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 II

W. A. Tilden

Phil. Trans. R. Soc. Lond. A 1903 **201**, 37-43
doi: 10.1098/rsta.1903.0012

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

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

Received December 8,—Read December 11, 1902.

IN the BAKERIAN LECTURE for 1900 ('Phil. Trans.,' A, vol. 194, p. 233) it was shown that the specific heats of very pure cobalt and nickel, when compared at temperatures from 100° C. down to the boiling-point of liquid oxygen, − 182°·5 C., steadily approach each other and together tend towards a least value which is at present unknown.

It was thought desirable to increase the number of determinations at successive points on the thermometric scale, and to extend the total range of the experiments so as to afford better data for calculation of the form of the curves. The following is an account of the results obtained.*

It has not yet been possible to arrange for the conduct of experiments at temperatures lower than − 182°·5, as this could only be done with the aid of liquid hydrogen. The temperatures above 100° C. have been obtained by the use of a bath of aniline vapour, melted fusible metal or melted lead, and were estimated by the use of a platinum resistance thermometer which was carefully calibrated, and of which the fixed points 0°, 100°, and 184° (boiling-point of aniline) were verified. The specific heats were determined in the same calorimeter and with the same precautions as described in the BAKERIAN LECTURE.

The holder employed in the experiments at low temperatures was found equally useful in the experiments above 100°. Between air temperature and 100° the steam calorimeter was again employed.

The figures given in the following Table I. are in nearly all cases the mean values deduced from several experiments which were always closely concordant.

The total amount of heat per unit mass measured in the calorimeter is equal to the product of the mean specific heat and the range of temperature, beginning in each case at 15° C. Taking the values given in the table, this product, Q, may be plotted as an ordinate, the higher absolute temperature, *t*, being the abscissa. The result is

* The nickel, cobalt, and platinum employed are the pure specimens prepared for the former series of experiments. Pure silver was obtained from Messrs. JOHNSON and MATTHEY. For the aluminium I am indebted to Professor J. W. MALLET; it was described as nearly pure.

shown in fig. 1. Cobalt has been omitted, as the metal apparently undergoes some oxidation at high temperatures and the results are less regular than the rest.

TABLE I.—Mean Specific Heats.

Range of temperature.	Aluminium.	Nickel.	Cobalt.	Silver.	Platinum.
° C.					
− 182 to + 15	·1677	·0838	·0822	·0519	·0292
− 78 ,, + 15	·1984	·0975	·0939	·0550	—
+ 15 ,, + 100	—	·1084	·1030	·0558	·0315
15 ,, 185	·2189	·1101	·1047	·0561	—
15 ,, 335	·2247	—	—	—	—
15 ,, 350	—	·1186	·1087	·0576	—
15 ,, 415	—	·1227	—	—	—
15 ,, 435	·2356	·1240	·1147	·0581	·0338
15 ,, 550	—	·1240	·1209	—	—
15 ,, 630	—	·1246	·1234	—	—
0 ,, 1000	—	—	—	—	·0377*
0 ,, 1177	—	—	—	—	·0388*

The general shape of the curves is the same and the connection between Q and t may be assumed as hyperbolic:

$$Q^2 + aQ + bt^2 + ct + f = 0.$$

The values of $k, = dQ/dt$, for the specific heats at successive temperatures on the absolute scale are given in the following table:—

TABLE II.—Specific Heats.

t abs.	Aluminium.	Nickel.	Silver.	Platinum.
° C.				
100	·1226	·0575	·0467	·0275
200	·1731	·0878	·0528	·0293
300	·2053	·1054	·0558	·0311
400	·2254	·1168	·0572	·0328
500	·2384	·1233	·0581	·0344
600	·2471	·1275	·0587	·0358
700	·2531	·1301	·0590	·0372
800	—	·1321	—	·0385
900	—	·1338	—	·0397
1000	—	—	—	·0409
1100	—	—	—	·0421
1200	—	—	—	·0432
1300	—	—	—	·0442
1400	—	—	—	·0452
1500	—	—	—	·0461

One important result of the extension of the experiments to other metals is that the assumption of a constant atomic heat at the absolute zero, which seemed justified

* VIOLLE, 'Comptes Rendus' (1877), vol. 85, p. 543; also 'Phil. Mag.' [5], vol. 4, p. 318.

