PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The Specific Heats of Metals and the Relation of Specific Heat to Atomic Weight. Part III

W. A. Tilden

Phil. Trans. R. Soc. Lond. A 1904 **203**, 139-149
doi: 10.1098/rsta.1904.0018

VI. *The Specific Heats of Metals and the Relation of Specific Heat to Atomic Weight.—Part* III.

By W. A. Tilden, *D.Sc., F.R.S., Professor of Chemistry in the Royal College of Science, London.*

Received March 9,—Read March 17, 1904.

The law of Neumann assumes that when an atom enters into chemical combination it retains the same capacity for heat as when in the uncombined or elemental state. This generalisation is, however, based on the values observed for the mean specific heats of elements and their compounds between 0° and 100° C.*

Attention was directed in Part II. of this investigation† to the great differences found in the influence of temperature on the specific heats of various metals, such as aluminium on the one hand, and silver or platinum on the other. The experiments now about to be described were undertaken with the object of ascertaining to what extent these differences persist in the compounds of such elements.

If the calculated atomic heats of elements in combination are equal at various temperatures through a considerable range to the sum of the atomic heats of the same in the separate state at the same temperatures, then the difference between any two must be due to a fundamental difference in the atoms of the elements concerned and not to a difference in their states of aggregation when separate.

The specific heats of nickel sulphide and silver sulphide have already been compared through a range of temperature from − 182° to + 324° C., but owing to the low melting-point of sulphur, and especially to the occurrence of several allotropic modifications of this element in the solid state, it was not thought worth while to attempt determinations of its specific heat at various temperatures for this purpose.

The only element which seemed to present the assemblage of characters required for the purpose contemplated was tellurium. I am indebted to Dr. T. K. Rose for a supply of tellurium which had already been refined by several dissolutions in aqua regia and precipitation by sulphurous acid. It was further purified by fusion with potassium cyanide, solution in water, and precipitation by exposure to air. Compounds of silver, nickel and tin with tellurium were made by the following

---

* Regnault, 'Ann. Chim. Phys.' [3], 1, 129; Kopp, 'Phil. Trans.,' 1865.

† 'Phil. Trans.,' A, vol. 201, p. 37 (1903).

process. Tellurium and the pure metals were weighed out in the proportions corresponding to the formulæ Ag_2Te, NiTe and $SnTe_2$ respectively, with a slight excess amounting to about 1 per cent. of tellurium. The materials were then fused together in a stream of hydrogen at a temperature sufficiently high to volatilise the excess of tellurium. The tellurides were obtained as black, crystalline, fusible substances, and were cast into cylindrical form by melting in a glass tube.

The nickel used in the preparation of the telluride was in the form of soft wire drawn from metal obtained by electrolysis. For this I am indebted to the kindness of Dr. J. WILSON SWAN, F.R.S. Its specific heat was determined in the steam calorimeter in order to compare it with the fused nickel made for the previous experiments, but which was not found to be sufficiently ductile to admit of being drawn into wire.

SOFT Nickel Wire.

Range of temperature.	Specific heat.	Mean.
° C.		
22 to 100	·1087	·1086
20 „ 100	·1082	
23 „ 100	·1088	

The mean specific heat adopted as the result of the previous experiments on fused nickel was ·1084 for the same range of temperature.*

Alloys of silver and aluminium have also been examined. They were prepared by melting together the exact proportions of the pure metals. In the first the silver largely predominates, being in the ratio required by the formula Ag_3Al. The second contains aluminium in proportion corresponding to the formula $AgAl_{12}$, which represents 75·1 per cent. of aluminium and 24·9 per cent. of silver.

As in the results set forth in the previous paper, the specific heat adopted is the mean of several closely concordant experiments made at each range of temperature. The figures followed by E are estimated from the others which are the direct results of experiment. It will be seen (Table I.) that the value for specific heat increases with rise of temperature in every case except silver telluride, where the mean specific heats found between 15° and 309° and 390° C. respectively are less than at lower temperatures. This irregularity is attributed to the fact that during the later experiments the mass cracked and it was found necessary to re-melt it several times. This was done in hydrogen gas, and though no change in appearance was observed, some slight change in composition or structure may have been produced. These figures have, therefore, not been used in the subsequent calculations.

---

* 'Phil. Trans.,' A, vol. 201, p. 38 (1903).

