

The Capacity for Heat of Metals at Different Temperatures, being an Account of Experiments Performed in the Research Laboratory of the University College of South Wales and Monmouthshire

E. H. Griffiths and Ezer Griffiths

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IV. *The Capacity for Heat of Metals at Different Temperatures, being an Account of Experiments performed in the Research Laboratory of the University College of South Wales and Monmouthshire.*

By E. H. GRIFFITHS, *Sc.D., F.R.S.*, and EZER GRIFFITHS, *B.Sc., Fellow of the University of Wales.*

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SECTION I.

Introductory.

A STUDY of the published determinations of the capacity for heat of the elements leads to the conclusion that further information of an accurate nature is desirable. It will be found that, in most cases, the values are deduced by observations of the heat absorbed or given out when the changes of temperature are large, and the conclusions

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derived therefrom are based on the assumption that the relation between the specific heat and the temperature is of a linear order.

Again, some, in fact a large majority, are comparative determinations and dependent on the capacity for heat of other bodies, as, for example, those which assume REGNAULT'S values for the capacity for heat of water at ordinary temperatures—values which we now know to be inaccurate.

The experimental difficulties connected with the method of mixtures are considerable and that method has probably been pushed to its extreme limits of accuracy. The agreement between the results obtained by different observers, and also between those resulting from repetition by the same observer, is rarely satisfactory. The temperature changes have, as a rule, been measured by means of mercury thermometers, without a proper appreciation of the difficulties attendant upon the use of those instruments for accurate work.

A further possible source of uncertainty is the effect of the sudden chilling of a metal when rapidly cooled from a high temperature.

The experimental conditions have not been varied sufficiently to demonstrate the absence of unsuspected causes of error and, according to the chemists, sufficient care has not been devoted to the detection and elimination of the impurities present in the samples used.

It is true that there are determinations of a high order of accuracy which may not justly be subject to this criticism, but such examples are few and it is difficult, when comparing the evidence, to assign to each determination its due weight.

As an illustration of the divergences which exist, we append the values given by leading authorities in the case of copper, a metal which does not appear to present any peculiar difficulties and one in which the values obtained by different observers are, on the whole, in better agreement than is the case with other metals.

All the observers agree with the conclusion that the capacity for heat of copper is a function of the temperature, but they differ markedly as to the value of the function. For example TOMLINSON ('Roy. Soc. Proc.,' 1885) gives

$$S_t = 0\cdot09008 + 0\cdot0000648t.$$

LORENZ gives values at 0° C., 50° C. and 75° C., from which the following expression is obtained :—

$$S_t = 0\cdot0898 + 0\cdot0000204t + 0\cdot000000317t^2,$$

an expression which denotes that the specific heat increases more rapidly than the temperature.

GAEDE ('Phys. Zeitschr.,' 4, 1902) gives values at various temperatures between 17° C. and 92° C., from which the following expression can be deduced :—

$$S_t = 0\cdot090135 + 0\cdot000058t - 0\cdot00000017t^2.$$

This would give a maximum capacity for heat at a temperature of 341° C.

If we consider the endeavours to ascertain the mean capacity over the range 0° C. to 100° C., the same lack of agreement is evident. For copper we have—

Temperature range. ° C.	Specific heat.	Observer.
15–100	0·09331	BEDE.
0–100	0·09332	TOMLINSON.
At 50	0·09169	LORENZ.
17–100	0·09333	NACCARI.
23–100	0·0940	TROWBRIDGE.
15 100	0·09232	TILDEN.
At 50	0·09261	GAEDE.

The methods described in this paper, although they doubtless present their own peculiar difficulties, are, we believe, free from many, if not all, of the sources of error above referred to. The method is briefly indicated in the following numbered paragraphs:—

1. The energy was supplied electrically and the conclusions are not dependent upon any assumption concerning the capacity for heat of other bodies than those under consideration.

