

Bakerian Lecture: The Specific Heats of Metals, and the Relation of Specific Heat to Atomic Weight

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VI.—BAKERIAN LECTURE.—*The Specific Heats of Metals, and the Relation of Specific Heat to Atomic Weight.*

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With an Appendix by Professor JOHN PERRY, *F.R.S.*

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THE experiments recorded in the following pages were begun nearly five years ago, at a time when opinion was still much divided as to the atomic weight of cobalt and nickel. It seemed to me that it would be a step in advance if it could be settled which of the two is the greater, for while perhaps the majority of chemists represented the atomic weight of cobalt as greater than that of nickel, some still assigned to them both the same value, while MENDELÉEFF* did not hesitate to invert the order by making Co = 58·5 and Ni = 59. After taking into account all the best evidence on the subject, it appears certain that the atomic weight of cobalt is greater than that of nickel, but the fact remains that the values differ from each other by an amount which is less than the difference between any other two well established atomic weights, the respective numbers being variously represented by different authorities as follows:—

	F. W. CLARKE.	T. W. RICHARDS.†	Committee of German Chemical Society.‡
	H = 1.	H = 1.	O = 16.
Co	58·55	58·55	59·0
Ni	58·24	58·25	58·7

The object of my experiments, however, soon developed into a wider field, for it appeared that the results obtained with these two metals might be made the means of further testing the validity of the law of DULONG and PETIT, inasmuch as temperatures at which the specific heats would be determined are not only very remote, but about equally remote, from the melting points of these two metals.

* 'Principles of Chemistry' (English translation, 1891), vol. 2, p. 333, and table at beginning.

† 'Amer. Chem. J.,' vol. 20, p. 543, 1898.

‡ 'Ber. d. Deutsch. Chem. Gesell.,' vol. 31, p. 2761, 1898.

Both metals are now obtainable in a pure state, and after melting and solidification under the same conditions are presumably in the same state of aggregation. Their atomic weights, though not known exactly, are undoubtedly very near together, as are also the densities of the metals and other of their physical properties.

The specific heats of cobalt and nickel were estimated by REGNAULT, using the method of mixtures, with the following mean results :—*

Nickel, ·1090. Cobalt, ·1067.

The metal in both cases contained carbon, and the cobalt probably contained nickel.

In the choice of the method for estimating the specific heat, my attention was drawn to the excellent results obtained by Professor J. JOLY in the use of his differential steam calorimeter.

It is unnecessary for me to describe the apparatus I have used, for it has been very carefully described by its inventor,† to whom I am greatly indebted for instructing the makers of the instrument in my possession. In using the instrument, all I have done by way of modification is to add a condenser for the escaping steam, and to take great precautions in determining the temperature of the space within the inner cylinder of the calorimeter by jacketing the thermometer and reading with a telescope; also in protecting the substance in the carrier from drip. The weights were all reduced to their equivalent *in vacuo*, due allowance being made for the exchange of the atmosphere of air for one of steam at 100°.

The following formulæ were used in the calculations :—

$$S = \frac{w\lambda}{W(t_2^\circ - t_1^\circ)} \dots \dots \dots (1),$$

where S is the specific heat, W the weight of the metal *in vacuo*, w the number of grams (or cubic centimetres) *in vacuo* of water condensed by the metal, t_1° the temperature of the calorimeter full of air before the admission of steam, t_2° the temperature of the steam in the calorimeter, and λ the latent heat of steam at barometric pressure; and

$$w = w_1 + w\delta - (V_1D - V_2\delta)$$

or

$$w = \frac{w_1 - V_1D + V_2\delta}{1 - \delta} \dots \dots \dots (2),$$

in which w_1 is the apparent weight in steam of water condensed by the substance, V_1 is the volume of the substance at t_1° , V_2 is the volume of the substance at t_2° , D is the density of the air at t_1° and barometric pressure corrected to 0°, δ is the density of the steam at t_2° and barometric pressure. A small correction (·0003 gram) had to be applied to one carrier to make it calorimetrically equal to the other.

* 'Ann. Chim. Phys.' [3], vol. 63, p. 23.

† 'Roy. Soc. Proc.', vol. 47, p. 241.

AND THE RELATION OF SPECIFIC HEAT TO ATOMIC WEIGHT.

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The values for λ were taken from Professor JOLY'S paper, those required being contained in the following abstract :—

Temperature and latent heat of steam.			
t° .		λ .	
99·37	to	99·48	536·9
99·52	„	99·63	536·8
99·67	„	99·78	536·7
99·82	„	99·89	536·6
99·93	„	100·07	536·5
100·11	„	100·22	536·4
100·25	„	100·36	536·3

The value of δ was taken uniformly as ·0006.

The first metal operated upon was a specimen of commercial sheet cobalt obtained from MESSRS. WIGGIN, of Birmingham, for the analysis of which I am indebted to Mr. F. R. PENN, Assoc. R.C.S. It contained

Copper	·62 per cent.
Iron	1·92 „
Nickel	8·30 „
Carbon	·49 „
Cobalt (by difference)	88·67 „
	<hr/>
	100·00 „

The specific gravity of the cobalt was 8·96.

The following data and results were obtained. The boiling temperature, t° , was usually taken from observation of the barometer.

W.	w_1 .	w .	t_1° .	t_2° .	S.
23·3580	·3544	·3530	22·64	100·07	·10480
23·3334	·3678	·3665	19·41	99·65	·10506
23·3105	·3768	·3753	18·00	99·93	·10550
23·3102	·3749	·3735	18·93	100·08	·10593
23·3111	·3688	·3675	19·43	99·82	·10523
23·2824	·3752	·3738	18·51	99·93	·10580
			Arithmetical mean		·10539
	Or omitting the first experimental		„ „		·10550
42·9247	·6828	·6803	19·48	99·96	·10565
42·9245	·6856	·6832	18·92	99·98	·10535
			Arithmetical mean		·10550

These preliminary experiments showed that with a little practice it is possible to get results which are uniform to the third place, and could therefore be trusted as a basis for calculating the atomic weight if the pure metal were used.

