratios observed between the weights of the elementary substances that unite together. The pains taken for some years past to determine the proportions of most chemical compounds, leave but slight uncertainties respecting the data which we have employed; but as no precise method exists of discovering the real number of atoms of each kind which enter into a combination, there must always be something arbitrary in the choice of the specific weight of the elementary molecules: this uncertainty, however, can only be in the choice of two or three numbers which have the most simple relation to each other. The reasons which have directed our choice will be understood from what follows. There is none of the numbers on which we have fixed which does not agree with the best established chemical analogies.

From the data contained in the preceding table we may now easily calculate the ratio which exists between the capacity of atoms of a different kind. In order to pass from the specific heats

heats furnished by the observations of those of the particles themselves, it is sufficient to divide the former by the number of particles contained in the same weight of the substances which we compare : but it is obvious that the number of particles for equal weights of matter are reciprocally proportional to the density of the atoms. We shall, therefore, obtain the desired result by multiplying each of the capacities deduced from experiment by the weight of the corresponding atom. These different products are presented in the last column of the table.

The approximation apparent on a bare inspection is too remarkable by its simplicity, not to indicate the existence of a physical law capable of being generalized and extended to all elementary substances. These products, which express the capacities of the different atoms, approach so near equality, that the slight differences must be owing to trifling errors either in the measurement of the capacities or in the chemical analyses ; especially if we consider that, in certain cases, these errors, derived from these two sources, may be on the same side, and, consequently, be found multiplied in the result. The number and variety of the substances on which we operated not allowing us to consider the relation thus indicated as merely accidental, we are authorized to deduce from them the following law :—*The atoms of all simple bodies have precisely the same capacity for heat.*

By recollecting what has been stated respecting the kind of uncertainty that exists in fixing the specific weight of the atoms, it may be easily conceived that the law which we have just established will change, if we adopt for the density of the particles a supposition different from what we have chosen ; but, in every case, the law will exhibit a simple ratio between the weights and the specific heats of the elementary atoms ; and it is obvious that, when we had to choose among hypotheses equally probable, we should naturally be led to prefer that which established the most simple relation between the elements which we compared. But whatever opinion be adopted respecting this relation, it will enable us afterwards to control the results of chemical analysis ; and, in certain cases, will give us the most exact method of arriving at the knowledge of the proportions of certain combinations : but if, in our subsequent experiments, no fact occur to invalidate the probability of the opinion we now hold, we shall find, in this method, the advantage of fixing in a certain and uniform manner the specific weight of the atoms of all simple bodies that can be submitted to direct observations.

The law we have announced, seems to be independent of the form which bodies assume, provided that we always consider them under the same circumstances. This, at least, is a consequence deducible from the experiments of MM. Laroche and Berard on the

the specific heat of the gases. The numbers given by them for oxygen and azotic gases do not differ from what they ought to be to agree accurately with our law, except by a quantity less than the probable errors of such experiments. The number for hydrogen is rather too small; but on examining, with attention, all the corrections which the authors were obliged to make on the immediate results of their observations, it may easily be seen that the quickness with which hydrogen lowers to the temperature of the surrounding bodies, compared with other elastic fluids, ought necessarily to introduce into the determination relative to that gas an inaccuracy from which they did not attempt to free it. By taking into consideration this source of error, we are enabled to explain the difference to which we have alluded, without being compelled to make any false supposition.

Having thus established the law of specific heats for elementary bodies, it became very important to examine, under the same point of view, the specific heats of compound bodies. Our process applying indifferently to all substances, whatever their conductivity or state of aggregation may be, we were enabled to subject to experiment many bodies whose proportions may be considered as fixed; but when we attempt to ascend from these determinations to that of the specific heat of each compound atom, by a method analogous to that which we employed for the simple bodies, we find ourselves soon stopped by the number of equally probable suppositions among which we must make our election. Since the method of fixing the weight of the atoms of simple bodies has not yet been subjected to any fixed rule, that of the atoms of compound bodies has been, *à fortiori*, deduced from suppositions purely arbitrary. But instead of adding our own to the conjectures before advanced on the subject, we choose rather to wait till the new order of considerations which we have established can be applied to a sufficiently great number of bodies, and in circumstances sufficiently varied to place the opinions that may be adopted, on decisive conclusions. For the present we shall only remark, that in abstracting each particular supposition, the observations we have hitherto made tend to establish this remarkable law,—*that there always exists a very simple ratio between the capacity of the compound atoms and that of the elementary atoms.*

Another consequence very important for the general theory of chemical actions may likewise be deduced from our researches; namely, *that the quantity of heat developed at the instant of the combination of bodies has no relation to the capacity of the elements: and that in the greater number of cases, this loss of heat is not followed by any diminution in the capacity of the compounds formed.* Thus, for example, the combination of oxygen

gen and hydrogen, or of sulphur and lead, which produces so great a quantity of heat, occasions no greater alteration in the capacity of water, or of sulphuret of lead, than the combination of oxygen with copper, lead, silver,—or of sulphur with carbon, produces in the capacity of the oxides of these metals, or of carburet of sulphur.

These facts cannot be easily reconciled with the generally received ideas respecting the production of heat in chemical phenomena; for, to do so, it would be necessary to admit the improbable supposition that heat exists in bodies in two very different states, and that the portion which we consider as united to the particles of matter is entirely independent of the specific heats. There is, besides, much vagueness and incoherence in the explanations relative to the kind of phenomena of which we speak. The opinions entertained respecting them differ so widely that they can neither be regularly discussed, nor exposed to complete refutation.—It may perhaps be useful to recall briefly the principal facts, and the inductions belonging to this important branch of the science.