2. The substances were raised across a given temperature through very small ranges of temperature (extreme limit of range, about $1^{\circ}4$ C.).

3. These temperature changes were measured by means of differential platinum thermometers, for which purpose these instruments are admirably adapted.

4. Large masses of the substances were used, ranging from 1 to 4 kgr.

5. The apparatus was constructed with all its parts duplicated. The metals examined were suspended by quartz tubes in similar air-tight brass cases which were placed side by side in a large tank containing rapidly stirred water or oil. This tank was electrically controlled with great constancy at any given temperature, θ_0 .

One of the metal blocks remained at the tank temperature throughout an experiment while the other, having been previously cooled below θ_0 , was raised to a somewhat similar temperature above it by a supply of heat electrically developed in the centre of the block, the difference in temperature between the two blocks being determined at regular intervals by means of the differential platinum thermometers.

All changes in the surrounding conditions would therefore affect both blocks equally; hence, by measuring the difference of temperature only, many possible causes of error were eliminated.

6. The equation connecting the various quantities is

$$M \cdot S \cdot (\theta_2 - \theta_1) = \frac{E^2 \cdot t}{J \cdot R} \pm Q,$$

where M = total mass, S its specific heat; θ_1 the initial temperature, and θ_2 the final temperature; E , the potential difference at the extremities of the resistance

coil R ; $*J = 4.184 \times 10^7$; and Q , the number of thermal units lost or gained during time t from sources other than the electrical supply.

In these experiments the values of θ_1 and θ_2 were so arranged that Q was in every case small or negligible, and, if necessary, could be estimated with sufficient accuracy.

7. With two exceptions, the samples of metals used were supplied by Messrs. Johnson and Matthey, to whom we wish to express our sincere thanks for the trouble they have taken in the matter. Their certificate concerning the degree of purity is in each case appended. Information regarding the remaining metals (Cu and Fe) will be found in the sections dealing with those two elements.

8. Experiments on identical samples at the same temperature were repeated under very varied conditions, in order to enable us to detect unsuspected sources of experimental error. Two separate methods of experiment, involving different data and methods of reduction, were employed. Three different sets of differential platinum thermometers were used. The rate of heat supply was varied in the ratio of 9:1. The determination of S at a given temperature with a particular sample was in several cases repeated after the lapse of some months; the quartz tubes and cover were replaced by others of different masses &c. We were thus enabled to ascertain causes of error which would otherwise have remained undetected (see p. 139).

9. The results of our observations have been deduced from the actual experimental numbers and in no case from "smoothed curves."

The most serious difficulty presented by this method of experiment is that of determining the mean temperature of the block of metal when its temperature is altering. Temperature gradients must necessarily exist, since equalisation of temperature by stirring is an impossibility. The manner in which this difficulty was surmounted is described in later sections.

When embarking on this investigation we proposed to extend our range of temperature to the lowest point obtainable by means of liquid air, limiting the inquiry to the study of two or three metals only. Owing, however, to delay by the contractors in the delivery of the liquid-air plant, we were compelled to postpone that portion of our investigation dealing with temperatures below 0°C. to a later date, and therefore enlarged the scope of our inquiry so as to include the following metals, namely, Aluminium, Iron, Copper, Zinc, Silver, Cadmium, Tin and Lead.

As the data already accumulated concerning the capacity for heat of these metals over the range 0°C. to 100°C. may be useful to other observers, we see no reason for delaying the publication of the work already completed.

SECTION II.

Outline of Apparatus and of the Method of Experiment.

A diagrammatic sketch of the apparatus within the tank is indicated in fig. 1.

* For a full discussion of the reasons for selecting this value of J , see p. 110 of the 'Thermal Measurement of Energy,' by E. H. GRIFFITHS (Camb. Univ. Press).