Experiments on Pure Cobalt.

Preparation.—Commercially pure cobalt nitrate was dissolved in cold water and fractionally precipitated by the addition of weak solution of bleaching powder, leaving at least a quarter of the cobalt in solution. The oxide was collected, washed with hot water, dissolved in moderately strong hydrochloric acid, and the solution boiled to expel a part of the chlorine. Solution of ammonia was then added in excess, and the solution filtered through paper to remove a small brown precipitate containing iron and probably a little alumina.

The solution on being evaporated gave a deep red crystalline precipitate of purpureo-cobaltic chloride, leaving a pale mother liquor. The precipitate, drained, well washed with hydrochloric acid, and dried, was heated strongly in a platinum dish till fuming ceased. The dark blue crystalline mass of cobalt chloride was then dissolved in water and precipitated hot by excess of pure sodium carbonate. The precipitate was filtered off, washed, and heated to redness in a platinum dish. The resulting oxide was washed with hot water till free from alkali and dried. The oxide was then packed in a glass combustion tube and reduced at a red heat in pure hydrogen. The spongy metal was allowed to cool in hydrogen, and was then compressed into cylindrical blocks by a Spring compressor under a pressure of 64 tons to the square inch.

The rods thus formed were heated in a vacuum, when they gave off a little water and about their own volume of gas, consisting almost wholly of carbon dioxide, apparently absorbed from the air.

On exposing this metal to contact with steam and subsequently drying, it was found to increase appreciably in weight. Moreover, on attempting a calorimetric estimation with the metal, the first considerable increase of weight due to condensation of steam was followed by a small but continuous loss of weight, probably due to the slow expulsion of occluded gas. No accurate determination of specific heat was therefore possible. The metal was therefore supported upon a block of pure lime and melted in an oxyhydrogen flame. On the first attempt it was found that the melted mass on cooling ejected a considerable quantity of gas, giving rise to hollow excrescences upon the surface, the phenomenon closely resembling the expulsion of oxygen from melted silver in the process of solidification. After several experiments, it was found best to employ a considerable excess of oxygen at the end of the fusion, and though some loss of metal was incurred through oxidation of the fused button, much less escape of gas occurred on cooling. The buttons obtained were bright, but often hollow, the sides of the cavity being white and silvery. The metal breaks with a brilliant crystalline fracture.

A portion of the compressed but unmelted metal placed in a porcelain crucible and covered with glass was heated till the latter was melted and the crucible much softened. The metal in this case contracted visibly but was not melted, and it was preserved separately for a further attempt to determine the specific heat with the object of observing the difference, if any, between the melted and the unmelted metal.

Series II.

W.	w_1 .	w .	t_1° .	t_2° .	S.
Pure Cobalt. After fusion.					
21·9273	·3338	·3325	21·26	100·16	·10310
21·9311	·3258	·3245	23·50	99·99	·10378
21·9333	·3368	·3355	20·56	100·15	·10310
21·9314	·3266	·3253	23·14	99·99	·10355
21·9320	·3347	·3335	21·42	100·04	·10373
21·9377	·3310	·3297	22·33	100·13	·10362
Arithmetical mean . . .					·10348
Pure Cobalt. Not fused.					
12·3493	·1848	·1840	22·52	99·96	·10323

The density of the fused cobalt was determined by weighing in benzene, the density of which was specially determined. Two experiments gave 8·7171 and 8·7191 respectively, or a mean of 8·7181 for the density of the metal at $21^\circ/4^\circ$.

This cobalt was afterwards found to leave a minute trace of black substance on dissolution in nitric acid.

A fresh and larger supply of the metal was therefore made as follows: The purpureo-chloride was first prepared and precipitated from aqueous solution by adding strong hydrochloric acid, the precipitate being well drained, re-dissolved in boiling water, and again precipitated by hydrochloric acid. The salt was then heated in a platinum dish till converted into the anhydrous chloride, which was then transformed into sulphate, and finally into ammonio-sulphate by addition of pure ammonium sulphate. The double salt was crystallised from water in small crystals, which were well drained and washed. From a concentrated solution of this salt in water the metal was deposited by electrolysis, using as anode the cobalt of the preceding series of experiments.

After fusion in oxyhydrogen flame the metal gave the following values for the specific heat :—

Series X.

W.	w_1 .	w .	t_1° .	t_2° .	S.
17·1332	·2617	·2607	20·84	99·98	·10315
17·1332	·2582	·2573	21·81	99·98	·10306
17·1319	·2601	·2592	20·98	99·78	·10303
17·1317	·2590	·2581	21·15	99·74	·10289
Arithmetical mean.					·10303
Probable error					\pm ·000013

This result is very slightly lower than the result of the previous series.

Experiments on Pure Nickel.

For the metal used in these determinations I am indebted to the kindness of Dr. L. MOND, F.R.S. It had been deposited twice from the carbonyl compound by heating in a glass tube. It was afterwards found to contain a minute quantity of sulphur. In the form in which it was received it was, doubtless, somewhat porous, and when heated in a vacuum it gave off a small quantity of gas,* and this is probably the chief reason why the results obtained in estimating the specific heat are somewhat less uniform than those obtained with fused cobalt, and, as will be seen later, with fused nickel. The deposited but unfused nickel was not acted upon perceptibly by steam at 100°.

Series III.

Pure Nickel. Deposited from $\text{Ni}(\text{CO})_4$.

W.	w_1	w .	t_1° .	t_2° .	S.
22·1614	·3551	·3538	20·99	99·88	·10859
22·1605	·3592	·3579	19·87	99·96	·10820
22·1600	·3550	·3538	20·54	100·04	·10775
22·1601	·3545	·3533	21·32	100·29	·10829
22·1605	·3502	·3490	21·84	100·46	·10744
22·1618	·3516	·3504	21·58	100·12	·10798
Arithmetical mean.					·10804

* Ackworth and Armstrong found hydrogen in Russell's pure nickel, but not in fused commercial nickel nor in Russell's pure cobalt, though in the latter case it was surmised that hydrogen had been originally present, but the metal examined had undergone oxidation, all but the piece used in their experiments for solution in nitric acid, and which was "extremely dense and compact." ('Journ. Chem. Soc.,' 1877 [2], p. 82.)