Table I.—Mean Specific Heats.

Range of temperature.	Tellurium.	Tin.	Silver-telluride. Ag_2Te.	Nickel-telluride. NiTe.	Tin-telluride. $SnTe_2$.	Silver-aluminium. Ag_3Al.	Aluminium-silver. $AgAl_{12}$.
° C.							
– 182 to 15	·0469	·0499	·0516	·0588	·0471	·0620	·1477
15 ,, 100	·0483	·0557	·0672	·0670	·0494	·0696	·1802
15 ,, 180	·0486 E	·0577	·0686	·0689	·0489	·0703	·1861
15 ,, 200	·0487	—	—	—	—	—	—
15 ,, 227	·0488 E	—	—	·0690 E	·0486	·0704	·1863 E
15 ,, 300	—	—	—	·0691	—	—	·1916
15 ,, 309	—	—	·0670	—	—	—	—
15 ,, 315	·0489	—	—	—	—	—	—
15 ,, 322	—	—	—	—	—	·0705	—
15 ,, 327	·0490 E	—	—	·0695 E	·0496	—	·1939 E
15 ,, 380	·0500	—	—	—	—	—	—
15 ,, 385	—	—	—	·0703	—	—	—
15 ,, 390	—	—	·0663	—	—	—	—
15 ,, 410	—	—	—	—	—	·0725	—
15 ,, 427	·0508 E	—	—	·0708 E	—	—	·2015 E
15 ,, 437	—	—	—	—	—	—	·2026
15 ,, 495	—	—	—	—	—	—	·2093

To these results may be added the mean specific heats of silver, nickel, and aluminium taken from the previous series of experiments.

Table II.—Mean Specific Heats.

Range of temperature.	Silver.	Nickel.	Aluminium.
° C.			
– 182 to + 15	·0519	·0838	·1677
15 ,, 100	·0558	·1084	·2100 E
15 ,, 180	·0561	·1101	·2189
15 ,, 227	·0565 E	·1120 E	·2208 E
15 ,, 327	·0577 E	·1175 E	·2247
15 ,, 427	·0581	·1233 E	·2356

The mean specific heats thus determined have been used, as in the former paper,* for the calculation of Q, the total heat measured in the calorimeter. The values of Q for the two elements tellurium and tin, the tellurides of nickel and tin, and the two alloys of aluminium and silver, have been plotted against absolute temperatures, and the results are shown in fig. 1, in which the curves are for the most part hyperbolic, those of tin, tellurium, and tin telluride approaching an elliptic form. In the case of tin, which melts at 232°, this is most probably due partly to incipient fusion at 180°, the highest experimental temperature, and is in accordance with experience.

---

* Part II., 'Phil. Trans.,' A, vol. 201.