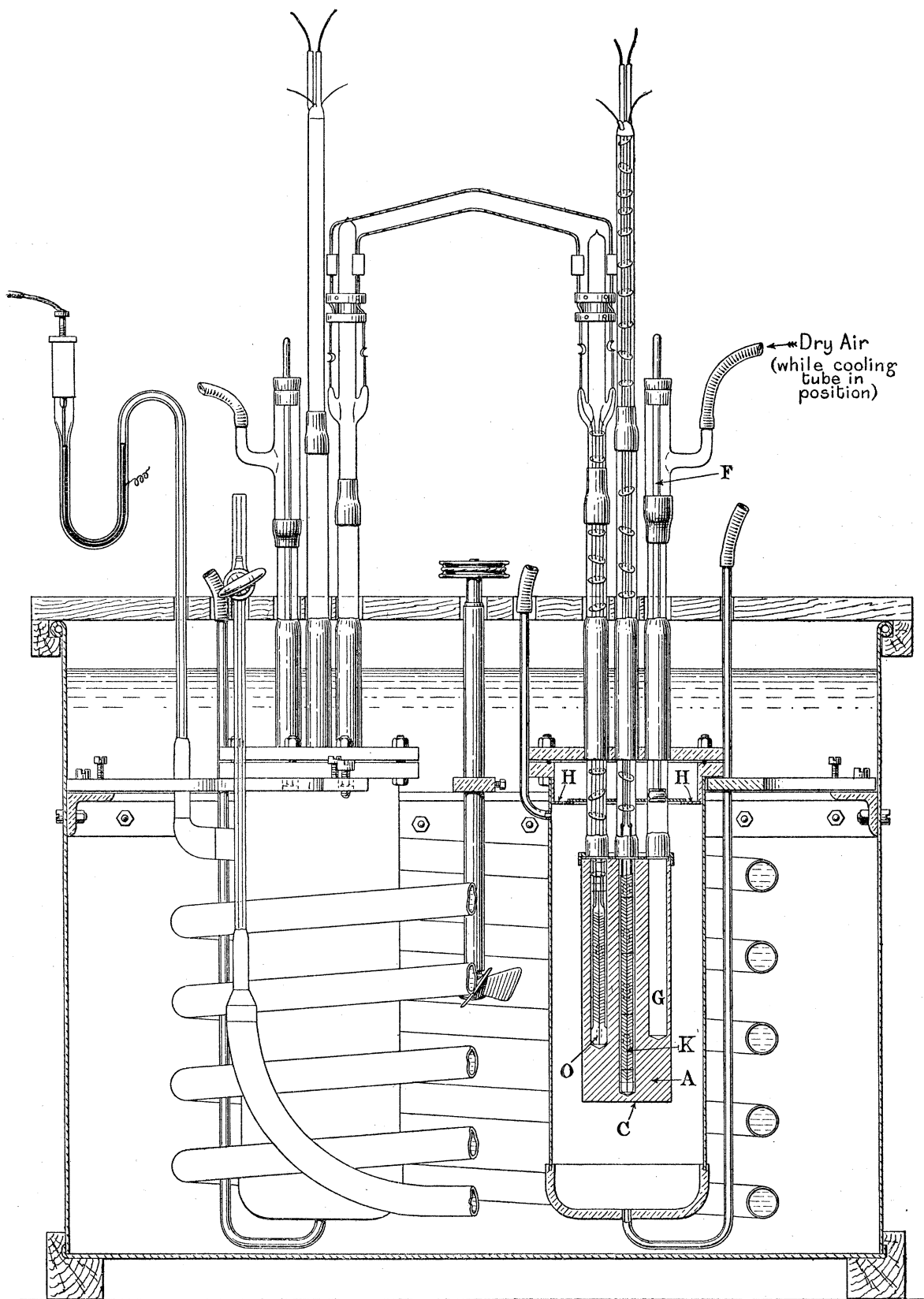


Fig. 1.

R 2

As the left-hand portion is a replica of the right, it will suffice to describe the latter only.