The density of the metal was found to be 8·8759 and 8·8776, or a mean of 8·8768 at 21°/4°.

Pure Nickel. The same, fused.

W.	w_1 .	w .	t_1° .	t_2° .	S.
12·6668	·2001	·1994	22·95	100·06	·10953
12·6683	·2003	·1996	22·71	100·22	·10910
12·6671	·1997	·1990	22·78	99·93	·10926
Arithmetical mean					·10930

The density of the fused metal was slightly *less* than that of the unfused, namely, 8·7903 at 22°/4°.

This specimen was afterwards found to contain a small quantity of sulphur. It was therefore dissolved in nitric acid and converted into the double ammonio-sulphate, and this, after recrystallisation, was submitted to electrolysis, using an anode composed of fused Mond nickel. Its specific heat was determined after fusion.

Series XI.

W.	w_1 .	w .	t_1° .	t_2° .	S.
14·5414	·2275	·2267	22·30	100·22	·10732
14·5423	·2324	·2316	21·39	100·17	·10844
14·5421	·2266	·2258	22·88	100·15	·10779
14·5409	·2309	·2301	21·60	100·15	·10806
14·5425	·2294	·2286	22·30	100·15	·10831
14·5411	·2311	·2303	21·35	100·23	·10770

The results not being so concordant as was desired, the metal was cut through, as it was suspected there might be cavities, which would render the drying difficult. No cavities were observable, but in the succeeding experiments the metal was dried over sulphuric acid in an exhausted desiccator before use.

W.	w_1 .	w .	t_1° .	t_2° .	S.
14·0912	·2231	·2223	22·16	100·24	·10838
14·0919	·2238	·2230	21·88	100·10	·10852
14·0926	·2218	·2210	22·43	100·05	·10839
14·0930	·2247	·2239	20·90	99·89	·10791
Arithmetical mean					·10830
Probable error.					± ·00006

Finally, another specimen of nickel deposited from the carbonyl compound in Dr. MOND'S laboratory was submitted to experiment. The whole was melted into a solid button free from cavities.

Series XII.

W.	w_1 .	w .	t_1° .	t_2° .	S.
15·1549	·2318	·2310	24·83	100·08	·10866
15·1535	·2379	·2371	22·52	100·10	·10818
15·1564	·2359	·2351	23·56	100·05	·10878
Arithmetical mean . . .					·10854
Probable error					\pm ·000047

The mean specific heats of pure cobalt and nickel after fusion may now be taken as follows :—

Cobalt ·10303 probable error . . . \pm ·000013

Nickel ·10830 } mean of means . . . ·10845
 ·10854 } with probable error . \pm ·000037

Arithmetical mean . ·10842

REGNAULT found the specific heat of cobalt made from the oxalate ·10696, and of nickel ·10863.

On multiplying these numbers by the atomic weights, the products are for cobalt $\cdot 10303 \times 58\cdot55 = 6\cdot03$, and for nickel $\cdot 10842 \times 58\cdot24 = 6\cdot31$, from which it is obvious that the atomic heats are not identical.

There is no other pair of metals so nearly allied together as cobalt and nickel, but with the object of testing the process further, gold has been compared with platinum and copper with iron, the atomic weights and densities in each case being pretty near together.

Gold and Platinum.—For the gold I am indebted to Professor Sir W. ROBERTS-AUSTEN. It was practically pure, containing, if anything, a minute trace of silver. It was supplied in the form of a rolled plate, and gave the following results :—

Series V.

Rolled Gold. S.G. 19·269 at 20°/20°.

W.	w_1 .	w .	t_1° .	t_2° .	S.
29·9920	·1395	·1386	18·27	100·10	·03029
29·9924	·1360	·1351	19·80	100·28	·03001
29·9924	·1362	·1353	19·80	100·19	·03010
Arithmetical mean . . .					·03013

The metal was then melted in a porcelain crucible by an oxyhydrogen flame applied outside.

Gold after fusion. S.G. 19·227 at 18°/18°.

W.	w_1 .	w .	t_1 .	t_2 .	S.
29·9886	·1432	·1423	17·23	100·60	·03052
29·9891	·1359	·1350	20·55	100·55	·03017
29·9892	·1396	·1387	18·75	100·46	·03035
Arithmetical mean . . .					·03035

There is very little difference between the two series, the value after fusion being a little higher.

REGNAULT'S mean value for the specific heat of pure gold is ·03244 by the method of mixture.

The platinum was prepared from scrap, chiefly foil. After successive treatment with hydrochloric acid, water, nitric acid, and washing, the metal was dissolved in aqua regia, the solution evaporated to dryness, and the residue was heated above 100 degrees for some time. The chloride was redissolved in water, the solution filtered, and excess of pure ammonium chloride added. The precipitate was bright orange yellow. It was washed with water, dried, and heated slowly to redness. The spongy metal was then compressed in a steel mould, and the resulting cylinders boiled in dilute hydrochloric acid, and then fused by an oxyhydrogen flame upon a support of pure lime. The buttons obtained were bright and lustrous, but the under surface which cooled less rapidly was blistered from the escape of gas. And from the specific gravity, which in various experiments was found to be 20·23, 20·33, 20·16, it was obvious that all were more or less permeated by cavities, although when this metal was heated to redness in a Sprengel vacuum it gave off no gas. Turnings obtained from one of these buttons had a specific gravity 21·323 at 18°/18°. After rolling one of them into a strip, it had a specific gravity 21·424 at 22°/22°.

Series VI.

Specific Heat of Platinum after fusion.

