

“On the Determination of Specific Heats, especially at Low Temperatures.” By H. E. SCHMITZ, M.A., B.Sc. Communicated by ARTHUR SCHUSTER, F.R.S. Received February 2,—Read February 19—Received in revised form June 3, 1903.

The specific heats at low temperatures of various metals have recently been determined by Professor Tilden,\* by U. Behn,† and by C. C. Trowbridge.‡ In the following table are given the values obtained by Tilden and by Trowbridge, and some of the numbers obtained by Behn; the numbers given represent the mean specific heats between the temperature of liquid air or of liquid oxygen and the atmospheric temperature.

	Tilden	Behn	Trowbridge
Aluminium .....	0·1676	0·173	0·1833
Iron .....	—	0·0853	0·0914
Nickel .....	0·0838	0·0857	—
Cobalt .....	0·0822	—	—
Copper .....	—	0·0796	0·0868
Silver .....	0·0519	0·0519	—

The differences in the method of cooling the metal probably furnish a partial explanation of the discrepancies here shown. Tilden used a portable metallic air chamber cooled by means of liquid oxygen, and assumed the initial temperature to be  $-182^{\circ}5$ . Behn used a fixed glass air chamber cooled by means of liquid air; the initial temperature was assumed to be that of the liquid air, which was measured by means of a thermo-electric couple. Trowbridge immersed the object directly in liquid air which had been boiling for some time, and assumed the initial temperature to be  $-181^{\circ}5$ .

The author of the present paper has made a series of determinations of the specific heats of several metals (i) between the temperature of liquid air and the atmospheric temperature (ii) for the ordinary temperature range,  $100^{\circ}$  to  $20^{\circ}$ . In the former case he has used two distinct methods, one being the method of mixtures. In the latter case he has used only the method of mixtures. The experiments were conducted mainly in the physical laboratory of the Owens College,

\* ‘Phil. Trans.’ A, 1900, vol. 194, pp. 246—250.

† ‘Wied. Ann.’ 1898, vol. 66, p. 237; also 1900, vol. 1, p. 257.

‡ ‘Science,’ 1898, vol. 8, p. 6, quoted in ‘Science Abstracts,’ 1898, No. 1325.

and the writer has pleasure in expressing his obligations to Professor Schuster for advice during the progress of the work.

*Platinum Thermometer.*

The temperature of the liquid air was obtained by means of a Callendar's platinum thermometer with exposed coil, made in accordance with instructions kindly given to the author by Mr. J. E. Petavel. It was found that, when the instrument was placed in a narrow test-tube containing the last remains of a quantity of liquid air made some time before, its resistance went up to a maximum at which it remained practically constant until nearly all the liquid air had evaporated. The steady maximum obtained on several occasions in this way was taken as the resistance at  $-182^{\circ}\cdot5$ , which (disregarding the variation with pressure) is very nearly the temperature of liquid oxygen. This value, together with the resistances at  $0^{\circ}$  and  $100^{\circ}$ , enabled Callendar's formula to be used. The lowest observed temperature of the liquid air obtained in this way was  $-191^{\circ}\cdot0$ .

*Calorimeter for Method of Mixtures.*

The inner vessel was of very thin brass or copper. Different quantities of water were used, as shown in the following list:—

Calorimeter	Apparent weight of water	Total water-equivalent
	Grammes	Grammes
A.....	70·0	73·8
B.....	200 0	203·7
C.....	400·0	405·1
D.....	550·0	562·2
E.....	700·0	712·8

In each case the vessel was nearly full of water, and the thermometer was immersed to a constant depth. The water equivalent of the thermometer bulb (from the mass of water displaced) was 0·9 gramme; the water equivalent of the whole immersed portion was estimated at 1·5 grammes.

*Mercury Thermometer.*

This was one of Goetze's Beckmann thermometers. It was carefully compared with a secondary standard of which the calibration corrections were known; in the final comparison the readings were taken at every tenth of a degree in a very slowly rising temperature. As a

result of the comparison it appeared that the relation between the Beckmann scale and the corrected scale of the secondary might be taken as linear throughout. In obtaining the value of a degree on the Beckmann in terms of a degree on the secondary standard, it was found necessary to exercise considerable care, as the observed values for the ice-point of the secondary varied between  $0^{\circ}\cdot61$  and  $-0^{\circ}\cdot04$  according to its previous state. The temperature  $t$  of the secondary was accordingly calculated from the reading  $T_t$  in accordance with the equation  $t = 100 (T_t - T_0 t) / (T_{100} - T_0^{100})$ .\* One degree on the Beckmann (kept, as regards the amount of mercury in the bulb, in a constant state during all except the earliest experiments) was found to be equal to  $1^{\circ}\cdot009$  on the secondary standard.