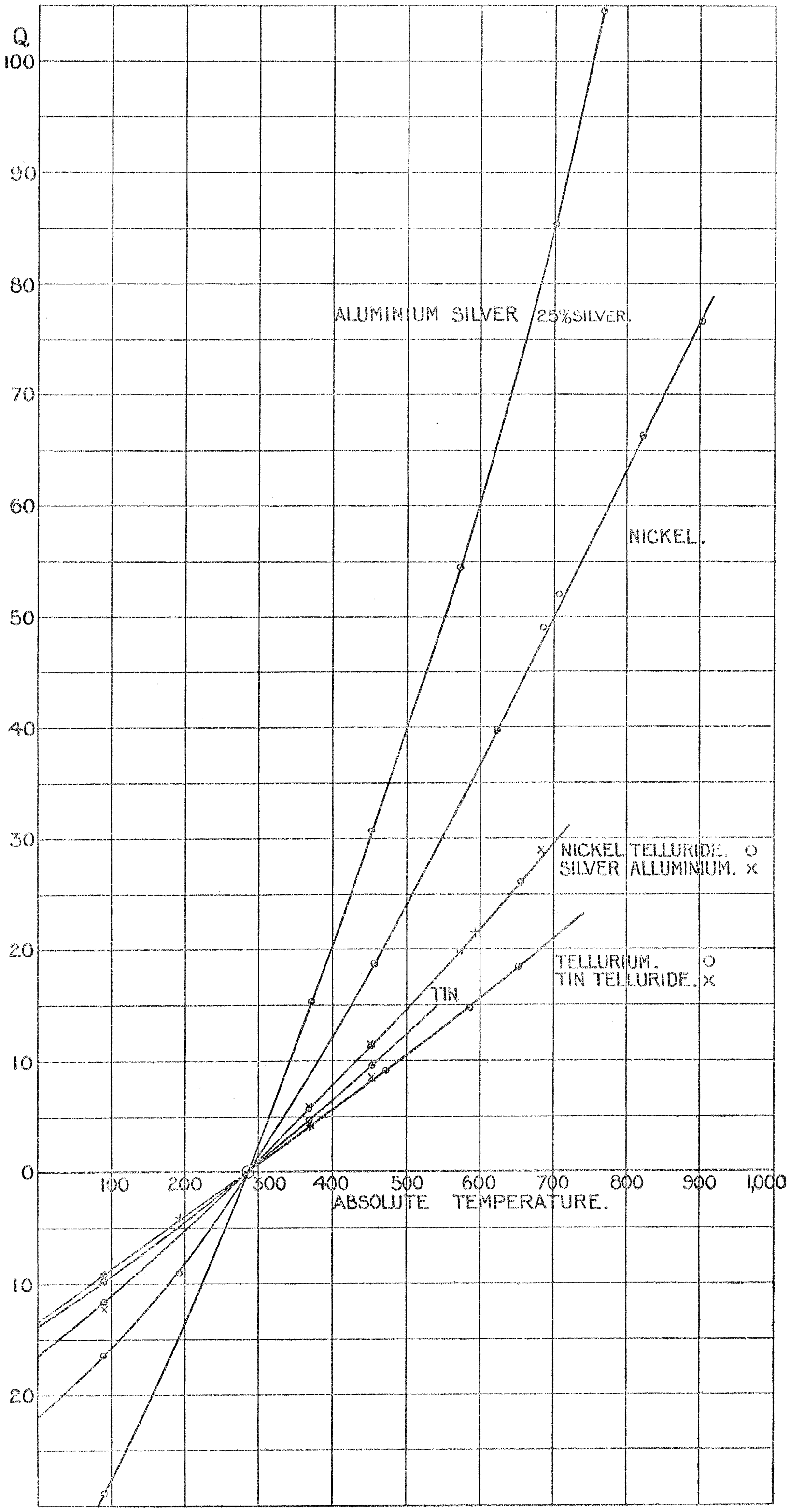
Q.
100
90
80
70
60
50
40
30
20
10
0
10
20
100
200
300
400
500
600
700
800
900
1,000
ABSOLUTE TEMPERATURE.
ALUMINIUM SILVER 25%SILVER.
NICKEL.
NICKEL TELLURIDE. ○
SILVER ALLUMINIUM. ×
TIN
TELLURIUM. ○
TIN TELLURIDE. ×

Fig. 1.

Regnault, for example, found the molecular heats of easily fusible alloys to be very much higher than those of alloys of higher melting-point.*

The values of the true specific heats at successive temperatures on the absolute scale are given in the following table, and are exhibited graphically in figs. 2 and 3 :—

Table III.—True Specific Heats.

t abs.	Tellurium.	Tin.	Nickel-telluride. NiTe.	Tin-telluride. $SnTe_2$.	Silver-aluminium. Ag_3Al.	Aluminium-silver. $AgAl_{12}$.
° C.						
100	·0462	·0462	·0453	·0467	·0591	·1233
200	·0471	·0504	·0614	·0472	·0628	·1510
300	·0480	·0548	·0671	·0479	·0662	·1731
400	·0489	·0596	·0699	·0488	·0693	·1917
500	·0498	—	·0711	·0502	·0722	·2060
600	·0507	—	·0718	—	·0748	·2166
700	·0516	—	·0722	—	·0771	·2260
800	—	—	—	—	—	·2340

It is obvious that the curves for the specific heats of the compounds are of the same character as those for the metals aluminium, nickel, and silver given in the previous paper, and that the inclination of each is determined by the principal ingredient. Thus the curve for aluminium-silver containing 92 per cent. of silver is very near to the curve for that metal, while the curve for the alloy containing 75 per cent. of aluminium approaches the curve for pure aluminium.

The atomic heats of the elements are obtained by multiplying the specific heats by the respective atomic weights, which have been taken from the International Table.