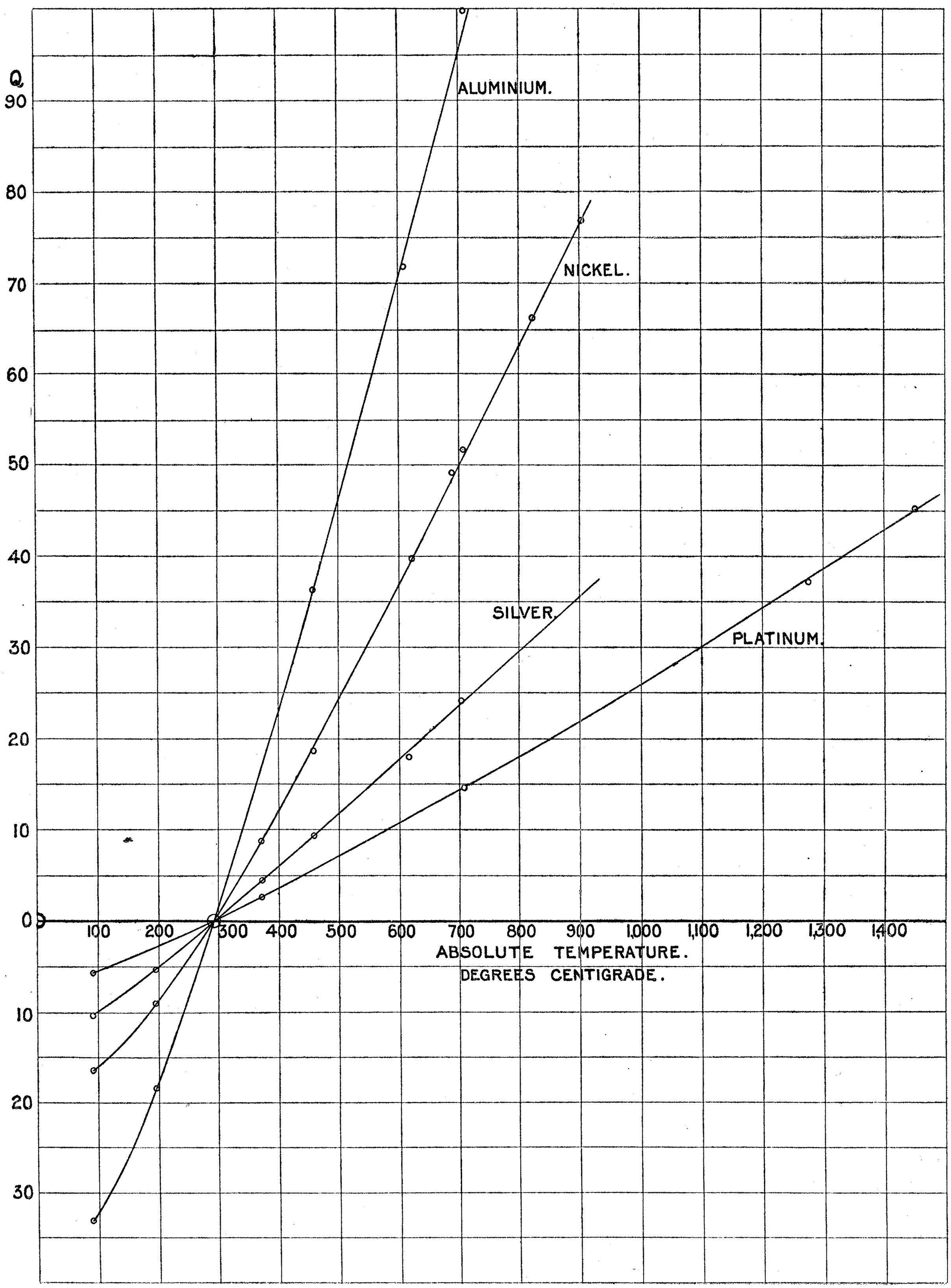

Fig. 1.

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

in the case of cobalt and nickel (see Appendix to BAKERIAN LECTURE), is apparently untenable.

Plotting the specific heats in Table II. against absolute temperatures, the curves shown in fig. 2 are obtained, from which it is obvious that unless some remarkable change in the specific heats of silver and platinum occurs below − 182° C. the curves representing *atomic* heats cannot meet at the absolute zero.