W.	w_1 .	w .	t_1 .	t_2 .	S.
29·0862	·1448	·1440	15·45	99·88	·03147
29·0860	·1405	·1398	18·16	100·00	·03150
29·0865	·1444	·1436	15·30	99·58	·03144
Arithmetical mean . . .					·03147

The same Platinum rolled thin.

W.	w_1 .	w .	t_1° .	t_2° .	S.
23·4692	·1158	·1152	17·30	100·12	·03177

REGNAULT'S mean value for the specific heat of platinum by the method of mixture is ·03243.

If we now compare gold with platinum

$$\text{S.H. of Gold} : \text{S.H. of Platinum} :: 1 : \frac{\cdot 03147}{\cdot 03035} = 1\cdot 0369.$$

In this case the atomic weights are known with a greater degree of certainty than those of cobalt and nickel. The value for the atomic weight of gold may be regarded as very accurately determined, while the atomic weight of platinum is still uncertain.

Assuming Au = 195·74 (H = 1), the atomic weight of platinum is $\frac{195\cdot 74}{\cdot 10369} = 188\cdot 8$, from which it is obvious that the law of DULONG and PETIT cannot be applied to such results in an absolute sense, for the atomic weight of platinum is approximately 193·41 (CLARKE).

Copper and Iron.—The copper was prepared by electrolysis from a solution of specially purified copper sulphate. After being washed and dried, the metal was fused in a covered ROSE crucible, supplied with a stream of hydrogen. The buttons on cooling gave off gas sufficient to produce a large cavity in each, but on afterwards heating to redness in a vacuum they yielded practically nothing. The metal was bright within and without.

Series IV.

Specific Heat of Copper.

Pure and after fusion. S.G. 8·522 at 20°/20°.

Specific heat.

·09248

·09241

·09205

·09234

Arithmetical mean . . . 09232

Assuming the value 63·12 preferred by CLARKE for the atomic weight of copper, and the specific heats determined by REGNAULT and by KOPP, we obtain the following product of their combination :—

$$63\cdot 12 \times \cdot 09515 \text{ (REGNAULT).} \quad . \quad = 6\cdot 00$$

$$63\cdot 12 \times \cdot 0925 \text{ (KOPP).} \quad . \quad = 5\cdot 81$$

$$63\cdot 12 \times \cdot 0923 \text{ (W. A. T.)} \quad . \quad = 5\cdot 82$$

REGNAULT'S copper on analysis gave "only traces of foreign matters." KOPP used "commercial copper wires."

The iron used in my first experiment was prepared by dissolving fine iron wire in hydrochloric acid, boiling the solution with nitric acid, and precipitating with excess of ammonia. The completely washed precipitate was dried and heated strongly in a platinum dish, then introduced into a glass tube and heated to redness in a stream of hydrogen made by dissolving aluminium foil in solution of caustic potash, and purified by passing through a moderately strong solution of potassium permanganate. The spongy metal was compressed into short rods in a steel cylinder, and then melted in an oxyhydrogen flame upon a support of lime. The buttons in solidifying gave off a considerable quantity of gas, presumably hydrogen. They were then rolled into moderately thin strips.

A sample analysed by solution in cupric ammonium chloride and combustion indicated 0·01 per cent. of carbon. This must be derived from atmospheric dust, as every precaution had been taken to exclude carbon compounds from the gases used in the preparation.

Iron in this state is apparently unaltered by contact with pure steam at 100°, but a small amount of rusting occurred during the subsequent cooling in the presence of atmospheric air.

The results were not as uniform as could have been desired, the two former experiments yielding results appreciably higher than the two latter. This may possibly be due to the presence of occluded hydrogen, which was gradually oxidised or expelled; at any rate no other explanation presents itself, as the experiments passed off successfully.

Specific Heat of Iron nearly pure and after fusion and rolling.

S.G. 7·75 at 18°/18°.

Specific heat.

·11022

·11037

·10946

·10926

Arithmetical mean . . . ·10983

The nature and amount of impurities present in a metal affect the value of the specific heat seriously. This is well known, and an instance is afforded by the results quoted at the beginning of this paper relating to impure cobalt. REGNAULT showed that the specific heat of a specimen of white cast iron, containing perhaps 6 per cent. of impurities, was ·12728, while that of malleable iron was ·11380. There are no data for estimating the effect of carbon by itself upon the specific heat of a metal,

but it might be expected to reduce the specific heat rather than raise it, as seems to be the case. In view of the uncertainty of the present state of knowledge, I have made some direct experiments upon the influence of impurities, the results of which are given briefly below. From these experiments it appears that the presence of a non-metal affects the result far more than the presence of a second metal, which produces very little effect upon the specific heat till the quantity of it is large enough to be felt through the difference of atomic weight (see Copper-tin). The influence of a *small* amount of carbon is proportionately much greater than the effect of a large amount.

Three samples of electrical iron, for which I am indebted to Messrs. J. SANKEY and SONS, of Bilston, were then examined. Their composition is stated below. The metal was fused in the oxyhydrogen flame, as in all the previous experiments.

Sample A.	B.	C.
Carbon	·025	·030
Phosphorus	·030	·080
Sulphur	·004	·062
Silicon	·046	·040
Manganese	trace	·430

Percentage of non-metallic constituents.	S.H. experimental numbers.	Arithmetical mean.
A. ·060	{ ·11085 ·11101 ·11011 ·11104 ·11144 }	·11089
B. ·105	{ ·11073 ·11010 ·11104 ·11070 ·11112 ·11050 }	·11070
C. ·212	{ ·11134 ·11130 ·11134 }	·11133

There seems to be no doubt that the presence of *non-metallic* impurities tends to raise the specific heat of a metal. Iron, however, is a metal which does not afford the best experimental material.

An attempt to discriminate between two samples of copper wire differing considerably in electrical conductivity failed, inasmuch as they gave practically the same

specific heats. For the samples and measurement of their resistances I am indebted to Professor AYRTON.

I. Specific resistance at $17\cdot7^{\circ} = 2\cdot75$ microhms per cub. centim. Analysed yielded no bismuth. Minute trace of antimony and $\cdot154$ per cent. of arsenic.