Table IV.—Atomic Heats.

t abs.	Tellurium. Te = 126·6.	Tin. Sn = 118·1.	Silver. Ag = 107·12.	Nickel. Ni = 58·3.	Aluminium. Al = 26·9.
° C.					
100	5·85	5·46	5·00	3·35	3·30
200	5·96	5·95	5·65	5·12	4·66
300	6·08	6·47	5·98	6·14	5·52
400	6·19	7·04	6·13	6·81	6·06
500	6·30	—	6·22	7·19	6·41
600	6·42	—	6·29	7·43	6·65
700	6·53	—	6·32	7·58	6·81
800	—	—	—	7·70	—
900	—	—	—	7·80	—

---

* 'Ann. Chim. Phys.,' [3], 1, 137 and 183.

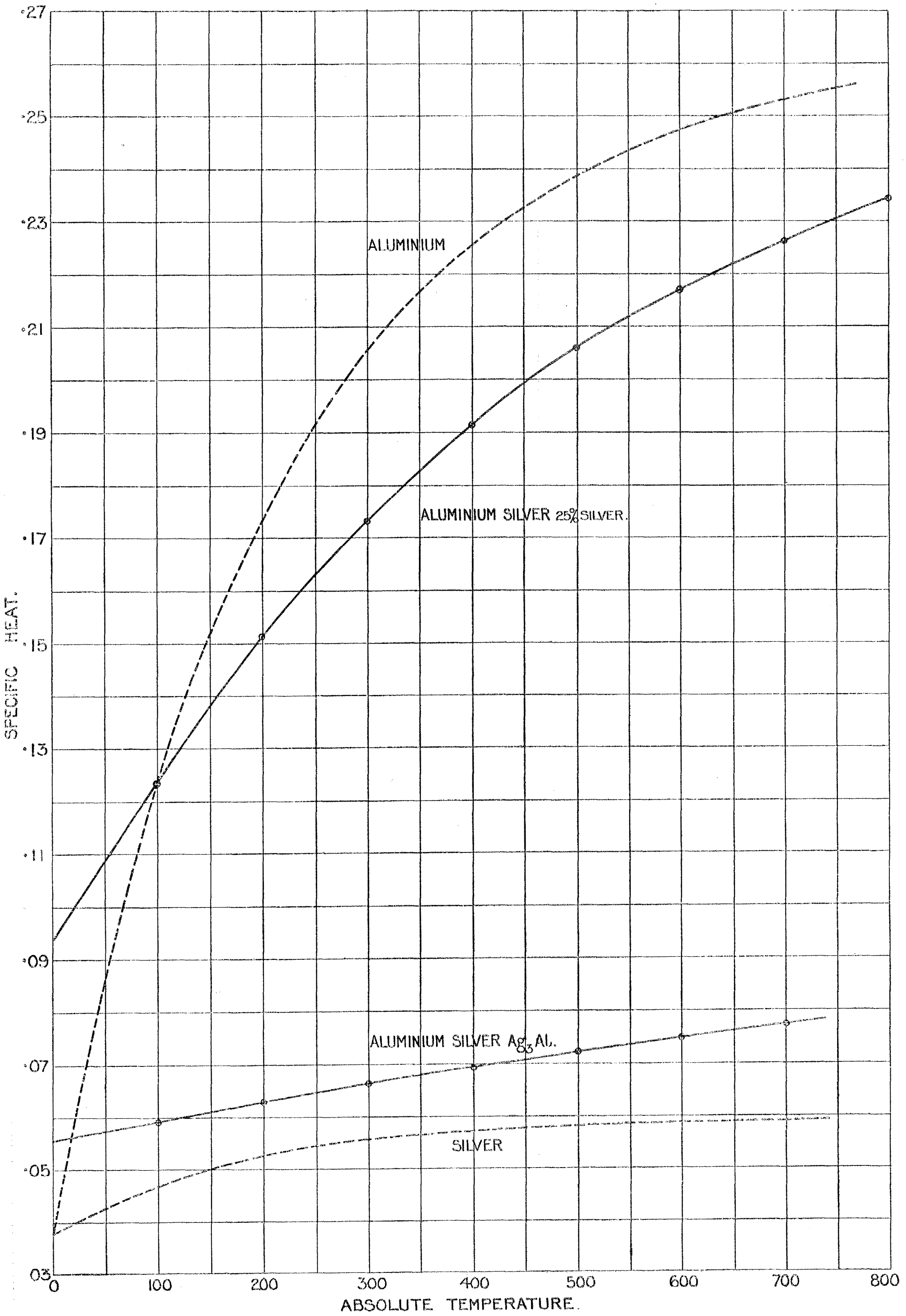
·27
·25
·23
·21
·19
·17
·15
·13
·11
·09
·07
·05
·03
SPECIFIC HEAT.
ALUMINIUM
ALUMINIUM SILVER 25% SILVER.
ALUMINIUM SILVER Ag$_3$ Al.
SILVER
0
100
200
300
400
500
600
700
800
ABSOLUTE TEMPERATURE.