The metal (A), whose capacity for heat was to be determined, was cast and then "turned" into the form of a cylinder 15.2 cm. long and 5.7 cm. in diameter.

This cylinder fitted accurately into a thin copper case (C) of mass, apart from the lid, of 149 grms. Thus the actual radiating surface surrounding the metal blocks was similar throughout all experiments.

Two small copper pins attached A in its proper position to the copper lid to which the case was fastened by a copper ring bearing a screw thread.

Three quartz tubes passed through the brass pipes fixed in the lid of the external case, and supported the copper case and block within the outer brass cylinder.

These quartz tubes having been previously platinized were soldered at their lower ends into short copper ferrules which formed parts of the copper lid and at their upper extremities to the top of the brass tubes which, for 7 cm. of their length, were washed by the tank liquid.

Between the case-lid and the outer brass lid a mica disc of nearly the diameter of the brass cylinder was placed and through it passed the three quartz tubes.

After the metal block had been fixed in its case and pins and ring firmly screwed home, the case and contents were lowered into the outer brass vessel, the edges of the mica disc (which were slightly padded with cotton wool) resting on a projecting circular ring (H) about 3.5 cm. above the top of the copper lid. Thus the effect of the flow of convection currents from inner to outer case, or *vice-versâ*, was diminished. The brass lid was firmly screwed down over a lead ring by eight bolts.

After the parts were assembled, the air-tightness of the apparatus was ascertained both by pressure and exhaust tests. The lateral clearance between the inner and outer cases was 2 cm.; the vertical, between the lids, 6.5 cm.; and between the bases, 6.5 cm.

The volume of air contained in the brass case after insertion of the metal block was about 1500 c.c. A pressure gauge containing a light oil was connected by means of a 3-way tap with one of the tubes leading from this case to the exterior of the tank. Observations of the air pressure within the case were taken immediately before and after an experiment. The air being slightly warmed, the pressure rose during that interval, and thus the presence of any leakage could be detected.

The annular air space could be regarded as the bulb of a constant volume air thermometer, and from the change in pressure during an experiment, the change in the average temperature of the enclosed air could be deduced.

It was found that this change was about one-sixth of that of the contained block.

The approximate magnitude of any correction rendered necessary by the capacity for heat of the contained air could thus be ascertained (see Section VI.).

In our preliminary experiments the copper case was placed within specially constructed "vacuum vessels," the exterior walls of which fitted closely into the

surrounding brass vessels. The reasons for discarding their use are given on p. 159.

A cylindrical hole (K), 9 mm. in diameter and 14 cm. in length, was bored down the centre of each metal block, co-axial with the central quartz tube.

Into this was fitted the "heating coil," the wire of which was wound on a light mica frame of the X section used for platinum thermometers. The edges of the frame were deeply serrated to prevent any possible contact between the wire and the surrounding metal walls. This hole was filled, at low temperatures, with liquid paraffin (previously boiled and placed *in vacuo* to drive off volatile constituents), and at the higher temperatures with a heavy hydro-carbon oil.

Small mica "baffle plates" were inserted at intervals into the triangular sections of the mica rack, in such a manner as to deflect the convection currents outwards.

The hole O (depth 10.3 cm., diameter 1.1 cm.), co-axial with the left-hand quartz tube, contained one of the differential thermometers, the other being inserted into the corresponding hole in the left-hand block.

The position of the hole O was such that about half the total mass of metal was contained in the annular ring whose outer surface was in contact with the copper case, and whose inner passed through the centre of the hole. The various precautions taken to secure accuracy in the use of these differential thermometers will be described in Section III.

The third hole (G) was used for the purposes of cooling the block below the surrounding temperature, by the insertion of a thin-walled glass tube containing ether and connected with a water pump.

When the bath temperature was high the cooling process was a rapid one, but somewhat tedious at lower temperatures.