The value of the Beckmann degree was however more satisfactorily ascertained by comparison with a Baudin thermometer, No. 12772, the corrections for which are very accurately known from the work of Schuster and Gannon.† The comparison was made at two points, distant each about half a degree from one of the extremities of the Beckmann scale. A considerable number of readings were taken in the neighbourhood of each of the two points; all were rejected except those which indicated in the case of each thermometer a very slowly rising temperature. The corrections of the Baudin for calibration and unequal division, though small, were relevant. The only other correction requiring consideration was that for stem temperature. Since in the specific heat determinations no correction for the exposed part of the Beckmann (scale-length  $5^{\circ}$ ) is applied, the uncorrected Beckmann should be compared with the corrected Baudin. The Baudin was exposed from division 12, and the temperatures of comparison were approximately  $15^{\circ}$  and  $19\frac{1}{2}^{\circ}$ . On the range of  $4\frac{1}{2}^{\circ}$ , the correction for exposed stem might possibly approach 1 part in 1000, but would probably be much less than this. Disregarding the stem correction, the following values were obtained for the Beckmann degree in terms of the Baudin degree,  $1\cdot0101$ ,  $1\cdot0117$ ,  $1\cdot0110$ ,  $1\cdot0086$ ,  $1\cdot0093$ ,  $1\cdot0103$ ,  $1\cdot0113$ ,  $1\cdot0109$ ,  $1\cdot0111$ ,  $1\cdot0110$ , mean  $1\cdot0105$ . Making an allowance for the stem correction, this has been called  $1\cdot011$ . To reduce an interval  $t_B$  on the Baudin (used vertically) to the corresponding interval  $t$  on the French hard-glass scale, the following relation has been given by Schuster and Gannon,  $t = t_B (1 - \cdot00135)$ . The Beckmann degree is therefore equivalent to  $1\cdot010^{\circ}$  on the French hard-glass scale of the mercury thermometer. The results which follow are expressed in the first instance in terms of the French hard-glass scale. An interval on this scale lying between  $14^{\circ}$  and  $20^{\circ}$  is reduced to the scale of the

\* 'Phil. Trans.,' A, 1895, p. 428.

† 'Phil. Trans.,' A, 1895, p. 432, *et seq.*, also 'Owens College Book of Standards.'

hydrogen thermometer by subtracting  $0.003^{\circ}$  per degree ; this reduction is made use of in Table IV.

The absolute value of the Beckmann reading was given with sufficient accuracy by the comparison with the secondary standard. The correction was approximately  $+14^{\circ}.55$  at the lower extremity of the Beckmann scale and  $+14^{\circ}.60$  at the upper extremity.

### *Specific Heat of Water.*

The specific heat of water at  $17^{\circ}.5$  has been taken as unity, as recommended by Griffiths. In all except a few of the earlier of the experiments on copper, it was not necessary to apply a correction for variation of the specific heat of water ; where necessary, the correction was made by means of the values given by Griffiths, "Thermal Measurement of Energy," Table VII.

### *Method of Cooling the Metal.*

Experiments were made with a view to finding a satisfactory method of cooling the metal in an air chamber, surrounded or partly surrounded by liquid air, but these were not successful. The method of direct immersion in the liquid air was therefore adopted. This method has the disadvantage that a certain quantity of liquid air adheres to the body after its extraction from the bath ; this, if carried into the calorimeter, causes an error of more or less importance. Again, it is possible that the temperature of the body may *fall* slightly after its withdrawal from the bath, owing to the rapid evaporation of liquid air from its surface ; a marked effect of this kind was observed in the case of the platinum thermometer, but in this case the mass was small and the surface large ; in the experiments described below this effect is probably negligible.

### *Copper.*

A number of preliminary experiments on pieces of copper of various shapes led the author to the conclusion that the error, caused by the adhesion of liquid air, would be comparatively small if the piece of metal were massive in comparison with its surface. The amount of liquid air entering the calorimeter may moreover be materially lessened by shaking the piece of metal during its transference from the bath of liquid air to the calorimeter. Thus a cylinder of copper, suspended in the bath with its axis vertical, gave, in two experiments in which it was rapidly and steadily transferred to the calorimeter, 0.0815 and 0.0811 for the apparent specific heat. On the other hand, when it was shaken during a transference lasting about 5 seconds, it gave in two experiments 0.0801 and 0.0799. It will presently appear

that the difference between these numbers and the previous numbers is not, or is not in the main, due to variation in the time of transference. The effect of a variation in the time of transference is shown in Table I. This table gives the results of fourteen experiments on a copper cylinder, the time of transference being varied from experiment to experiment. The cylinder here used was not the same as that to which the previous numbers refer; it was however cut from the same casting of pure copper. It was made with a conical upper end, so that it might be the less able to carry liquid air on its upper surface; its edges also were rounded off. It was always slightly shaken during the transference.