Specific heat . . .	$\cdot09266$
„ . . .	$\cdot09267$

II. Good copper. Specific resistance at $17\cdot7^{\circ} = 1\cdot69$ microhm per cub. centim.

Specific heat . . .	$\cdot09274$
„ . . .	$\cdot09272$

Some specimens of copper to which phosphorus was added were then prepared, and the specific heat compared with that of the pure metal employed in their preparation.

Metal.	Specific heat.
Pure copper fused in hydrogen	$\left. \begin{array}{l} \cdot09265 \\ \cdot09234 \end{array} \right\}$
The same containing $\cdot002$ per cent. phosphorus.	$\left. \begin{array}{l} \cdot09368 \\ \cdot09336 \end{array} \right\}$
„ $\cdot44$ „	$\left. \begin{array}{l} \cdot09347 \\ \cdot09320 \end{array} \right\}$
„ $3\cdot49$ „	$\left. \begin{array}{l} \cdot09870 \\ \cdot09910 \end{array} \right\}$

The amount of phosphorus in each specimen was carefully determined after its preparation.

Some further data as to the effect of metallic or metalloidal impurity are provided in the following results :—

	Specific heat.
Copper, pure, fused in air, possibly containing oxide.	$\left. \begin{array}{l} \cdot0936 \\ \cdot0938 \end{array} \right\}$
„ with $\cdot49$ per cent. tin.	$\cdot0936$
„ „ $3\cdot29$ „	$\left. \begin{array}{l} \cdot0927 \\ \cdot0924 \end{array} \right\}$
„ „ „ „	$\cdot0905$
„ „ $6\cdot64$ „	$\left. \begin{array}{l} \cdot0905 \\ \cdot0556 \end{array} \right\}$
Cadmium, pure	$\cdot0556$
„	$\cdot0553$
„ with $\cdot2$ per cent. of silver	$\left. \begin{array}{l} \cdot0561 \\ \cdot0558 \end{array} \right\}$
„ „ „ „	$\cdot0558$
„ „ $\cdot1$ „	$\left. \begin{array}{l} \cdot0554 \\ \cdot0558 \end{array} \right\}$
„ „ „ „	$\cdot0558$

The specific heat of a metal is affected by a variety of other circumstances, of which its mechanical condition is the most important. REGNAULT found the specific heat of hammered copper $\cdot 0935$ and that of annealed copper $\cdot 0952$. According to my results porous unfused metals all gave slightly lower values for the specific heat than the same after fusion.

As explained at the outset, all the determinations described up to this point were made in the steam calorimeter, and the results represent the average specific heats of the metals between the temperature of air, say 15° , and that of steam 100° . On applying the rule of DULONG and PETIT it has been shown that, notwithstanding the high degree of purity of the metals nickel and cobalt, the extreme care taken in determining their specific heats under the same conditions, and the close approximation of the physical properties of these two metals to each other, the numbers representing the atomic heats within the range of temperature of 15° to 100° differ appreciably.

The specific heat represents the relative amount of energy consumed in giving to the molecules of the solid the vibratory motion corresponding to temperature and in separating the molecules from one another, and so causing expansion. I am indebted to Mr. A. E. TUTTON, F.R.S., for determinations of the coefficients of expansion of the two pure metals, and his results have been published in the 'Proceedings of the Royal Society' (vol. 65, pp. 161 and 306). He finds the coefficient of linear expansion at t° for nickel $10^{-8} (1248 + 1\cdot48t)$ for cobalt $10^{-8} (1208 + 1\cdot28t)$, a difference of about 3·2 per cent. at 0° . His determinations also indicate that this difference increases with rise of temperature, and amounts to 4·3 per cent. at 100° . These differences of expansibility correspond very closely with the differences in the specific and atomic heats of the two metals.

I have also to thank Mr. THOMAS TURNER, Assoc. R.S.M., F.I.C., for observations with his sclerometer,* on the relative hardness of the two metals. He reports that the cobalt is harder than the nickel, the relative hardness being on his scale about Co = 17 and Ni = 12 or 13. The cobalt is harder than soft wrought iron, while the nickel is softer than wrought iron. The difference is therefore very distinct.

These differences of expansibility and of specific heat are the result of observations at and above atmospheric temperatures. As the specific heat of solids increases with rise of temperature and diminishes with fall of temperature, it was thought desirable to make some estimations of specific heat at successively lower temperatures in order to find out if the difference between the two metals was maintained. At absolute zero it is probable that they would exhibit the same capacity for heat, and if temperatures low enough could be employed an estimate could be made of the absolute atomic heat of the solid metals.

A series of calorimetric experiments has, therefore, been made at the tempera-

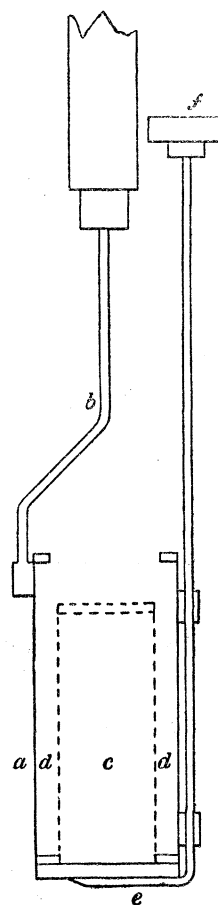
* 'Journ. Chem. Soc.,' 1885, vol. 47, p. 904; and 1887, vol. 51, p. 145.

ture of solid carbon dioxide, which was taken as -78.4° , and again at the temperature of boiling oxygen taken as -182.5° .