Fig. 2.

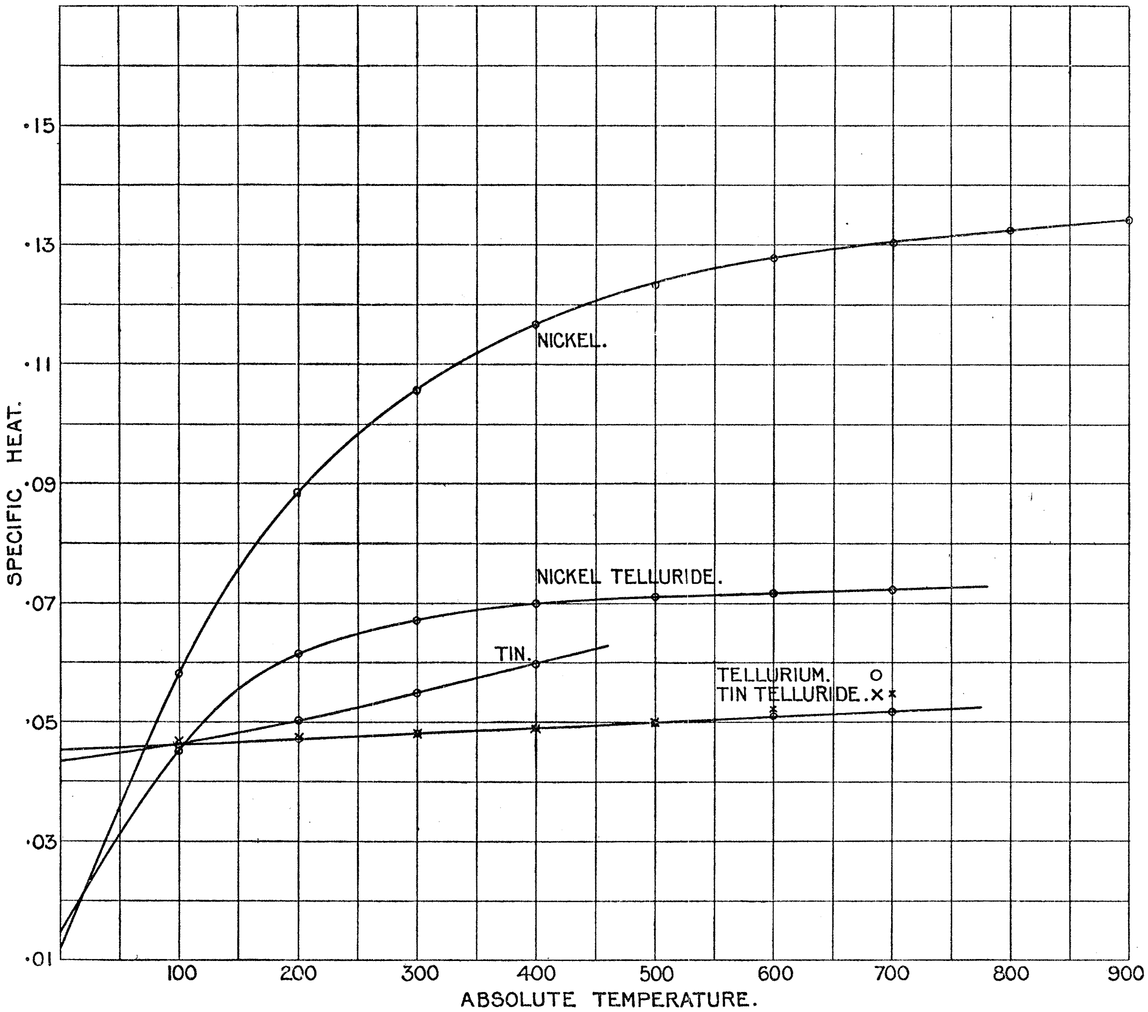

Fig. 3.