On graphical examination of the numbers in Table I, it appeared that if the relation between time and apparent specific heat in Experiments 8 to 14 be assumed linear, then the apparent specific heat in Experiments 1 to 7 is on the average slightly greater than that given

Table I.

Number of experiment	Time of transference in seconds	Apparent specific heat
1	1	0·08025
2	2	0·0798
3	3	0·0806
4	4	0·0794
5	5	0·0799
6	7½	0·0797
7	10	0·0797
8	15	0·0795
9	20	0·0784
10	30	0·0783
11	40	0·0774
12	60	0·0762
13	80	0·0742
14	120	0·0724

Table II.

Number of experiment	$x$	10,000 $y$	10,000 $\Delta$
1	1	800·7	+ 1·8
2	2	800·0	- 2·0
3	3	799·3	+ 6·7
4	4	798·7	- 4·7
5	5	798·0	+ 1·0
6	7½	796·3	+ 0·7
7	10	794·6	+ 2·4

Table II.—*continued.*

8	15	791·3	+ 3·7
9	20	787·9	- 3·9
10	30	781·2	+ 1·8
11	40	774·5	- 0·5
12	60	761·1	+ 0·9
13	80	747·7	- 5·7
14	120	720·9	+ 3·1

by the line representing the results of Experiments 8 to 14. This would be explained by supposing that in Experiments 1 to 7, or in some of them, some of the liquid air had not been got rid of by shaking and entered the calorimeter. From later work it appeared that anomalous results, such as those of Experiments 3 and 4, were probably due more to a chance variation in the amount of liquid air carried over than to other errors of experiment.

In Table II the numbers of Table I are reduced according to the following plan:—Experiments 8 to 14 are represented by the equation  $y = c - mx$ , where  $y$  is the apparent specific heat for time of transference  $x$ . The method of least squares gives  $c = 0·080135$ ,  $m = 0·0000671$ . Table II gives the values of  $y$  for Experiments 1 to 7 as well as for Experiments 8 to 14, and in the last column the differences between these numbers and the numbers in Table I.

The mean of Experiments 1 to 5 (Table I) is 0·0800, which differs but little from the value of  $c$  above, and is adopted by the author as representing the specific heat of copper, the principle being that the small amount of liquid air, not got rid of by shaking during a short transference, approximately compensates for the heating effect of the atmosphere during the transference. Results for other metals were obtained on the same principle. As a standard shape for the specimens, a short cylinder with approximately hemispherical ends was adopted where possible. The number in brackets after each result for the specific heat of a given metal indicates the time of transference in seconds. This time was generally 3 or 5 seconds; it was in general found that any difference between a result for 3 seconds and a result with the same piece of metal for 5 seconds was covered by the experimental errors. Five seconds was found to be a more convenient time than three, allowing for a more deliberate treatment and greater uniformity of shaking.

The mercury thermometer was read to 0°·001, the temperature observations being made in accordance with the following scheme:—

Reading of platinum thermometer.

Period of 2½ minutes, with readings of mercury thermometer at end of every half-minute.

Interval of  $2\frac{1}{2}$  minutes, reading of platinum thermometer during the interval.

Period of  $2\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

Immersion of object in calorimeter (half a minute after the last reading).

Period of  $7\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

Interval of  $2\frac{1}{2}$  minutes.

Period of  $2\frac{1}{2}$  minutes, with readings of mercury thermometer at end of every half-minute.

The first ten readings of the mercury thermometer gave the initial rate of change of temperature and also the temperature at the moment of immersion; the last ten gave the final rate of change. The final temperature was obtained as the mean of the later of the corrected intermediate readings. It was found that equilibrium of temperature was attained in about 3 minutes in the case of the copper cylinder of Tables I and II. The weight of this cylinder was approximately  $161\frac{1}{2}$  grammes; calorimeter D was used, and the fall of temperature was approximately  $4^{\circ}6$ .

The initial readings were always made with a falling temperature, but this circumstance did not seem to introduce any important uncertainty. During the final readings the temperature was sometimes rising, sometimes falling.

The copper used was obtained from Johnson, Matthey and Co., and described as pure.

### *Thallium.*

The original object of the investigation was to determine the specific heat of this metal, but as the amount used was small, the experimental error is here probably larger than in the case of the other metals. The first specimen examined weighed about 30 grammes. After forming the material into a single mass, approximately cubical, it gave in two experiments 0.0299 (4) and 0.0298 (4) for the specific heat. A second specimen, of nearly double the weight of the first and similarly molten and compressed into a compact mass, gave 0.0298 (4) and 0.0301 (3). The two specimens together gave 0.0302 (4), 0.0300 (3), 0.0301 (3), mean 0.0301. Calorimeter B was used, and the fall of temperature in the last three experiments was approximately  $2^{\circ}5$ .