For this purpose a thin brass cylindrical vessel holding 400 c.c. of water, provided with an efficient stirrer in the form of a horizontal brass plate, perforated with rather large holes, was used. This calorimeter was supported by silk cords within a bright tin double-walled cylinder, the annular space being filled with water. The top of the tin casing was covered by asbestos card to prevent air currents, but arranged so as to allow the passage of the thermometer and the silk cord carrying the stirrer. The thermometer was divided into large tenths of a degree, and could easily be read to $.01^{\circ}$. The zero had been verified by ourselves, and it had been compared with a standard at Kew at each degree, the correction to the nearest $.01^{\circ}$ being supplied. So far as the observations of temperature in the calorimeter, the determination of the mass of water used and of the water equivalents of the brass, the thermometer, &c., were concerned, the usual procedure was adopted, and no details are necessary.

The problem of how to convey the cooled metal into the water of the calorimeter without appreciable heating in the air required a special contrivance. This is represented in the accompanying figure. The metal for experiment was placed in the interior, *c*, of a double brass tube, *a*, so constructed that the space, *d*, between the inner and outer tubes will hold liquid. The top of the inner tube, shown by the dotted line, is closed, while the top of the outer tube is open. The rod, *b*, by which the tube is held, is extended into a long wooden handle. The metal is retained in its place within *c* by means of a brass plate, *e*, working smoothly upon the mouth of the tube which it closes, and capable of being turned aside by rotating the head, *f*, of the rod which is attached to it at one side. The metal being introduced and supported by *e*, the holder was gradually plunged into liquid oxygen contained in a large cylindrical vacuum vessel till the double brass tube was completely immersed and the space, *d*, filled with liquid. The whole was left in the liquid till ebullition had practically ceased, or was proceeding at the same slow rate as the oxygen in a second vessel kept for comparison alongside. This happened in about 10 minutes after immersion. The metal was then assumed to be at -182.5° very nearly. On lifting out the brass holder the annular space between the two tubes remained full of liquid by which the temperature of the whole was kept down, and bringing the tube over the water in the calorimeter, the dish *f* was turned and the metal fell into the water.

The cold tube when brought into the air is of course attended by a cloud of cold air and mist which flows downward. In order to prevent the entrance of this mist into the calorimeter or its water-jacketed case a



stream of air was blown by means of bellows across the mouth of this vessel at the moment at which the cold tube was brought over it, and the metal dropped.

After reading the thermometer the calorimeter and its contents were weighed. The metal was previously weighed separately. All the weighings were reduced to a vacuum.

The following results were obtained :—

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at $-182\cdot5^{\circ}$.		Specific heat.
Cobalt, 39·15 grammes.				
1	415·74	13·33	11·79	·0842
2	414·29	12·75	11·27	·0808
3	414·09	13·81	12·30	·0820
4	413·84	13·88	12·37	·0819
Arithmetical mean . . .				·0822
Nickel, 40·42 grammes.				
1	416·02	13·34	11·74	·0848
2	414·21	12·84	11·24	·0846
3	413·96	13·95	12·39	·0819
Arithmetical mean . . .				·0838

Experiments at the temperature of solid carbon dioxide were carried out in a similar manner. The holder containing the metal was thrust into a cavity scooped out of a large mass (originally 50 pounds) of compact solid carbon dioxide, and the space between the inner and outer tubes was packed with the same. The apparatus remained in contact and surrounded by the solid for half-an-hour. The uniformity of the results which follow seems to prove that the metal had acquired the temperature of the cold mass.

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at $-78^{\circ}\cdot4$.		Specific heat.
Cobalt, 39·15 grammes.				
1	427·10	17·23	16·41	·0943
2	427·15	17·03	16·21	·0945
3	426·77	17·86	17·03	·0929
Arithmetical mean . . .				·0939

Expt. No.	Water + equivalent of calorimeter, &c.	Temperatures before, after immersion of metal at -78.4° .		Specific heat.
Nickel, 40.42 grammes.				
1	424.75	16.13	15.25	.0987
2	424.40	16.49	15.62	.0971
3	424.05	16.99	16.12	.0966
Arithmetical mean . .				.0975

The mean specific heats of the two metals within three successive ranges of temperature now stand as follows :—

Temperature.	Cobalt.	Nickel.
From 100° to 15°	.10303	.10842
„ 15° „ -78.4°	.0939	.0975*
„ 15° „ -182.5°	.0822	.0838
and by calculation from the last two results		
From -78.4 to -182.5°	.0712	.0719

Mere inspection shows that the change in value proceeds regularly in both cases, but that the value for nickel declines more rapidly than for cobalt, and the consequence is that the specific heats of the two metals steadily approach each other. If the numbers given above for the specific heats are multiplied by the atomic weights, the products are very nearly identical.

Thus $.0822 \times 58.55 = 4.81$ atomic heat of cobalt, and $.0838 \times 58.24 = 4.88$ the atomic heat of nickel.

Or $.0712 \times 58.55 = 4.169$ and $.0719 \times 58.24 = 4.187$.

* Other recorded attempts to determine specific heats at low temperatures are as follows :—

Metal.	Temperature.	Sp. heat.	Temperature.	Sp. heat.	Authority.
Lead . . .	100° to 10°	.03140	10° to -77.75°	.03065	Regnault.
Platinum . .	100° „ 20°	.03295	20° „ -78°	.03037	Schuz.
Tin	100° „ 20°	.05564	20° „ -78°	.05416	„

The falling off is in each case less than in my experiments, but the probability is that in these old experiments the metals were not really at the low temperature assumed when introduced into the calorimeter. (See note, p. 250.)

Hence the absolute "atomic heat" of the two metals, cobalt and nickel, is almost exactly 4.

It appears probable, therefore, that if the experiments could be carried further the specific heats would stand in exactly the inverse ratio of the atomic weights.

It remains to be seen whether the value of the atomic heat for other metals agrees with this.* If such turns out to be the case the original expression of the law of DULONG and PETIT, which is only roughly applicable at atmospheric and higher temperatures, would be completely justified.

In conclusion I desire to record my appreciation of the skilful assistance I have received throughout these experiments from Mr. SIDNEY YOUNG.

APPENDIX BY PROFESSOR JOHN PERRY, F.R.S.