On the hypothesis that each atom in a compound behaves as it does in the solid element, the sum of the atomic heats of the elements entering into the compound should be equal to the molecular heat of the compound. The following table contains a comparison of the sum of the atomic heats, A, with the molecular heats, B, of the several compounds, that is, the product of the observed specific heat of the compound multiplied by the molecular weight in each case.

TABLE V.—Molecular Heats of Compounds.

t abs.	$SnTe_2$. A.	$SnTe_2$. B.	NiTe. A.	NiTe. B.	Ag_3Al. A.	Ag_3Al. B.	$AgAl_{12}$. A.	$AgAl_{12}$. B.
° C.								
100	17·16	17·33	9·20	8·38	18·30	20·58	44·60	53·01
200	17·87	17·51	11·08	11·35	21·61	22·38	61·57	64·92
300	18·63	17·77	12·22	12·41	23·46	23·06	72·12	74·42
400	19·42	18·10	13·00	12·92	24·45	24·14	78·85	82·41
500	—	—	13·49	13·15	25·07	25·15	83·14	88·56
600	—	—	13·85	13·28	25·52	26·05	86·09	93·12
700	—	—	14·11	13·35	25·77	26·85	88·04	97·16
800	—	—	—	—	—	—	—	—

A = calculated from the atomic heats of the elements.

B = calculated from the observed specific heats of the compounds.

The figures contained in this table show that in the cases of tin-telluride, nickel-telluride and the silver-aluminium alloy containing 92·28 per cent. of silver, there is a remarkably close approximation of the values under B to those under A, the differences between the two columns being throughout well within the limits of variation due to experimental error.

With regard to the aluminium-silver alloy containing only 24·9 per cent. of silver, however, there are differences which are somewhat greater. The values for silver-telluride must be regarded as open to suspicion, for reasons which have already been indicated, and they are not included in the table. If the *mean* atomic heats of silver-telluride are compared, it is found that the difference between the sum of the atomic heats and the molecular heat of the compound increases considerably with the temperature, as seen below:—

Temperature.	A.	B.	Difference.
° C.			
−182 to + 15	17·06	17·59	0·53
15 „ 100	18·07	22·90	4·83
15 „ 180	18·17	23·38	5·21

This is perhaps due to some change taking place in the constitution of the solid. This, however, does not seem to be the explanation in the case of the aluminium-silver alloy, in which the differences between the two columns of figures, though not constant, do not increase appreciably—

$$\begin{aligned} B - A \text{ at } 100^\circ &= 8{\cdot}41, \\ 200 &= 3{\cdot}35, \\ 300 &= 2{\cdot}30, \\ 400 &= 3{\cdot}56, \\ 500 &= 5{\cdot}42, \\ 600 &= 7{\cdot}03, \\ 700 &= 9{\cdot}12. \end{aligned}$$

Remembering what a large factor, 429·9, is used in calculating these figures, it will be seen that the differences are really small, being about 15 per cent. of the molecular heat at the lowest temperature and falling to about 3 per cent. at 300° abs. It will be noticed that in this case B is throughout larger than A.

The results of these experiments show that NEUMANN'S law may be regarded as approximately valid for the specific heats at all temperatures. They also confirm the view that the specific heat of a solid is not a measure of the work done in separating the molecules of the substance, but that its amount is determined almost entirely by the nature of the atoms composing the physical molecules.

All the facts at our disposal show that there is not a great difference between the specific heats of elements in the solid and liquid states, but that in every case the latter is the greater, as shown in the following examples:—

TABLE VI.—Specific Heats.

Name.	Solid.	Liquid.	Authority.
Lead	·034	·040	PERSON.
Bromine	·084	·107	ANDREWS.
Gallium	·079	·080	BERTHELOT.
Phosphorus	·202	·204	PERSON.
Mercury	·032	·033	KOPP.
Bismuth	·030	·036	PERSON.
Tin	·058	·063	SPRING.

