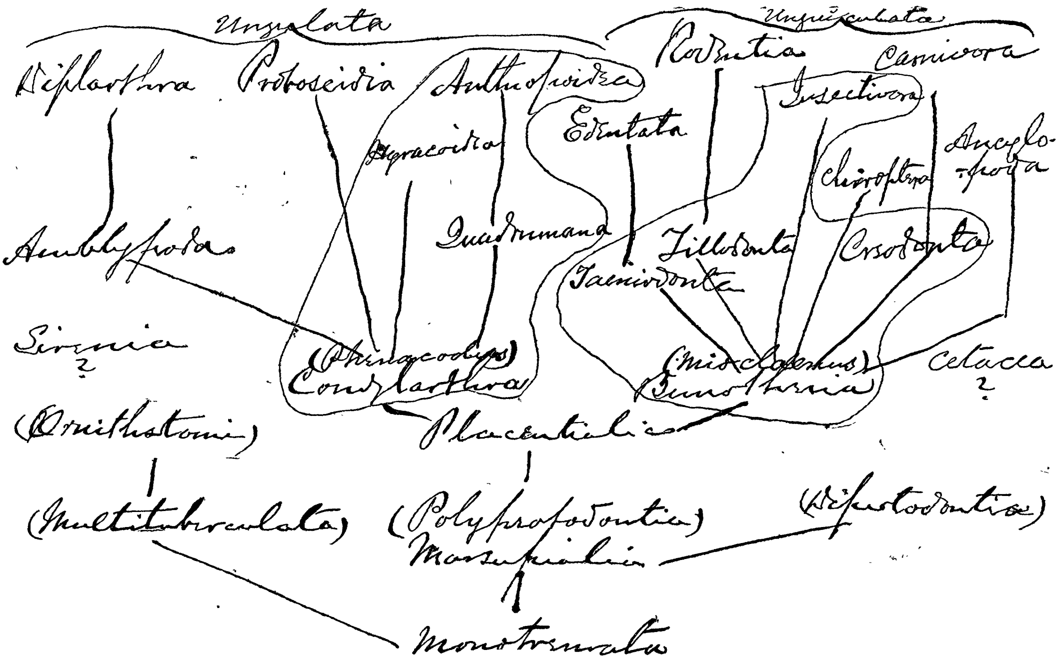

tremes as true surviving ancestral types, as the table might seem to suggest.

It is merely justice to him to add that he regarded the whole subject as a problem for further investigation, and that he by no means looked upon his own conceptions at that time as final.

Charles S. Minot.

RECENT EXPERIMENTS ON CERTAIN OF THE CHEMICAL ELEMENTS IN RELATION TO HEAT.*

The discovery that different substances have different capacities for heat is usually attributed to Irvine, but there can be no doubt that Black, Crawford and others contributed to the establishment of the idea. The fact that equal weights of different substances, in cooling down through the same number of degrees, give out different amounts of heat, may be illustrated by the well-known experiment in which a cake of wax is penetrated with different degrees of rapidity by balls of different metals heated to the same temperature. But, for the quantitative estimation of the amounts of heat thus taken up and given out again—that is, the *specific heats*—the physicist must resort to other forms of experiment, each of which presents difficulties of its own. Broadly speaking, three principal methods have been used in the past for this purpose. The first is based upon the observation of the exact change of temperature produced in a known mass of water, by mixing with it a known weight of the substance previously at a definite temperature above or below that of the water. The second consists in determining the quantity of ice melted, when the heated body is brought into contact with it in such a way that no heat from any other source can reach the ice. And the third method consists in observing the rate at which the temperature of the heated body falls through a definite range of degrees, when suspended in a vacuous

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*A Lecture delivered before the Royal Institution of Great Britain on May 13, 1898, by Professor W. A. Tilden, D.Sc., F.R.S.

space, as compared with the rate of cooling of another body taken as the standard.

The process of intermixture with water was used by the earlier experimenters in the last century, and some of the best results extant have been obtained by this method, which, however, is not so easy as it appears when the highest degree of accuracy is desired.

Lavoisier and Laplace, in 1780, devised the ice calorimeter which bears their name; and in a most interesting memoir, which is reprinted among Lavoisier's works, they show that they were familiar with the idea which in modern times is expressed as the principle of the conservation of energy. In this memoir they give the results of experiments, in which the specific heats of iron, mercury and a few other substances are estimated with a very tolerable approach to accuracy. Although many of the metals were known to them, and supposing they had persisted in this work, it would not have been possible for them to make the discovery which was reserved for Dulong and Petit thirty-five years later, for the atomic theory had not then been conceived, and no elemental combining proportions had been determined.