Dr. TILDEN has asked me to write the following short appendix to his paper. In making the tedious calculations I was assisted by two of our students, Mr. E. R. VERITY and Mr. H. L. MANN.

The law connecting the p , v , and t of unit mass of any substance in the solid condition is not sufficiently well known for the general application of the laws of thermodynamics.

If we take it that there is an atomic or molecular specific heat k_0 of an elementary substance which is constant in all states of the substance, and which is represented

* *Note added March 3.*—Experiments made since this paper was written, upon the metals silver, copper, iron, and aluminium show that further investigation is necessary. The mean specific heat of silver, for example, was found to be $\cdot 0558$ between 100° and 15° , and $\cdot 0519$ between 15° and $-182\cdot 5$. The decrease of specific heat at the lower temperature is, therefore, much less than in the case of cobalt and nickel.

A paper by U. BEHN in the 'Annalen der Physik' (No. 2 for 1900, p. 257), issued on Feb. 16, did not come into my hands till some time after the date of my communication to the Royal Society. My attention was drawn by this paper to the fact that in 1898 the Author had commenced a series of determinations of the specific heats of metals at low temperatures, and that about the same time some experiments on the specific heats of three metals,—copper, iron, and aluminium,—at the temperature of liquid air, had been published by C. C. TROWBRIDGE in the American periodical 'Science' (N.S. 8, p. 6, 1898).

The results of the latter cannot claim to be very important, as no information is given concerning the composition of the metals, and there is great uncertainty about the temperature of the liquid in which they were cooled. The numerical values given by TROWBRIDGE are considerably higher than those of BEHN, as also in the one case, aluminium, in which a comparison can be made with my results; the mean specific heat between the temperature of air and that of boiling oxygen being $\cdot 1833$ according to TROWBRIDGE, and $\cdot 1676$ according to my experiments.

BEHN'S results are highly interesting, though for various reasons they must be inaccurate in some cases and are probably to a slight extent inaccurate in all; inasmuch as no special means were taken to avoid access of heat in transferring the mass from the cold bath to the calorimeter, and as liquid air was used instead of liquid oxygen, the temperature of the cooling liquid was somewhat uncertain.

by its specific heat at constant volume when in the state of a perfect gas. If α is its atomic weight, then

$$\alpha k_0 = 2.414$$

for all elements, because it is of this amount for hydrogen.

Thus if $\alpha = 58.55$ for cobalt, and 58.24 for nickel, $k_0 = .04123$ for cobalt, and $.04145$ for nickel.

It is, perhaps, not unreasonable to assume that in no state can the substance have a smaller specific heat than this atomic specific heat.

If the specific heat of a substance at constant volume is k , and at constant pressure K , it is interesting to note that K and k are very nearly equal for solid metals, and, indeed, that the heat required to raise a gramme of solid metal 1° in temperature is not very different under all ordinary conditions as to pressure and volume. The ratio of K to k is known to be the ratio of the elasticity at constant entropy to the elasticity at constant temperature, or what we sometimes call the *quick* and the *slow* elasticity. The slow may be measured with a piezometer, or calculated from YOUNG'S modulus and the modulus of rigidity, the quick may be obtained from sound vibration experiments.

Thermodynamics of a Solid.

If we say that α is the real coefficient of expansion under constant pressure, we mean that

$$(dv/dt) = \alpha v.$$

When we say that ϵ is the volumetric elasticity at constant temperature, we mean that

$$(dv/dp) = -v/\epsilon.$$

In all probability α and ϵ are functions of the temperature, and practically of nothing else.

The thermodynamic coefficients become, all energy being measured in ergs,

$$\begin{aligned} K - k &= \alpha^2 \cdot \epsilon \cdot v \cdot t, \\ l &= \alpha \epsilon t, \\ L &= -\alpha v t, \end{aligned}$$

where K is specific heat at constant pressure, and k is specific heat at constant volume, and the significations of l and L are given by the following expressions for the heat, dH given to unit mass of the stuff when its t , p , and v become $t + dt$, $p + dp$, and $v + dv$.

$$dH = k \cdot dt + l \cdot dv = K \cdot dt + L \cdot dp.$$

Mr. TUTTON has measured what are ordinarily known as the coefficients of expan-

sion of pure nickel and cobalt with temperature. We have taken his observed numbers, and found what may roughly be taken to be the *true* coefficient of cobalt. As he had only two changes of temperature, we are compelled to assume that α is a linear function of the temperature, and we find

$$\alpha = (2.598 + .003775t)10^{-5}$$

We can therefore say that the heat (in gramme-centigrade degrees) given to 1 gramme of cobalt during an increase of temperature dt , and an increase of pressure dp , is, taking JOULE'S equivalent as 4.2×10^7 ergs,

$$dH = K . dt - (6.186 - 0.008988t)t . v . 10^{-13} . dp.$$

If instead of change of state being expressed in terms of dt and dp , it is expressed in terms of dt and dv , we can only use this result if we can calculate dp . This needs a knowledge of ϵ , which we do not possess for either cobalt or nickel, even at one temperature. It is, however, worth while making the following rough approximation.

In pounds per square inch ϵ is, for iron, 2.1×10^7 (KELVIN'S article on Elasticity); for copper, 1.7×10^7 (BUCHANAN); and 2.4×10^7 (KELVIN'S Elasticity).

We cannot do better in making a first approximation than to take ϵ for solid cobalt as 2×10^7 lbs. per square inch, or in C.G.S. units

$$\epsilon = 1.38 \times 10^{12} \text{ degrees per sq. centim.}$$

under all conditions.

We shall not be far wrong in assuming that, within Dr. TILDEN'S range of temperature, the above value may be taken for α .

Mean temperature of each range.	α .	v .	t .	K/k .
57.5° C.	38.45×10^6	.1149	330.5	1.018
- 31.7° C.	35.1×10^6	.1145	241.3	1.012
- 83.7° C.	34.4×10^6	.1143	189.3	1.010

We have taken v at 21° C. as $1 \div 8.7181$, or 0.1148 cub. centim.