Of all the chemical actions considered as sources of heat, none were recognised till lately, except combustion. To search for a plausible theory for this mode of producing heat, before the epoch marked by the memorable discoveries of Lavoisier, would be folly. This illustrious chemist, having more particularly considered the action of oxygen in the state of gas, formed an opinion respecting the cause of this phenomenon, suggested by the observations of Black on latent heat. Hence the idea that the heat liberated during combustion comes from the change of state of the oxygen. The determination which, in concert with Laplace, he made, of the quantities of heat disengaged by the combustion of several substances, appeared to furnish a powerful argument in favour of his conjectures; for experiment showed that when the same quantity of oxygen was united, successively, with phosphorus, hydrogen, and carbon, it disengaged more heat in the first case than in the second, and more in the second than in the third. This might have been expected from the theory; the result of the first combustion being solid, that of the second liquid, and that of the third gaseous: but on considering that the two elements which concur to produce water, lose both the gaseous state, and that, notwithstanding, the heat developed is less than what results from the combustion of phosphorus naturally solid, he was necessarily led to conclude that the latent heat of oxygen must be superior to that of the other elastic fluids. Another difficulty soon after presented itself: nitric acid, in which the oxygen has already lost the gaseous form, and still more nitre, which is in a solid state, produce, when decomposed by combus-

tibles, quantities of heat very different from what would be produced by a weight of gaseous oxygen equal to that which they contain. This fact, which ought to have excited doubts respecting the first explanation, only restricted its generality: it was then supposed that the oxygen, in certain combinations, was capable of retaining a dose of caloric almost as great as that which it contains in the elastic state. Later observed facts could not be explained according to the theory, without admitting that oxygen in certain combinations retained a quantity of heat, even superior to what it contains when in the elastic state: such are the detonations produced by mixtures of chlorate of potash with certain combustibles, or the spontaneous explosions of Davy's euchlorine, and of the chloroide and iodide of azote.

This mode of explanation was afterwards extended to all combinations. It was considered as a principle sufficiently established, that a body, in combining with a certain number of others, might abandon a greater or less portion of its heat, according as, in each case, the different degrees of affinity of the elements in contact occasioned the molecules to approach more or less nearly to each other. It is the degree of this approach, essentially variable, that has been designated by the word *condensation*, so frequently employed by chemists. This is the theory adopted almost generally in France. Several foreign chemists have pointed out its inaccuracy, and modified it in several points, but without producing any conclusive proof, either against the opinion which they combat, or in support of that which they would substitute.

It thus appears that the different explanations relative to the development of heat, in chemical combinations, are reducible to simple assertions derived from the first hypothesis of Lavoisier: and it is wonderful that, since this doctrine was first proposed, it has not been more closely examined; and that, even from the results already known, all the arguments which they are capable of furnishing against it have not been drawn from them. The relations which we have pointed out between the specific heats of simple bodies and those of their compounds, preclude, we think, the possibility of supposing that the heat developed by chemical actions owes its origin merely to the heat produced by changes of state, or to that supposed to be combined with the material molecules. We have even a better reason for rejecting this purely gratuitous hypothesis, as we can explain the phenomenon in a manner more satisfactory. In fact, Davy has long ago shown that when the two poles of a Voltaic pile are united by means of pieces of charcoal placed in a gas incapable of supporting combustion, the charcoal may be kept in a state of strong ignition as long as the pile remains in activity, and without the charcoal undergoing any chemical change. On the other hand, we are warranted to conclude,

conclude, from many Galvanic experiments made by Hissinger and Berzelius, and by Davy, that all bodies which combine are, with respect to each other, at the moment of combination, precisely in the same electric conditions as the two poles of the pile. Is it not then probable that the cause which produces the incandescence of the charcoal in the beautiful experiment just mentioned, is likewise the cause of the greater or less elevation of temperature of a body during the act of combustion? At least this conclusion is founded on the strongest analogies, and ought to be followed through all its consequences. We by no means contend that the changes of constitution which result from chemical combinations have no part in the development of heat with which they are accompanied: we only mean to say that, in very energetic combinations, this cause produces, in general, but a very small part of the total effect.

In closing this memoir, we cannot pass in silence another very important application, to which the exact knowledge of the specific weight of the atoms will lead. If, as we have reason to think, we have by the foregoing considerations succeeded in determining this element with accuracy, we may, setting out from the proper densities of bodies, calculate the ratios which exist between the distances of their atoms: and it is easy to see how important it will be, in many physical theories, to be able to establish a comparison between the distances of the particles, and certain phenomena which may naturally be supposed to stand connected with the new element. For example, it is by examining the question of the dilatations under this new point of view, that we may expect to arrive at simple laws, at present quite unknown. Some essays made on the observations of different philosophers, and on some of our own, (made with a different object,) lead us to consider it very probable that there exists a simple relation between the dilatability of liquids and the distances of their particles. The fine observations of Gay-Lussac on the identity of the contractions of carburet of sulphur and alcohol, setting out from their respective boiling points, support our opinion; for these two liquids present this remarkable particular, that, at the temperatures at which they were compared, the distances between their particles are nearly identical. Before, however, pursuing the researches on this subject, it will be necessary to elucidate, as much as possible, the question of specific heats, and to deduce from it all the consequences to which it may lead relative to the knowledge of the constitution of bodies.