The first specimen was from Dr. Schuster, the second was bought as pure. An analysis of the second specimen by Mr. Joseph Race gave thallium 99 per cent., oxygen (probably due to surface oxidation of the fragments analysed) 1 per cent., traces of iron and zinc.

*Lead.*

A specimen supplied by Johnson, Matthey and Co., of a purity of about 99·9 per cent., gave 0·02942 (3), 0·02933 (4), 0·02936 (5), 0·02924 (7), mean of the first three 0·0294. Mass of lead approximately 250 grammes, calorimeter C, fall of temperature approximately 3°·6.

Table III gives the results of ten experiments on commercial sheet lead. The object of these experiments was to test the comparability of the results when the mass and also the proportion of surface to mass was varied. The shapes of the specimens are given in Table VI. All the calorimeters made use of in the investigation were included in this series of experiments, with the secondary object of testing the comparability of results obtained with different calorimeters.

Table III.

Calorimeter	Mass of lead	Approximate fall of temperature	Specific heat
	Grammes.		
A .....	35·06	2·8	0·0294 (5)
B .....	64·51	1·9	0·0293 (5)
B .....	129·3	3·8	0·0292 (5)
B .....	140·9	4·1	0·0292 (5)
C .....	"	2·1	0·0292 (5)
C .....	246·3	3·6	0·0292 (5)
C .....	285·8	4·2	0·0294 (5)
D .....	246·3	2·6	0·0293 (5)
D .....	285·8	3·0	0·0293 (5)
E .....	"	2·4	0·0293 (5)

Five further experiments with the piece of lead of mass 285·8 grammes, using calorimeter C, gave 0·0295 (3), 0·0296 (3), 0·02945 (3), 0·0295 (4), 0·02945 (5). Mean result for sheet lead 0·02935. An analysis by Mr. Race showed lead 99·5 per cent., tin 0·13 per cent., traces of iron, copper and antimony.

*Aluminium.*

A specimen supplied by Johnson, Matthey and Co., was analysed by Mr. Race and found to contain 98 per cent. of aluminium, 1 per cent. of zinc, 0·7 per cent. of iron, small quantities of silica, etc. It gave in the first instance in two experiments 0·1725 (4), 0·1733 (5). For these experiments the piece of metal had been only roughly trimmed in the lathe. As a comparatively large quantity of liquid air was evidently, in these two experiments, carried into the calorimeter, the piece of metal was reshaped with a very smooth surface. It now gave 0·1731 (3), 0·1721 (4), 0·1721 (5), mean 0·1724. Mass of aluminium approximately



72 grammes, calorimeter E, fall of temperature approximately  $3^{\circ}5$ . In the second set of experiments the amount of liquid air entering the calorimeter was distinctly less than in the first; the inference, therefore, that may be drawn from the approximate identity of the results in the two sets of experiments is that in neither case was the amount of liquid air calorimetrically of much consequence.

A commercial casting gave, after a rough trimming in the lathe  $0.153$  (3),  $0.154$  (3), and, after a final shaping and smoothing,  $0.153$  (3),  $0.1525$  (3). Mass (in the second pair of experiments) approximately 88 grammes. An analysis by Mr. Race showed aluminium 88 per cent., zinc 7 per cent., copper 4 per cent., the balance lead, iron, silica, etc., with a trace of nickel. The specific heat found is much lower than would be indicated by this analysis and Regnault's law of mixtures.

#### *Iron.*

A ball of cast-iron, mass approximately  $110\frac{1}{2}$  grammes, gave in two experiments  $0.0897$  (3),  $0.0889$  (5). These experiments were made merely for comparison with the results given by the ice method described later.

#### *Nickel.*

A specimen supplied by Johnson, Matthey and Co., was found by Mr. Race to contain nickel and cobalt 98.5 per cent. (cobalt approximately 0.9 per cent.), iron 0.6 per cent., copper 0.7 per cent., some silica. It gave  $0.0848$  (5),  $0.0842$  (5),  $0.0840$  (5), mean  $0.0843$ . Mass approximately 192 grammes, calorimeter E, fall of temperature approximately  $4^{\circ}5$ .

#### *Cobalt.*

A specimen supplied by Johnson, Matthey and Co., was found by Mr. Race to contain cobalt and nickel 97.5 per cent. (nickel 0.5 per cent. approximately), iron 1.9 per cent., small quantities of copper, lead, carbon and a trace of zinc. It gave  $0.0843$  (5),  $0.0846$  (5),  $0.0841$  (5), mean  $0.0843$ . Mass approximately 165 grammes, calorimeter E, fall of temperature approximately  $3^{\circ}9$ .