Dulong and Petit[*] seem to have used at first the method of mixtures, and to have found, by direct experiment, that the specific heat of solids (metals and glass) increases with the temperature. They also studied (after Leslie) the laws of cooling of bodies; and two years after the publication of their first paper on the subject they (Petit and Dulong, *sic*) arrived at the remarkable general expression which is associated with their names.[†]

After pointing out that all the results of previous experiments except those of Lavoisier and Laplace are extremely incorrect they describe their own conclusions obtained by the method of cooling, conducted with many precautions to avoid error. The numerical expression of their experimental results is given in the following table:

COPY OF TABLE BY PETIT AND DULONG.

(Ann. Chim. Phys. 1819, X., 403.)

—	Specific Heats.	Atomic Weights (0 = 1).	Atomic Weight × Specific Heat.
Bismuth	.0288	13.30	.3830
Lead	.0293	12.95	.3794
Gold	.0298	12.43	.3704
Platinum	.0314	11.16	.3740
Tin	.0514	7.35	.3779
Silver	.0557	6.75	.3759
Zinc	.0927	4.03	.3736
Tellurium	.0912	4.03	.3675
Copper	.0949	3.957	.3755
Nickel	.1035	3.69	.3819
Iron	.1100	3.392	.3731
Cobalt	.1498	2.46	.3685
Sulphur	.1880	2.011	.3780

The statement of the relation indicated in the last column of figures is expressed in the following words of the authors, page 405: "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur."

Here the question rested, till resumed

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[*] Ann. Chim., 1817, VII., 144.

[†] Ibid., 1819, X., 395.

many years later (1840) by Regnault, who in his first memoir* pointed out the difficulties which attend the acceptance of the statement of Petit and Dulong in the form in which they gave it. He then discussed the three principal experimental methods: viz. (1) fusion of ice; (2) mixture with water or other liquid; and (3) cooling; and decided in favor of the second, which he used throughout his researches. The general form of the apparatus used by the great physicist has been a model for the guidance of successive experimentalists since his time.

Another quarter of a century elapsed before the question of the specific heats of the elements was resumed by Hermann Kopp. His results were communicated to the Royal Society, and are embodied in a paper printed in the *Philosophical Transactions* for 1865. After reviewing the work of his predecessors he described a process by which he had made a large number of estimations of specific heat, not only of elements, but of compounds of all kinds in the solid state. Concerning his own process, however, he remarks that "The method, as I have used it, has by no means the accuracy of that of Regnault" (p. 84).

In 1870 Bunsen introduced his well-known ice-calorimeter. This is an instrument in which the amount of ice melted by the heated body is not measured by collecting and weighing the water formed, but by observing the contraction consequent upon the change of state. The results obtained by Bunsen himself are uniformly slightly lower than those of Regnault for the same elements.

Since that time experiments have been made by Weber, Dewar, Humpidge and others, in connection especially with the influence of temperature in particular cases.

Setting aside the elements, carbon, boron, silicon and berryllium, as providing an entirely separate problem, the question is whether the law of Dulong and Petit is strictly valid when applied to the metals. Kopp, in the discussion of his subject, came to the conclusion that it is not; but the grounds for this conclusion are unsatisfactory, since neither the atomic weights nor the specific heats were at that time known with sufficient accuracy. It has been customary to assume that the divergences from the constant value of the product, At. Wt. × Sp. Ht. are due partly to the fact that at the temperature at which specific heats are usually determined, the different elements stand in very different relations to their point of fusion; thus, lead at the temperature of boiling water is much nearer to its melting point than iron under the same conditions. The divergences have also been attributed to temporary or allotropic conditions of the elements. As to the relation to melting point, the specific heats of atomic weights seem to be practically the same in separate metals and alloys of the same which melt at a far lower temperature. For example, the atomic heat of cadmium is 6.35; of bismuth, 6.47; of tin, 6.63; and of lead, 6.50; while the mean atomic heat in alloys of bismuth with tin, and lead with tin, ranges from 6.40 to 6.66 (Regnault), which is practically the same. Again, while the melting point of platinum is at a white heat, the metal becomes plastic at a low red heat, and yet the specific heat at this lower temperature is very little less than it is near the melting point. The properties of many other metals, notably zinc and copper, change considerably at temperatures far removed from their melting points without substantial change in their capacity for heat.

As to allotropy, it is a phenomenon which is comparatively rare among metals, and in the marked cases in which it occurs we have no information as to the value of the specific heats in the several varieties, such

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*Ibid., 73, 5.

as the two forms of antimony and the silver-zinc alloy of Heycock and Neville, and they may be left out of account. Bunsen compared the so-called allotropic tin, obtained by exposing the metal to cold for a long time, and found it .0545 against .0559 for the ordinary kind.[*] In dimorphous substances there is often no difference. Regnault found for arragonite .2086 and for calcite .2085 respectively. The differences between metals hammered and annealed, hard and soft, were also found by Regnault to be very small.[†]

Hard steel ...	.1175.	Same, softened ...	.1165.
Hard bronze ...	.0858.	Same, softened ...	.0862.