It will be observed that the influence of rise of temperature on the specific heat is in the inverse order of the atomic weights of the metals compared, being greatest in the case of aluminium and least in the case of platinum. This appears to be generally true and is supported by the experiments of BEHN ('WIEDEMANN'S Ann.,' vol. 66, p. 237). It appears, therefore, that the usual application of the law of DULONG and PETIT to the rectification of atomic weights is a rough empirical rule which, setting aside boron, carbon, silicon, and beryllium, is only available when the specific heats have been determined at comparatively low temperatures, usually, and most conveniently, between 0° and 100° C.

What mechanical properties of the metals are concerned in affecting the value of the specific heat is not known. The work done in expansion has apparently very little to do with it. Lead and platinum, for example, the atomic weights and specific heats of which are near together, have very different coefficients of expansion, that of lead being nearly ten times as great as that of platinum. I have, however, on the suggestion of Professor PERRY, thought it of some interest to determine the specific heat of the remarkable nickel steel which is said to have a smaller dilatation than that of any other metal. The sample used was found by analysis to contain 35·92 per cent. of nickel, practically 36 per cent., with ·11 of carbon and about ·30 of manganese. The mean specific heats observed at four widely separate temperatures show that there is decidedly an increase with rise of temperature to an extent about the same as in the case of nickel itself.

Range of temperature.	Mean specific heat of nickel steel.
− 182° to + 15°	·0947
15 „ 100	·1204
15 „ 360	·1245
15 „ 600	·1258

Evidence as to the cause of the difference between two such metals as nickel and silver has been sought by making comparative experiments with the two metals in the form of sulphide. These compounds were prepared by precipitation by hydrogen sulphide from solutions of the sulphate and nitrate respectively, and subsequent fusion of the dry sulphide with an excess of sulphur. If the differences between the metals are due to peculiarities of the atoms of each, similar differences would be