To prevent the entrance of laboratory air within the brass cases during cooling—which, by the deposition of moisture, might have had a serious effect, especially when the tank temperature was 0° C.—a current of well-dried air was passed by a branch tube into a larger one (F) which formed a continuation of the quartz tube leading to the cooling hole. This rapid up-flow of dry air was continued until the cooling tube had been withdrawn and replaced by a glass stopper, the lower end of which reached within 3 cm. of the inner copper lid, and thus prevented convection currents.

Our methods of experiment involved measurements of the following quantities:—

- (1) Temperature ;
- (2) Resistance of heating coil ;
- (3) Potential difference at ends of heating coil ;
- (4) Mass ;
- (5) Time ;
- (6) Thermal capacities of such bodies as oil, quartz, &c., whose temperature changed with that of the metal blocks.

The validity of our final conclusions is dependent upon the accuracy with which these quantities were determined, and in the following sections will be found a description of the methods adopted for their measurement. An error of 1 in 1000 in Nos. 1, 2, 4 and 5 *supra*, and an error of 1 in 2000 in No. 3 would affect our final results by 0·1 per cent. The thermal capacities of the bodies mentioned in (6), however, were so small, as compared with the capacities of the blocks, that the effect of an error of 1 to 5 per cent. in their valuation would fall below the 0·1 per cent. referred to.

We have, however, no reason to suspect that errors approaching such limits exist in any of the measurements above enumerated.

SECTION III.

Measurement of Temperature.

The platinum thermometers were of the standard form, thick platinum leads and compensators connecting the coil with the heads. All connections, both to the thermometers and the bridge, were made by means of small cups hard soldered to the ends of the leads and containing a fusible metal which expanded on solidification. The electrical connection thus formed was a perfect one and easily disconnected and re-made.

In our earlier experiments two thermometers, labelled AB and CD, were used. The constants of these thermometers have been previously published, and as far as we can detect, show no signs of change over a lapse of 15 years.

Their resistance was ascertained by means of a Callendar and Griffiths "self-testing" bridge,* containing bare Pt-Ag coils immersed in rapidly stirred oil.

Thus, the temperature of the coils could be ascertained with great accuracy.

The bridge was carefully calibrated at the beginning of this work and all its coils and bridge wire divisions expressed in terms of the mean box unit; the absolute value of which, for the purposes of temperature measurements, was of no consequence.

The slight inequality (but 27 parts in 1,000,000) of the "equal arms" (s_1 and s_2) was ascertained in the usual manner by observations of the apparent alteration in the resistance of a platinum thermometer immersed in ice, caused by exchanging the positions of s_1 and s_2 .

The resulting correction has been applied to all our measurements of resistance taken with this box.

All the precautions previously published by one of us were observed, and we do not

* Hereafter referred to as "Box A." This bridge was last used in 1900, and it was then observed that one of its larger coils was showing signs of change. That coil was replaced by another one, and hence a recalibration of the whole bridge was necessary.

think it necessary to encumber the paper with a full table of the results. By the introduction of the new coil, the mean bridge unit (approximately $\frac{1}{100}$ of an ohm) suffered alteration. Hence the values of R_1 and R_0 for AB and CD differ somewhat from those previously published. The alteration, however, is in the unit employed, rather than in the thermometers themselves, and the value of R_1/R_0 and δ may be regarded as unchanged.

One addition to the bridge, however, is worthy of mention, as it may be found useful in other cases. To obtain good contact by means of plugs, considerable pressure has to be exerted. As the insulating surface holding the brasses (in this case marble) is always somewhat yielding, the tendency of the brasses is to gape and thus contact is only made round a small horizontal section of the plug.