The *atomic* heat in the liquid state is thus in all cases greater than in the solid, and in the above cases ranges from 5·6 to 8·5. In the gaseous state at constant volume the atomic heat is, however, much smaller, being approximately for hydrogen 2·42, for oxygen 2·48, and for iodine, a solid at common temperatures and in some characters approaching the metals, 3·3. In respect to specific heat, therefore, the liquid state is not intermediate between the solid and the gaseous states. This may possibly be explained by the assumption that in the solid and in the gas at constant volume every molecule in the mass remains in the same condition relatively to every other molecule, for in the solid all are rigidly bound together by "cohesion," and in the gas all are equally free. In the liquid state there is reason to believe that there is a mixture of clusters or aggregates of molecules having different degrees of complexity, and that the effect of rise of temperature upon these is to cause dissociation of the more complex into simpler groups, a process which necessarily implies work done.

Notwithstanding the validity of NEUMANN's law, the attempts which have been made to deduce the atomic heats of elements, such as oxygen, which do not admit of experiment in the solid state, cannot, however, be regarded as satisfactory. It is obvious that in such calculations whatever change in the molecular heat of the compound is induced by slight alteration of density, or of structure in the solid, is concentrated upon one element in the compound of any two, when it is assumed that the other enters into combination with the atomic heat it possesses in the elemental state. Taking the figures for the compounds containing silver, for example, the value deduced for the atomic heat of silver is found to vary considerably according to the nature of the compound selected. To calculate the atomic heat of silver from the mean molecular heat of the telluride—which is $\cdot 0672 \times 340\cdot 8 = 22\cdot 90$ at the usual temperature of experiment, 0° to 100° C.—the value for tellurium is deducted and the remainder divided by 2. The result is 8·39.

Similarly the atomic heat of silver in the silver-aluminium, Ag_3Al, comes out as 6·19, and in the aluminium-silver, $AgAl_{12}$, as 9·67. The variations are still greater if a comparison is made over different ranges of temperature. Hence it appears probable that the values which have been calculated for hydrogen, oxygen, nitrogen and chlorine in the solid state are very far from the truth.

KOPP estimated the atomic heats of these elements in the solid state to be as follows:—

Hydrogen	2·3	Nitrogen	6·4
Oxygen	4·0	Chlorine	6·4

From its various compounds no approach to a uniform value for the atomic heat of carbon is to be found, but KOPP preferred the value 1·8, which is deduced from the specific heat of diamond.

Without here entering into a discussion of all these elements, it may be mentioned that in the case of hydrogen gas at constant volume the atomic heat is practically identical with that deduced from the specific heat of solid compounds, while that of oxygen is less, and that of carbon in the form of carbon dioxide gas is greater than the estimates thus made. JOLY found[*] the specific heat of air between 15° and 100° C. to be ·172, that of carbon dioxide gas ·173, and that of hydrogen 2·41, when under approximately equal pressures. The atomic heat of hydrogen gas is therefore 2·41. Assuming the specific heat of oxygen at constant volume very near to that of

---

[*] 'Phil. Trans.,' A, vol. 182, p. 73 (1892).

air, as it was shown to be many years ago, when at constant pressure, by Regnault, its atomic heat is about 2·7, which is a little greater than 2·48, the value deduced theoretically from Regnault's experiments at constant pressure. Lastly, taking ·173 for carbon dioxide and multiplying by 44, the value 7·61 is obtained as the molecular heat of carbon dioxide gas. If it be assumed that in the gaseous, as in the solid, state the atomic heat of each element is preserved in the compound, the atomic heat of gaseous carbon is left when the atomic heat of the oxygen in the dioxide is deducted. We thus obtain the value 2·65.

This is greater than 1·8, the value chosen by Kopp, but falls between 2·89 and 2·42, the atomic heats of carbon, in the form of wood charcoal and natural graphite respectively, deduced from the experiments of Regnault between 0° and 100° C.

This deduction from data belonging wholly to the gaseous state is of interest because it is in accordance with the theoretical view that specific heat in a gas is not dependent on the temperature.

On the other hand, as the above experiments prove, atomic heats in the solid state, and probably also in the liquid state, are largely dependent on the temperature, the variation being abnormally great in solid carbon. It has also been shown that at the same temperature the atomic heats are widely different for different elements in the solid state; but notwithstanding this fact it has been proved that the molecular heat of a solid compound is approximately the sum of the atomic heats of its constituents at each temperature.

In conclusion, I desire again to express the obligations I am under to Mr. Sidney Young and to Mr. Leonard Bairstow for their assistance.