In each case, therefore, it is easy to find $K-k$, or $\alpha^2 . \epsilon . vt$, which must be divided by JOULE'S equivalent 4.2×10^7 , to convert the specific heats from ergs to heat units. The last column shows that the two specific heats are nearly equal.

It is interesting to note, not merely in cobalt and nickel but in any metal, that if we take K to be either the specific heat at constant volume or pressure, the ratio of K to k_0 is very large at ordinary temperatures. Thus taking values from the tables prepared by Professor GRAY for the Smithsonian Institute :—

Substance.	^a . Atomic weight.	k_0 .	K.	K/k_0 .
Cu at 17° C. . .	63·6	·0378	·0924	2·444
„ 100° C. . .			·0942	2·492
„ 200° C. . .			·0963	2·548
„ 300° C. . .			·0985	2·605
Pb at 15° C. . .	206·9	·01167	·0299	2·563
„ 100° C. . .			·0311	2·665
„ 200° C. . .			·0324	2·841
Ag at 23° C. . .	107·9	·02247	·0550	2·447
„ 100° C. . .			·0566	2·520
„ 200° C. . .			·0588	2·617
„ 300° C. . .			·0609	2·710

These values are given for cobalt and nickel in a table below.

Our ignorance of the molecular state of a solid is so great that we cannot even speculate on how it is that when 1 gramme of cobalt at 50° C. rises in temperature to 51° C., whether it is allowed to expand freely or is subjected to great hydrostatic pressure which prevents expansion, the energy ·041 enters it as what may be called the real sensible heat, and the energy ·062 (or one and a half times as much) enters it as some kind of energy of disgregation necessary because of change of temperature and having nothing to do with change of volume or pressure. The facts are not explainable by assuming that the atomic weights are wrong, because as we see from cobalt and nickel, K approaches the value k_0 at low temperatures.

A table of temperatures may be made out at which for all metals the product of atomic weight and specific heat has any constant value. Thus we take it that at -273°C . this product is the same as it is for hydrogen or any elementary gas. At the following temperatures the product is 2·6 times what it is for hydrogen, and the product of K and atomic weight is in every case 6·28.

	Lead.	Copper.	Silver.	Nickel.	Cobalt.
Temperature . .	50° C.	290° C.	180° C.	52° C.	167° C.

We have no doubt if we had information to prepare exact tables of this kind (dealing with k/k_0 rather than K/k_0) we should find these temperatures related to other physical properties.

Dr. TILDEN's measurements of the mean specific heat of cobalt and nickel in the following ranges of temperature are :—

Range of temperature.	Cobalt.	Nickel.
100° C. to 15° C. . . .	·1030	·1084
15° C. to -78·4° C. . . .	·0939	·0975
15° C. to -182·5° C. . . .	·0822	·0838

We know so little of the molecular constitution of solids that any empirical formula which we may use for the calculation of the actual values of K , the specific heat, must be regarded as having no application higher than 100° C. and lower than -182·5° C. ; nor indeed can it have much correctness near these limits.

We have used $K = a + bt + ct^2$, and found the best values of a , b , and c for calculating K from the given mean values ; but we find that according to this law K both for cobalt and nickel reaches a maximum at 167° C. and rapidly diminishes for higher temperatures, and this is certainly wrong.

As it is possible that K is always greater at higher temperatures we were tempted to use

$$K = a + \frac{bt}{1 + ct}$$

But a came out negative. Now as a is the value of the specific heat at -273° C. or $t = 0$ we cannot imagine it ever negative. Indeed it is probably never less than k_0 the atomic specific heat. We therefore tried

$$K = k_0 + bt + ct^2 + et^3,$$

but the values of the constants are such that this causes K to reach a maximum at 270° C., and rapidly diminish afterwards.

To satisfy all our notions we know of better formulæ to use, but the labour of calculating the constants of these more promising formulæ coming after our other failures seemed too great.

We have, however, found a formula, easy to use, which fits Dr. TILDEN'S results with some accuracy, which gives $K = k_0$ when $t = 0$, and which causes K to continually increase with temperature. It is of the form

$$K = k_0 + \frac{bt^3}{1 + ct^3}$$

	Cobalt.	Nickel.
k_0	·0412	·0415
b	$1·764 \times 10^{-8}$	$1·764 \times 10^{-8}$
c	$2·55 \times 10^{-7}$	$2·35 \times 10^{-7}$

In all probability these formulæ give fairly correct values of K from -180° C. to 100° C. In spite of the danger of extrapolation, we give in the following table some values beyond this range, to show that the formula expresses the sort of change known to occur in metals generally at high temperatures. Close to the zero there must be greater doubt as to its suitability:—

θ° C.	t .	Cobalt.		Nickel.	
		K .	K/k_0 .	K .	K/k_0 .
1327	1600	·1103	2·677	—	—
727	1000	·1101	2·673	·1162	2·801
527	800	·1098	2·666	·1159	2·794
327	600	·1092	2·651	·1151	2·774
127	400	·1063	2·580	·1119	2·696
77	350	·1046	2·539	·1098	2·646
27	300	·1016	2·465	·1038	2·501
— 23	250	·0965	2·342	·1005	2·422
— 73	200	·0876	2·126	·0905	2·181
— 123	150	·0732	1·776	·0747	1·800
— 173	100	·0552	1·340	·0558	1·345
— 223	50	·0433	1·051	·0436	1·051
— 253	20	·0413	1·002	·0416	1·002
— 273	0	·0412	1·000	·0415	1·000

[April 27, 1900.—The following formula reproduces Dr. TILDEN'S results with greater accuracy. It is probably of a nature to suit all metals which exhibit no recalescence effects.

$$K = k_0 \left(1 + \frac{bt^n}{c + t^n} \right)$$

when the values of the constants for nickel and cobalt are

	Cobalt.	Nickel.
k_0	·0412	·0415
b	1·695	1·892
c	$1·002 \times 10^6$	$0·932 \times 10^6$
n	2·73	2·68