Alexis-Thérèse Petit (1791-1820) and Pierre-Louis Dulong (1785-1838)

Recherches sur quelques points importants de la Théorie de la Chaleur

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The considerations founded on the laws relative to the proportions of chemical compounds enable us to form respecting the constitution of bodies, ideas which, though arbitrarily established in several points, cannot, however, be regarded as absolutely vague and sterile. Convinced likewise that certain properties of matter would present themselves under more simple forms, and could be expressed by more regular and less complicated laws, if we could refer them to the elements upon 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. The success which we have already met with makes us hope not only that his kind of consideration may contribute materially to the further progress of physics; but that the atomic theory itself will receive from it a new degree of probability, and will from it derive sure methods of determining the truth among different hypotheses all equally probable.

Among the properties of matter to which the considerations just mentioned are applicable, we shall choose, in the first place, as having more particularly fixed our attention, those which depend upon the action of heat. By directing our observations in a suitable manner, we have been led to discover simple relations between phenomena, the connexion of which had not been previously attended to; but the numerous points of view under which these phenomena may be examined, giving to our researches an extent which does not permit us to embrace the whole at one time, we have thought that it might be useful at present to make known the results to which we have come.

These first results relate to specific heats. The determination of this important element has been, as is well known, the object of the labours of many philosophers, who have extended to a great number of bodies the methods which they have either contrived or improved. Several of them have likewise endeavoured to confirm, by their own experiments, some consequences deduced from the notions which they have formed to themselves of the nature of heat, and of its mode of existence in bodies. Accordingly Irvine and Crawford, admitting that the quantity of heat contained in bodies is proportional to their capacity, have concluded, that whenever the specific heat of a compound is greater or less than the sum of the specific heats of its elements, there ought to take place at the instant of combination either an absorption or disengagement of heat; but this principle, which Irvine had already applied to the circumstances which accompany the changes in the state of aggregation, and which Crawford made the basis of his theory of animal heat, is in opposition with too many facts to be adopted. The same is the case with a very ingenious hypothesis proposed by Mr. Dalton. According to the ideas of this celebrated philosopher, the quantities of heat united to the elementary particles of the elastic fluids are the same for each. Hence we may, setting out from our knowledge of the number of particles contained in the same weight or the same volume of the different gases, calculate the specific heats of these bodies. This M. Dalton has done; but the numbers which he obtained, and those likewise deduced from several other better founded hypotheses on the constitution of gases, are so inconsistent with experiment that it is impossible for us not to reject the principle upon which such determinations are founded, which Dalton has presented merely in a theoretic manner. The attempts hitherto made to discover some laws in the specific heats of bodies have then been entirely unsuccessful. We shall not be surprized at this if we attend to the great inaccuracy of some of the measurements; for if we except those of Lavoisier and Laplace (unfortunately very few) and those by Laroche and Berard for elastic fluids, we are forced to admit that the greatest part of the others are extremely inaccurate; as our own experiments have informed us, and as might indeed be concluded from the great discordance in the results obtained for the same bodies by different experimenters. 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 then was necessarily 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 mixture of bodies with water is employed, may doubtless, when properly conducted, lead to very exact results; but the greater number of the substances on which it is indispensable to operate can rarely be obtained in sufficient mass to enable us to apply either of these methods. It was necessary, therefore, to have recourse to a different method. The one which we have chosen appears to us to unite all the requisite conditions.

It is founded upon the laws of cooling. It is known that there exist between the velocity 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. The first application of this principle was by Mayer, who satisfied himself that the capacities determined in this way differ little from those obtained for the same bodies by the method of mixture. Mr. Leslie, who has adopted the method of Mayer, has pointed out an additional precaution, of which the latter did not suspect the necessity; namely, to enclose the body on which we operate in an envelope, which must be always the same, in order to avoid the error which would result from any inequality in the radiating power of the surfaces. But the most important of all the causes of uncertainty, and to which neither Mayer nor Leslie paid any attention, is that which results from the unequal conductibility of the substances compared with each other. the influence of this cause is so much the less, the smaller the volume is of the bodies operated upon, and the slower the heat makes its escape from it. Our object then must be to fulfil these two conditions; but it is difficult to reconcile them, because when we diminish the mass of a body, we augment the velocity with which its heat is dissipated. However, by endeavouring to unite all the causes which contribute to retard the cooling of a given mass, we are enabled, as the experiments have shown, to place it in such circumstances that the difference in the conductibility of the substances operated on has non longer any sensible influence on the measure of the capacities.

The first method which presents itself for attaining that end is not to begin the observation till the temperature of the body is only a few degrees higher than that of the surrounding bodies. Accordingly all our experiments were made in an interval of temperature included between 10° and 5° centigrade of excess above the ambient medium. It is indispensable to measure the changes of temperature with the greatest possible care; for even a slight error in the estimation might occasion a great mistake in the result which it is the object to obtain. By operating, as we have said, 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 glass, we can increase the size of its degrees so much as not to commit an error exceeding the 50th of a degree, which occasions a degree of uncertainty respecting the specific heat that may be overlooked. It is well known that all these precautions would be delusive if the temperature of the ambient medium were not rigorously the same in each case, and during the total duration of every experiment.; but this condition was likewise fulfilled, for the body was always plunged into a vessel, the sides of which were blackened interiorly, and covered on all parts with a thick coating of melting ice.