#### *Zinc.*

A specimen of Dr. Mond's metal, supplied by Johnson, Matthey, and Co., gave  $0.0838$  (3),  $0.0839$  (4),  $0.0840$  (5), mean  $0.0839$ . Mass approximately 169 grammes, calorimeter E, fall of temperature approximately  $4^{\circ}0$ .

A second specimen, nominally pure, gave  $0.0849$  (5),  $0.0854$  (5). Mass approximately 71 grammes. In this specimen Mr. Race found 99.7 per cent. zinc, no trace of any other metal.

A commercial casting gave 0.0835 (3), 0.0835 (5). Mass approximately  $106\frac{1}{2}$  grammes. Mr. Race found 99.5 per cent. zinc, a small quantity of tin, traces of arsenic, copper, lead, aluminium.

#### *Silver.*

A specimen of bar silver, supplied by Elkington and Co., was found by Mr. Francis Jones to contain silver 98.06 per cent., gold 0.17 per cent., the balance being at least partly copper. It gave 0.05133 (5), 0.05147 (5), 0.05129 (5), mean say 0.0514. Mass approximately 176 grammes, calorimeter C, fall of temperature approximately  $4^{\circ}5$ .

#### *Tin.*

A specimen supplied by Johnson, Matthey and Co., practically pure, gave 0.04993 (3), 0.04973 (4), 0.04963 (5), mean say 0.0498. Mass approximately 173 grammes, calorimeter E, fall of temperature approximately  $2^{\circ}4$ . An additional experiment, calorimeter C, gave 0.04997 (5).

A commercial specimen gave 0.0502 (3), 0.0503 (3), 0.05001 (5), 0.04997 (5). Mass approximately 130 grammes. In this case the casting contained numerous small air-holes, and was only roughly trimmed in the lathe. A considerable amount of liquid air was carried into the calorimeter, and this probably makes the results a little too high. Mr. Race found tin 99.3 per cent., lead 0.45 per cent., traces of iron and zinc.

#### *Summary.*

In Table IV are collected the results already given. For comparison Behn's numbers are added in the last column.

Table IV.

Metal	Specific heat		
	Mercury scale	Hydrogen scale	Behn
Copper, pure .....	0.0800	0.0798	0.0796
Thallium, approx. pure .....	0.0301	0.0300	—
Lead, pure .....	0.0294	0.0293	0.0296
Lead, commercial .....	0.02935	0.0293	—
Aluminium, approx. pure .....	0.1724	0.1719	0.173
Aluminium, commercial .....	0.153	0.152	—
Cast iron .....	0.0893	0.0890	—
Nickel, approx. pure .....	0.0843	0.0840	0.0857
Cobalt, approx. pure .....	0.0843	0.0840	—
Zinc, pure .....	0.0839	0.0836	0.0842
Zinc, approx. pure .....	0.085	0.085	—
Zinc, commercial .....	0.0835	0.083	—
Silver, approx. pure .....	0.0514	0.0512	0.0519
Tin, pure .....	0.0498	0.0497	0.0501
Tin, commercial .....	0.050?	0.050?	—

*Ice Method.\**

When an object cooled by means of liquid air is plunged in water, a firm coating of ice is rapidly formed. If the water is not stirred, the ice remains unmelted for a considerable time. This suggested the weighing of the ice as a possibly practical method of determining the specific heat of the material. After a number of preliminary experiments, it was found that the method was capable of yielding very consistent results. Thus five experiments were made with a ball of commercial zinc weighing  $106\frac{1}{2}$  grammes, giving the following numbers:—

Initial temperature	Mass of ice	Specific heat
	Grammes	
—185°·8	20·74	0·0838
—182°·6	20·39	0·0838
—190°·0	21·26	0·0840
—186°·4	20·85	0·0840
—184°·6	20·56	0·0836

The calorimeter contained water kept at very nearly 0° C. by means of an ice jacket, and the time of immersion in the calorimeter in each of the above experiments was five minutes. The initial temperature was deduced from the reading of a platinum thermometer observed  $\frac{1}{4}$  or  $\frac{1}{2}$  minute before extracting the object from the bath of liquid air. After removal from the calorimeter, the object was transferred to a vessel in which the ice was dried by contact with filter-paper cooled by means of melting ice, and was finally transferred to another vessel in which the ice was weighed. The number assumed for the latent heat of water is 80·0, this appearing to the author the best value he could take for the purpose of reducing his results to the unit used in the preceding part of the investigation.

The method appeared to offer advantages in its comparative simplicity and in its avoidance of thermometrical difficulties, and the author felt encouraged to attempt an extended examination of the method, with a view to the estimation of the relative importance of the sources of error. He here selects the more important considerations.