Kopp came to the conclusion, *first* that each element in the solid state, and at a sufficient distance from its melting point, has *one* specific or atomic heat, which varies only slightly with physical conditions ; and *secondly*, that each element has essentially the same specific or atomic heat in compounds as it has in the free state. This last is practically identical with the statement which is known as Neumann's law. With Kopp's conclusion I agree, but from some of Regnault's results, coupled with my own, the effect of *small* quantities of carbon, and perhaps of sulphur, upon the specific heats of metals is greater than has been supposed. If we take the results of Regnault and of Kopp and combine them with the most accurately known atomic weights the products are still not constant.

The 'Law' of Dulong and Petit is therefore only an approximation ; but this may perhaps be due to inaccuracy in the estimation of the specific heat, owing to impurity in the material used. That is the problem which I have endeavored to solve.

The introduction by Professor J. Joly of a new method of calorimetry, which depends upon the condensation of steam upon the cold body, and the excellent results obtained by the author in the use of the differential form of his instrument,[‡] led me to think that with due attention to various precautions—such as exact observations of the temperatures, and practice in determining the moment at which the increase of weight due to condensation is completed—results of considerable accuracy might be obtained.

The problem is to find two elements, very closely similar in density and melting point, which can be obtained in a state of purity, and then to determine with the utmost possible accuracy the specific heat of each under the same conditions.

The two metals cobalt and nickel were selected for the purpose. They were examined by Regnault, but the metals he used were very impure.

The cobalt employed in my experiments was prepared by myself. For the nickel I am indebted to Dr. Ludwig Mond. Both were undoubtedly much more nearly pure than any metal available in Regnault's time. The results obtained are as follows :

ATOMIC WEIGHTS MOST ACCURATELY KNOWN (1897) COMBINED WITH SPECIFIC HEATS.

	A. W. (H=1).	S. H. Regnault.	S. H. Kopp.	At. Ht Regnault.	At. Ht. Kopp.
Copper	63.12	.09515	.0930	6.01	5.87
Gold	195.74	.03244	....	6.35	....
Iron	55.60	.11379	.1120	6.33	6.23
Lead	205.36	.03140	.0315	6.45	6.47
Mercury liq	198.49	.03332	....	6.61	....
" —79° to +10° sol	198.49	.03192	....	6.34	....
Silver	107.11	.05701	.0560	6.11	6.00
Iodine	125.89	.05412	....	6.81	....

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[*] Pogg Ann. 141, 27.

[†] Ann. Chim. [3], IX.

[‡] Proc. R. S. 47, 241.

SPECIFIC HEATS OF COBALT AND NICKEL.

Pure fused.

	Cobalt, S. G. $\frac{21^\circ}{4^\circ}$ 8.718.	Nickel, S. G. $\frac{21^\circ}{4^\circ}$ 8.790.	
	.10310	.10953	too high ?
	.10378	.10910	
	.10310	.10930	
	.10355		
	.10373		
	.10362		
Arith. mean	10348	.10931	

The value arrived at for cobalt is much lower than that (.1067) derived from Regnault's experiments, while that for nickel is practically identical with Regnault's, which is .1092. This is certainly too high.

Further experiments will be made, because a single well-established case of this kind is sufficient to decide the question. Already, however, I feel certain that Kopp's conclusion is right, and that the law of Dulong and Petit, even for the metals, is an approximation only and can not be properly expressed in the words of the discoverers. For, although the exact values of the atomic weights of these two elements, cobalt and nickel, are not known, it is certain that they are not so far apart as would be implied by these values for the specific heats.

Two other examples of somewhat similar kind are shown by gold and platinum, copper and iron.

For the gold I naturally applied to my colleague, Professor Roberts-Austen. The platinum I prepared from ordinary foil, by resolution and re-precipitation as ammonio-chloride and subsequent heating. Both metals were fused into buttons before use. The atomic heats come closer together than those of Co and Ni.

Copper and iron differ considerably in melting point, but both at the temperature of 100° are far removed from even incipient fusion. The copper was prepared from pure sulphate by electrolysis, the iron by reduction of pure oxide in pure hydrogen. Notwithstanding all our care, it was disappointing to find it contained .01 per cent. of carbon, the source of which I am at a loss to explain. This iron is purer than any examined by Regnault or Kopp.

SPECIFIC HEATS OF GOLD AND PLATINUM.

Pure fused.