To this first method of diminishing the rate of cooling, without any diminution of the requisite accuracy, we added another, the influence of which we could calculate from our knowledge of the laws of the communication of heat. It results from these laws that the velocity of cooling of a body may, *ceteris paribus*, be considerably diminished when its surface possesses but a very weak radiating power, and is plunged in an air very much dilated. To realize these circumstances, we resolved to operate upon solid bodies only in a state of very fine powder. In this state they were contained, and strongly pressed into a cylindrical vessel of silver very thin, very small, and the axis of which was occupied by the reservoir of the thermometer that served to point out the rate of cooling. This vessel was then placed in the centre of the vessel; and the air contained in it was dilated till its tension did not exceed two millimetres; and care was taken to reproduce the same vacuum in each experiment.

By the precautions just stated, we succeeded in making the cooling of very small bodies exceedingly slow, and consequently easy to observe with precision. To give an idea of the limit which we have obtained in this respect, it may be sufficient to say, that when we measured the capacities of the densest bodies, such as gold and platinum, the masses on which we operated did not exceed the weight of 30 grammes; and that in the cases in which the cooling was most rapid, its duration was not less than 15 minutes.

It would now be requisite to give the formula which served for the calculation of the observations; but the details into which we should be obliged to enter respecting the manner of making the different corrections depending on the method of proceeding would lead us into a discussion which we reserve for the publication of the definitive results of all the direct experiments which we have made on the subject. We shall 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, the remarkable agreement has afforded the most convincing proof of the accuracy of the process which we have adopted.

We shall now present in a table the specific heat of several simple bodies, restricting ourselves to those results about which we entertain no doubt.

	Specific heats	Relative weights of the atoms	Products of the weight of each atom by the corresponding capacity
Bismuth	0,0288	13,30	0,3830
Lead	0,0293	12,95	0,3794
Gold	0,0298	12,43	0,3704
Platinum	0,0314	11,16	0,3740
Tin	0,0514	7,35	0,3779
Silver	0,0557	6,75	0,3759
Zinc	0,0927	4,03	0,3736
Tellurium	0,0912	4,03	0,3675
Copper	0,0949	3,957	0,3755
Nickel	0,1035	3,69	0,3819
Iron	0,1100	3,392	0,3731
Cobalt	0,1498	2,46	0,3685
Sulphur	0,1880	2,011	0,3780

To make the law intelligible, which we propose to make known, we have joined, in the preceding table, to the specific heats of the different bodies, the relative weights of their atoms. These weights are deduced, as is known, from the ratios observed between the weights of the elementary substances that unite together. The care taken for some years in the determination of the proportions of most chemical compounds can only leave slight uncertainties with respect to 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, it is obvious that there must always be something arbitrary in the choice of the specific weight of the elementary molecules; but the uncertainty can be only in the choice of two or three numbers which have the most simple relation to each other. The reasons which have directed us in our choice will be sufficiently explained by what follows. We shall satisfy ourselves at present with saying, that there is none of the numbers on which we have fixed which does not agree with the best established chemical analogies.

We may now, in consequence of the data contained in the preceding table, calculate easily the ratio which exists between the capacity of atoms of a different kind. We may remark, that in order to pass from the specific heats furnished by the observations to 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 clear that the number of particles for equal weights of matter are reciprocally proportional to the density of the atoms. We shall obtain, therefore, the result wanted by multiplying each of the capacities deduced from experiment by the weight of the corresponding atom. These different products are contained in the last column of the table.

The simple inspection of these numbers exhibits an approximation too remarkable by its simplicity not to immediately recognize in it 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 slight 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 found multiplied in the result. The number and diversity of the substances on which we operated not permitting us to consider the relation thus pointed out, as simply accidental, we are authorized to deduce from them the following law:

The atoms of all simple bodies have exactly the same capacity for heat.

If we recollect what has been said above respecting the kind of uncertainty which exists in fixing the specific weight of the atoms, it will be easy to conceive that the law which we have just established will change if we adopt for the density of the particles, a supposition different from that which we have chosen; but in all cases 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 were naturally led to decide in favour of 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 hereafter 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 the subsequent part of our experiments, no fact occur to invalidate the probability of the opinion, which we entertain at present, 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 subjected to direct observations.

The law, which we have announced, appears to be independent of the form which the bodies affect, provided always that we consider them in the same circumstances.

This at least is a consequence deducible from the experiments of MM. Laroche and Berard on the specific heat of the gases. The numbers which they give 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 relative to hydrogen, it is true, 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 is easy to see that the rapidity with which hydrogen gas cools down 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 cause of error, we are enabled to explain the difference alluded to without being obliged to make any forced supposition.