(i) An object which carries a quantity of liquid air on its upper surface, for instance, a cylinder with axis vertical, may by the method

\* [Note added 27th May, 1903.—The author has learned that the method of weighing an ice-jacket is not new. It was briefly described by Joly in 'Nature,' 1895, vol. 52, p. 80, and was subsequently independently invented and used by Dewar. See also a paper by Bedford and Green, 'B. A. Report,' 1901, p. 544, in which is described a calorimeter resembling in some of its features that used by the author.

of mixtures give appreciably too high a result if the liquid air is allowed to enter the calorimeter. But in this method the corresponding error will probably be of trifling amount, as the bulk of the liquid air rises to the surface of the water immediately on immersion of the object in the calorimeter; it sometimes forms independent ice capsules floating on the water. There is no necessity from this point of view to attach much importance to the time of transference from the bath of liquid air to the ice calorimeter.

(ii) A minute quantity of liquid air is always vaporised in contact with the object, or in its immediate proximity, and is imprisoned within the ice coating. This causes the chief difficulty in the method as practised by the author. The difficulty arises, not from any calorimetrical effect, but from the fact that the vaporised air slowly and gradually escapes in small bubbles through one or more holes near the top of the ice coating, its place being taken by water drawn in some way into the interior of the ice coating and therefore necessarily weighed with the ice.

(iii) For the reason mentioned in the last paragraph, the shape as well as the size of the immersed object is of importance. The object should be large and should have a small surface. Its base should be well rounded, otherwise a bubble of air of considerable size may form at the base in the earliest stages of the formation of the ice coating; this may produce a large error in the manner above described.

(iv) On account again of the gradual suction of water into the ice coating, the result depends on the time of immersion in the calorimeter.

The statements of the three preceding paragraphs are illustrated by Tables V and VI. In Table V each of the numbers given is the mean of three, four, five or six. In Table VI the results of the

Table V.—Variable Immersion.

	Flat-ended copper cylinder, 101·15 grammes	Copper sphere, 62·49 grammes	Copper cylinder with rounded base, 161·57 grammes
	Apparent sp. h.	Apparent sp. h.	Apparent sp. h.
Immersion of 3 to 6 mins.	0·0798	0·0800	0·0790
Immersion of 10 mins. ...	0·0818	0·0816	0·0800
Immersion of 15 mins. ...	0·0816	0·0815	0·0801
Immersion of 30 mins. ...	0·0837*	0·0829	0·0817

\* This number is not quite comparable with the others in the table. In the experiments of which it gives the mean result, the calorimeter was in a more efficient state than in the other long-period determinations.

Table VI.—Constant Immersion of Five Minutes.

Mass of Lead	Shape, &c.	Approximate mass of ice (apparent)	Apparent specific heat	
			Exp. 1	Exp. 2
Grammes		Grammes		
35·06	Cube, fine wire ring for suspension	2·6	0·0316	0·0322
36·29	Sphere ditto	2·6	0·0309	0·0304
37·36	Sphere, flange for suspension ..	2·7	0·03145	0·0305
64·51	Flat-ended short cylinder, axis vertical, wire .....	4·8	0·0319	0·0317
129·3	Cylinder as before, but of twice the length .....	9	0·0309	0·0306
140·9	Sphere, flange .....	10	0·0304	0·0303
246·3	Short cylinder, with rounded ends, flange .....	17	0·0303	0·0304
285·8	Plummet, with tapering rounded base, wire .....	20	0·0303	0·0303

individual experiments are given. The material in the case of Table V is pure copper; the three objects described were cut from the same casting. In the case of Table VI the material is commercial sheet lead; all the objects described were made from the same sample.

The numbers in Table V might at first sight be supposed to indicate that the process of formation of the ice coating is a very slow one, and is not complete in less than half-an-hour. The author was led to reject this hypothesis after weighing the object with its ice coating during immersion. It will be sufficient to describe a single experiment on the copper sphere of  $62\frac{1}{2}$  grammes. The first observation was made two minutes after plunging the sphere in the calorimeter. The apparent weight rapidly decreased at first, indicating additional formation of ice. After a very short time the apparent weight began to increase, and continued to increase during the remainder of the hour during which the experiment was continued. The observed increase in apparent weight divided itself into two parts: (1) There was a very slow and nearly uniform increase due to the gradual melting of the coating of ice; (2) there was an occasional relatively large increase due to the escape of a bubble of air.\* From this and similar experiments the author concluded that the formation of ice might, in the case of the objects used by him, be considered as being practically complete in 5 minutes or less. The rate of melting in the experiment quoted was 3 per cent. of the total mass per hour; the calorimeter, however, was of a less efficient form than that finally adopted.

\* The presence of the enclosed air made it useless to attempt to deduce the weight of ice from the apparent weight in water.