Gold, S. G. $\frac{18^\circ}{18^\circ}$ 19.227.		Platinum, S. G. $\frac{18^\circ}{18^\circ}$ 21.323.	
	.03052		.03147
	.03017		.03150
	.03035		.03144
Arith. mean	.03035	Arith. mean	.03147
Atomic. heat	5.94	Atomic heat	6.05

SPECIFIC HEATS OF COPPER AND IRON.

Fused.

Copper (pure) S. G. $\frac{20^\circ}{20^\circ}$ 8.522.		Iron, S. G. $\frac{15^\circ}{15^\circ}$ 7.745, contains 0.01 per cent. carbon	
	.09248		.11022
	.09241		.11037
	.09205		
	.09234		
Arith. mean	.09232	Arith. mean	.11030
Atomic heat	5.83	Atomic heat	6.13

The differences observed between cobalt and nickel, and between gold and platinum, are manifestly not due to allotropes or to differences of melting point, which in these cases can have no effect on the result. So large a difference must be due to peculiarities inherent in the atoms themselves; and differences of atomic heat are to a certain extent comparable with the differences observed in other physical properties, which, like specific volume, specific refraction, etc., are approximately additive.

If we try to think what is going on in the interior of a mass of solid when it is heated, the work done is expended not only in setting the atoms into that kind of vibration which corresponds to rise of temperature, that is, it makes them hotter, but partly in separating the molecules or physical units from one another (= expansion) and partly in doing *internal* work of some kind, the nature of which is not known. A difference between metals and non-metals has been brought out by the researches of Heycock and Neville, who find that metals dissolved in metals are generally monotomic; whereas it is generally admitted that iodine, sulphur and phosphorus in solution are polyatomic. It is moreover remarkable that, although in respect to specific heat each element in a solid seems to be independent of the other elements with which it is associated, when the elementary substances are vaporized some rise in separate atoms like mercury, some in groups of atoms like iodine, sulphur, arsenic and phosphorus, and as the temperature is raised these groups are simplified with very varying degrees of readiness.

The two metals, cobalt and nickel, with which I began my inquiry, have very nearly the same atomic weight, the value, 58.24 for nickel and that for cobalt 58.49, being calculated by F. W. Clarke from the results of a great many analyses by many different chemists. They are so close together that for a long time they were regarded as identical, and Mendeléef does not hesitate even to invert the order by making Co = 58.5 and Ni = 59. These metals, nevertheless, differ from each other in several very important chemical characters. Nickel, for example, forms the well known and highly remarkable compound with carbonic oxide discovered by Dr. Mond. Cobalt, on the other hand, produces many ammino-compounds to which there is nothing corresponding among the compounds of nickel.

Having put aside the common excuses for the observed divergences from the constant of Dulong and Petit, we are compelled to look round for some other hypothesis to explain them.

The constitution of carbon compounds is now accounted for by a hypothesis concerning the configuration of the carbon atom introduced by Van't Hoff and LeBel twenty-five years ago, and which is now accepted by the whole chemical world. It seems not unreasonable to apply a similar idea to the explanation of those cases of isomerism which have been observed in certain compounds of the metals, notably chromium, cobalt and platinum. This has already been done by Professor Werner, of Zurich. If the constitution of compounds can be safely explained by such hypothesis, this implies the assumption of peculiarities in the configuration of the individual constituent metals around which the various radicles are grouped in such compounds; and hence peculiarities in the behavior of such metals in the elemental form may possibly be accounted for. For the atom of cobalt Professor Werner employs the figure of the regular octahedron. For nickel, therefore, which differs from cobalt in many ways, a different figure must be chosen. This, however, is for the present a matter of pure speculation.

PRELIMINARY NOTE ON THE GROWTH OF PLANTS IN GYPSUM.

IN the 'Handbook of Experiment Station Work' (1893), p. 176, the following passage occurs:

"The action of gypsum as a fertilizer is not well understood. It appears to act indirectly in the soil, setting free plant food, especially potash, already present, but contributing little directly to the support of plants * * * It also promotes nitrification. Gypsum is used as an absorbent in manure heaps to prevent loss of ammonia."

Nevertheless, plants will grow in nearly pure gypsum, as we propose to show.

On the east side of the San Andreas mountains, in southern New Mexico, is an immense deposit of white sand, which has the following composition, according to data kindly furnished by Mr. R. F. Hare, assistant chemist of the New Mexico Experiment Station:

$CaSO_4 + 2\,H_2O$ (Gypsum)	97.00	per cent.
$CaCO_3$ (Calcium Carbonate)	2.86	" "
$MgCO_3$ (Magnesium Carbonate)	.06	" "
$MgSO_4$ (Magnesium Sulphate)	.12	" "
K_2SO_4	.07	" "
Na_2CO_3	trace.	
NaCl	trace.	

In this deposit, locally known as the