The law of specific heats being thus established 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 be their conductibility or state of aggregation, we had it in our power to subject to experiment a great many bodies whose proportions may be considered as fixed; but wen we endeavour to mount 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 choose. If the method of fixing the weight of the atoms of simple bodies has not yet been subjected to any certain rule, that of the atoms of compound bodies has bee, *à fortiori*, deduced from suppositions purely arbitrary. But instead of adding our own conjectures to those which have been already advanced on the subject, we choose rather to wait till the new order of considerations which we have just established can be applied to a sufficiently great number of bodies, and in circumstances sufficiently varied that the opinion adopted may be founded on decisive conclusions. We shall satisfy ourselves with saying, that in abstracting every particular supposition, the observations which we have hitherto made tend to establish this remarkable law; viz. that there always exists a very simple ratio between the capacity of the compound atoms and that of the elementary atoms.

We may likewise deduce from our researches another very important consequence for the general theory of chemical actions, 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 greatest 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 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.

It would be very difficult to reconcile these facts with the ideas generally received respecting the production of heat in chemical phenomena; for in order to do so, it would be necessary to admit the very 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. Besides, there is so much vagueness and incoherence in the explanations relative to the kind of phenomena of which we speak. There exist with respect to them opinions so different that they cannot be subjected to a regular discussion, nor exposed to a complete refutation. But, perhaps, it will not be useless to recall in a few words the principal facts and the inductions belonging to this important part of science.

Of all the chemical actions considered as sources of heat, none has been recognized till very lately, except combustion. It would be useless to look for a plausible theory for this mode of the production of heat before the epoch marked by the memorable discoveries of Lavoisier. This illustrious chemist having more particularly studied the action of oxygen in the state of gas, he formed an opinion respecting the cause of the phenomenon in question naturally suggested by the observations of Black on latent heat. Hence the idea that the heat disengaged during combustion comes from the change of state of the oxygen. The determination which he made, together with M. Laplace, of the quantities of heat disengaged by the combustion of several substances appeared to furnish a powerful argument in favour of his conjectures. 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 was what might have been concluded from the theory, since the result of the first combustion is solid, that of the second liquid, and that of the third gaseous. But on considering that the two elements which concur to form water lose both the gaseous state and that notwithstanding the heat developed is less than what results from the combustion of phosphorus naturally solid, it was necessary 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 form of an elastic fluid, and still more nitre, which is in a solid state, produce, when decomposed by combustibles, quantities of heat very little different from that which would be produced by a weight of gaseous oxygen equal to that which they contain. This observation, which ought to have excited doubts respecting the primitive explanation, only restricted its generality. It was then supposed that in certain combinations the oxygen was capable of retaining a dose of heat almost as great as that which it contains when in the elastic state. Some facts more lately observed could not be explained according to the theory without admitting that the oxygen contained in certain combinations retained a quantity of heat superior to that which 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 the euchlorine of Davy, and of the chloride and iodide of azote.

This explanation was afterwards extended to all combinations, and it was considered as a principle sufficiently established that a body in combining with a certain number of others might abandon a more or less considerable part 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 oft his approach, essentially variable, which has been denoted by the word *condensation*, so frequently employed in the language of chemistry.

Such is the theory almost generally adopted in France. Several foreign chemists have pointed out its inaccuracy, and have modified it in different points, but without producing any conclusive proof either against the opinion which they combat, or in support of that which they wish to substitute in its place.

We see then 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. It is astonishing that since the time in which this doctrine originated, it has not been subjected to a more rigid examination; and that even from the results already known, all the arguments have not been drawn against it which they are capable of furnishing. We conceive that the relations which we have pointed out between the specific heats of simple bodies and those of their compounds prevents 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 still a better reason to reject this purely gratuitous hypothesis, as we can explain the phenomenon in a much more satisfactory manner.

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 or supporting combustion, the charcoal may be kept in a state of violent ignition as long as the pile remains in activity, and without the charcoal undergoing any chemical change. On the other side, we are warranted to conclude from a great number of galvanic experiments made by Hisinger 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 fine experiment just mentioned is likewise the cause of the greater or less elevation of temperature of a body during the act of combination? This conclusion at least is founded on the strongest analogies, and ought to be followed through all its consequences.

We are far from pretending that the changes of constitution, which are the result of chemical combinations, have no part in the development of the heat which accompanies them. We mean to say merely that in very energetic combinations this cause produces in general but a very small part of the total effect.

We cannot pass in silence, in termination this memoir, another very important application to which the exact knowledge of the specific weight of the atoms will lead. If, as we have reason to expect, we succeed by the foregoing considerations to determine 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. But it is easy to see how important it will be in a great many physical theories to be able to establish a comparison between the distances of the particles and certain phenomena, which it is natural to suppose connected with this new element. It is, for example, by examining the question of dilations under this new point of view that we may expect to arrive at simple laws, at present altogether unknown. Some trials made on the observations of different philosophers, and upon some of our own made with a different object, lead us to consider it as 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 the carburet of sulphur and alcohol, setting out from their respective boiling points, support our opinion; for these two liquids present this remarkable particularity, that at the temperatures in which they were compared, the distances between their particles are almost exactly the same. But before prosecuting the researches on this subject, it is 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.