The last six results in Table VI are in good agreement with one another, but are in excess of the result given by the method of mixtures. The author has no doubt that the difference is due to the water imprisoned in the ice coating.

Table VII exhibits the results of a final series of experiments by the ice method. These experiments were conducted so far as possible in a uniform manner, differing slightly from that previously employed. The time of transference was about 5 seconds, and during the transference the piece of metal was well shaken. The time in the calorimeter was approximately 5 minutes, the time in the drying apparatus  $\frac{1}{2}$  minute. In the case of nickel the ice-coated cylinder was too large for the drying apparatus, and was dried by hand.

Table VII.

Metal	Mass of Metal	Approximate mass of ice	Apparent specific heat		Specific heat by mixture (from Table IV)*
			Exp. 1.	Exp. 2.	
	Grammes	Grammes			
Copper, pure .....	161.6	30	0.07945	0.0792	0.0800
Lead, pure .....	250.4	18	0.0299	0.0301	0.0294
Aluminium, approx. p.	72.4	29	0.1724	0.1746	0.1724
Nickel, approx., pure	192.3	37	0.0826	0.0820	0.0843
Cobalt, approx., pure	165.0	32	0.0840	0.0833	0.0843
Zinc, pure .....	169.3	34	0.0849	0.0850	0.0839
Silver, approx., pure	176.2	22	0.0519	0.0520	0.0514
Tin, pure .....	172.9	21	0.0507	0.0510	0.0498

*Specific Heats for the Range 20° to 100°.*

In view of the uncertainty prevailing as to the effect on specific heat, not only of impurities, but also of physical state in respect of hardness and density, the author regarded it as of importance to determine the specific heats at ordinary temperatures of the actual specimens used in the low temperature determinations. He used the method of mixtures, the procedure being, so far as the different circumstances permitted, the same as in the low temperature determinations by the method of mixtures. It was necessary in this case to make the time of transference as short as possible. After numerous preliminary trials, the arrangement finally adopted was a fixed steam-heater

\* In comparing the two methods, it should not be forgotten that the ranges of temperature are not the same. The specific heat given by the ice method is for the range  $-185^{\circ}$  to  $0^{\circ}$ , while that given by the method of mixtures is for the range  $-185^{\circ}$  to  $+15^{\circ}$ .

standing a few inches above a fixed calorimeter, the latter protected from the direct radiation of the former (except during the short time occupied in transferring the hot body to the calorimeter) by a screen of metal and wood forming the base of the heater. The hot body could be very rapidly lowered into the calorimeter, probably without appreciable cooling. A chief cause of uncertainty appeared to lie in the temperature of the hot body; this was read on a thermometer with its bulb very near the body, but there was no doubt that the thermometer acquired the temperature of the surrounding hot air much more rapidly than did the comparatively massive piece of metal. To eliminate this source of error, the heating process was generally continued for 3 or 4 hours, and in certain cases for 6 hours.

The thermometer used in the steam-heater was graduated in tenths of a degree from  $95^{\circ}$  to  $105^{\circ}$ , the length of a degree on the scale being approximately 24 mm. It had been examined at Kew, but the corrections actually applied were obtained by the frequent use of the hypsometer, which showed during the determinations a progressive rise in the steam-point amounting altogether to  $\frac{1}{4}^{\circ}$ .

In the calorimeter a Beckmann thermometer was used. It was convenient in many of the experiments to use a different instrument from that used in the low temperature determinations. This second instrument was carefully standardised in the same manner as the first, but unfortunately proved to have a bore far from uniform. The results obtained with it are those for copper (all), thallium (both), aluminium approx. pure (first result), aluminium commercial (both), nickel (both), zinc approx. pure (both).

The quantity of water used was 200, 300 or 400 grammes, and the rise of temperature  $1^{\circ}\cdot1$  (thallium) to  $5^{\circ}\cdot6$  (nickel).

Table VIII gives the results of all the experiments made with the exception of the following: (1) preliminary tests of the method, made with copper, thallium, lead commercial, zinc commercial; (2) one experiment with lead pure, result 0.0301, rejected on the ground of probably insufficient time of heating; (3) one experiment with tin commercial, result 0.0551, rejected on the ground of an unduly long transference.

#### *Dulong and Petit's Law.*

In Table IX the specific heats of Tables IV and VIII are compared. The metals are here arranged in order of atomic weight. The atomic heats, calculated from the international atomic weights (oxygen 16) for 1903, are added. So far as the metals examined are concerned, the table shows that the proportional alteration of specific heat is relatively large for metals of low atomic weight. Hence the approximate constancy of atomic heat for the higher temperature range is not preserved for the lower temperature range. In fact for the lower

temperature range, the metals examined show a progressive rise of atomic heat with atomic weight.

