PHYSICS-CHEMISTRY

Specific Heats and Atomic Weights

"A Classic of Science"

Dulong and Petit Discover an Odd Constant of Nature, Atoms of All Simple Bodies Have Same Heat Capacity

RESEARCHES ON SOME IMPORTANT POINTS OF THE THEORY OF HEAT. By MM. Petit and Dulong. (Presented to the Academy of Sciences on April 12, 1819.) Translated from the Annales de Chimie et Physique, x. 396. Published in Annals of Philosophy, Vol. XIV, Sept. 1819.

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 fulfill 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 endeavoring 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 no longer any sensible influence on the measure of the capacities.

Determining Specific Heat

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.

The Ratio

	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 capacity.
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 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.

Heat Capacity of Atoms

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 be 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

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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 favor 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 bodies affect, provided always that we consider them in the same circumstances.

Science News Letter, April 11, 1931