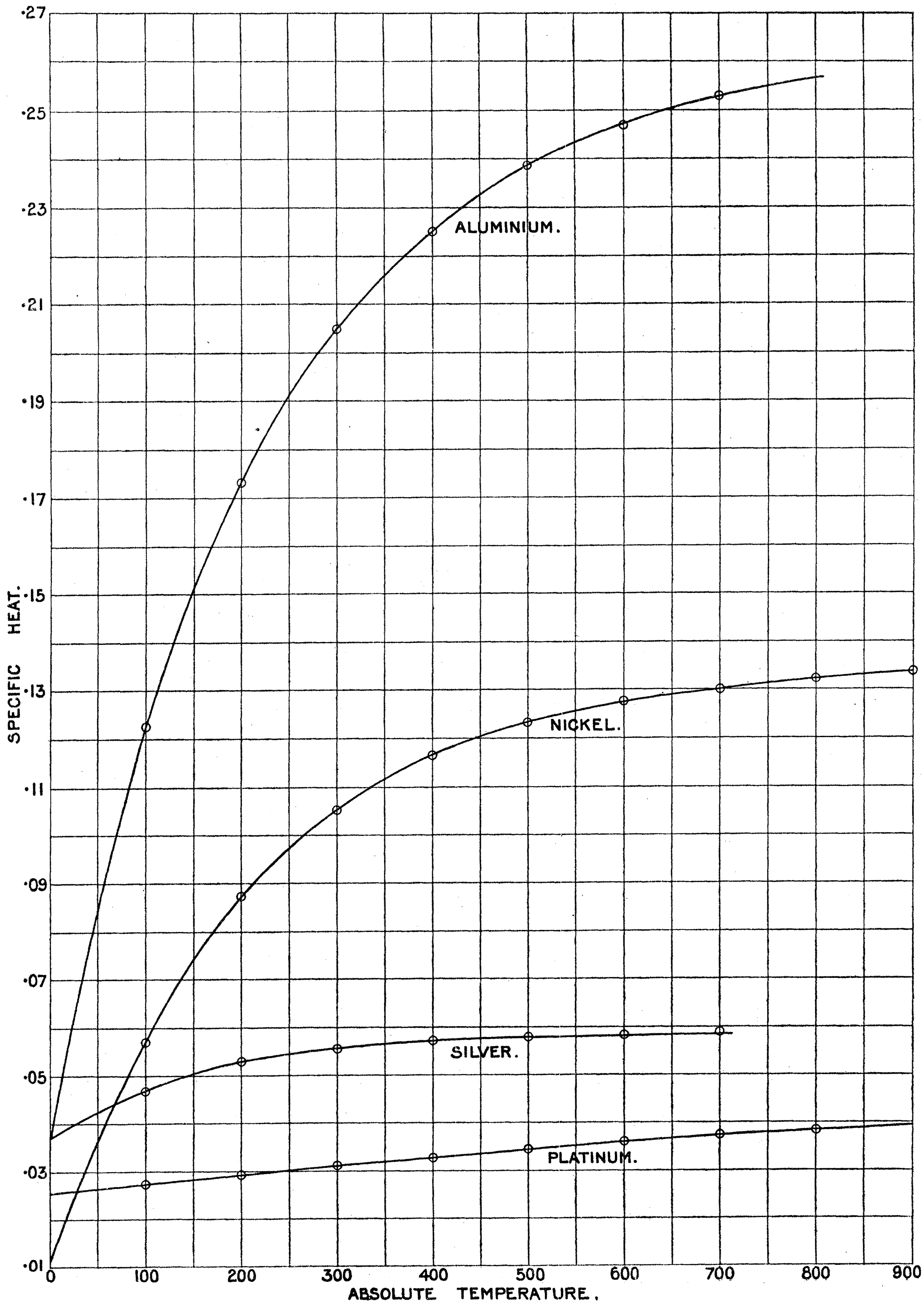

Fig. 2.

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

observed in the specific heats of their sulphides, in which presumably the atoms are separated. On the other hand, if the differences are due to molecular differences or to the properties of the metal in mass, somewhat different values for the specific heats might be obtained. In the result it was found that the mean specific heat of silver sulphide is less than that of nickel sulphide at all temperatures.

Range of temperature.	Mean specific heats.	
	Nickel sulphide.*	Silver sulphide.*
− 180° to + 15°	·0972	·0568
15 ,, 100	·1248	·0737
15 ,, 324	·1333	·0903

When these results are plotted in the same manner and on the same scale as shown for the metals in fig. 1, the two curves for the sulphides are seen to be very similar to those for the metals. See fig. 3.

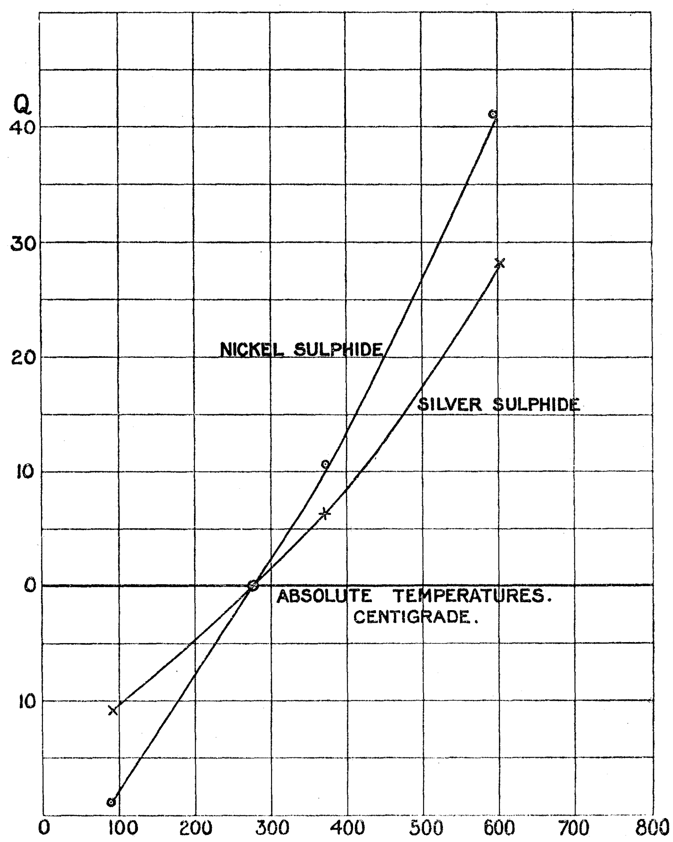

Fig. 3.

* REGNAULT found the mean specific heat of fused NiS to be ·1281 and of fused Ag_2S ·0746 between 0° and 100°.

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

This, however, takes no account of the sulphur in the compounds, and though the molecular heat of each may be calculated and the mean atomic heats of the two metals so obtained, the result is of little value without a knowledge of the rate at which the specific heat of sulphur increases with temperature.

In conclusion, I desire again to acknowledge the skilful assistance of Mr. SIDNEY YOUNG in the experiments. I have also to thank Mr. LEONARD BAIRSTOW, Whit. Sch., for valuable help in the calculations.