Table VIII.

Metal	Specific heat (hydrogen scale)		
	Exp. 1	Exp. 2	Mean
Copper, pure .....	0·0941	0·0941	} 0·0936
Ditto .....	0·0940	0·0929	
Ditto .....	0·0936	0·0936	
Ditto .....	0·0933	0·0932	
Thallium, approx. pure....	0·0325	0·0327	0·0326
Lead, pure .....	0·03044	0·03048	0·03046
Lead, commercial .....	0·03069	0·03058	0·0306
Aluminium, approx. pure	0·2182	0·2183	0·21825
Aluminium, commercial..	0·1917	0·1914	0·19155
Cast iron.....	0·1190	0·1188	0·1189
Nickel, approx. pure.....	0·1093	0·1095	0·1094
Cobalt, approx. pure.....	0·1080	0·1079	0·10795
Zinc, pure.....	0·0934	0·0928	0·0931
Zinc, approx. pure.....	0·0947	0·0938	0·09425
Zinc, commercial.....	0·0911	0·0913	0·0912
Silver, approx. pure .....	0·05595	0·05594	0·0559
Tin, pure .....	0·05524	0·05522	0·0552
Tin, commercial.....	0·05495	0·05514	0·0550

Table IX.

Metal	Specific heat for mean temperature :		Ratio of specific heats	Atomic heat for mean temperature :	
	-85°	+60°		-85°	+60°
Aluminium, approx. pure..	0·172	0·218	0·79	4·66	5·91
Aluminium, commercial...	0·152	0·192	0·79	—	—
Cast iron.....	0·0890	0·119	0·75	—	—
Nickel, approx. pure.....	0·0840	0·1094	0·77	4·93	6·42
Cobalt, approx. pure.....	0·0840	0·108	0·78	4·96	6·37
Copper, pure .....	0·0798	0·0936	0·85	5·08	5·95
Zinc, pure.....	0·0836	0·0931	0·90	5·47	6·09
Zinc, approx. pure.....	0·085	0·094	0·90	—	—
Zinc, commercial.....	0·083	0·091	0·91	—	—
Silver, approx. pure .....	0·0512	0·0559	0·92	5·53	6·03
Tin, pure .....	0·0497	0·0552	0·90	5·91	6·57
Tin, commercial.....	0·050?	0·0550	0·91?	—	—
Thallium, approx. pure....	0·0300	0·0326	0·92	6·12	6·65
Lead, pure .....	0·0293	0·0305	0·96	6·06	6·31
Lead, commercial .....	0·0293	0·0306	0·96	—	—



*Note on the Specific Heat of Aluminium, added May 27, 1903.*—A specimen of aluminium from the British Aluminium Company of an approximate purity of at least  $99\frac{1}{2}$  per cent., gave in three experiments. 0.2194, 0.2185, 0.2194, mean 0.2191, as the specific heat between  $20^{\circ}$  and  $100^{\circ}$ .

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“The Elasmometer, a New Interferential Form of Elasticity Apparatus.” By A. E. H. TUTTON, F.R.S. Received May 12,—Read May 14, 1903.

(Abstract.)

Being desirous of extending the investigation of the physical characters of the crystals of isomorphous salts to the subject of their elasticity, the question arose as to the best form of apparatus to employ for the determination of the coefficient of elasticity. The most accurate form hitherto devised is that of Koch\*. The amount of flexure of a thin plate of the crystal was determined by the interference method, sodium light being employed. The great convenience and high accuracy of the optical part of the interference dilatometer which the author has described to the Royal Society†, suggested the advantage of utilising it as interferometer for the measurement of the amount of the flexure of the plate, and many other possible improvements on the apparatus of Koch also suggested themselves. Eventually the instrument now described was devised. It has been constructed by Messrs. Troughton and Simms.

The observing telescope, with its auto-collimator and attached hydrogen Geissler tube, is exactly as used for the dilatometer, and its pedestal is mounted on a detachable plinth in front of the elasmometer. The rigid iron base on which the latter is mounted also accommodates, on its back portion, the pedestal of the vertical tube which carries the train of prisms to select the monochromatic C—or F—hydrogen light employed, and direct it on the interference apparatus. The interference chamber of the dilatometer is detached from the lower end of this tube, as the elasmometer carries its own interference tripod.

The elasmometer proper consists of the following seven essential parts:—

(1.) A pair of platinum-iridium wedges, arranged parallel to each other and with the knife-edges downwards, up against which the plate of the substance (not necessarily a crystal) is to be bent by a weight applied under its centre. They are carried by a pair of gunmetal

\* ‘Ann. der Phys.,’ N.F., 1878, vol. 5, p. 251.

† ‘Phil. Trans.,’ A, vol. 191, p. 313.