We therefore affixed to each pair of brasses an additional contact maker of the kind shown in fig. 2. The spring of the strip AB caused the wedge fastened on its lower surface to spring clear of its twin wedge on the block C when the screw-head E was sufficiently raised. The upright holding the screw passed through a slot in the strip without making contact therewith. The plug being firmly inserted in its hole, the head E was tightly screwed down; thus the wedge surfaces were firmly pressed together, and that with a sliding movement. The strain on the insulating surface was thus relieved, excellent contact was made by the wedge surfaces, also by the screw E connecting the strip with C and also by the plug itself. By this arrangement consistent results were obtained and one of the troubles of exact resistance measurements eliminated.

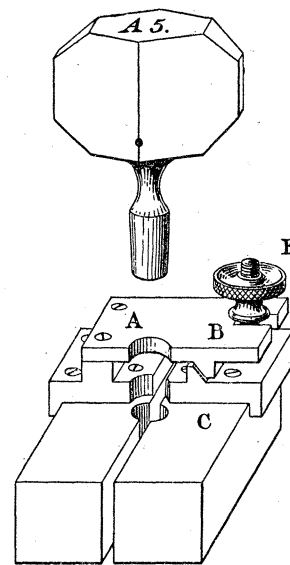


Fig. 2.

The constants of AB and CD were found to be as follows :—

Thermometer.	R_1 .*	R_0 .
AB	2449·201	1763·279
CD	2449·044	1763·308

The difference at 100° C. resulting from the separate standardisations is therefore $AB-CD = +0.157$.

The thermometers were then coupled up differentially and together immersed in the hypsometer. The differential reading was then found to be $+0.158$.

* The barometer used when observing R_1 was one whose scale coefficients, &c., had been determined by comparison with a French Standard of the Bureau International in 1896. Owing to an accident we had to refill it prior to this work; this was done with all the usual precautions.

In the same manner when in ice :—

$$\text{Difference when determined separately} = +0\cdot028.$$

$$\text{Difference when determined differentially} = +0\cdot027.$$

In the course of such a comparison, eight connections had to be undone, re-made separately in sets of four, and then replaced in the first position, *i.e.*, 12 removals and replacements. In the one case, a large number of the box coils were in use ; in the other, the bridge wire only. The identity of the results is sufficient proof of the accuracy of the methods employed. These thermometer coils were surrounded by very thin walled tubes of Jena glass which fitted closely into the holes in their respective blocks and thermal connection between these tubes and the surrounding walls was assisted by a thin film of oil of known weight.

Although the observations with AB and CD appeared satisfactory, it was decided, after a considerable number of determinations of specific heats had been made by their means, to alter the conditions and replace them by two other thermometers labelled AA and BB. In these, the platinum leads were fused through glass heads, while the protecting tube was cut off just above the top of the coils, leaving about $1\frac{1}{2}$ cm. to 2 cm. of glass projecting into the hole in the metal block.*

These thermometers were standardised by temporarily surrounding them with thin tubes containing sufficient oil to completely cover their coils, as we proposed to immerse them similarly when in the blocks. We afterwards found, however, that the effect of the oil was to increase, rather than decrease, the temperature "lag." Their coils were therefore freed from any traces of oil by washing with ether.

Their temperature then very rapidly responded to changes of temperature in the walls of their cavities, their heat capacity being very small as compared with their areas. The constants of AA and BB were as follows :—

Thermometer.	R_1 .	R_0 .	$R_1 - R_0$.
AA	2582·983	1863·367	719·616
BB	2582·341	1863·307	719·034

After a considerable number of experiments had been performed, the glass head of AA was fractured. It was replaced by another thermometer of the same type which had been in our possession for the last 13 years.

Its resistance, however, was slightly less than that of BB. It was necessary, therefore, to reduce the latter until the two became approximately equal. These thermometers were labelled AA' and BB'. Their constants were :—

* The tubes being wrapped round with threads of asbestos to prevent the passage of convection currents from the cavity.

Thermometer.	R_1 .	R_0 .	$R_1 - R_0$.	δ .*
AA'	2576·422	1859·579	716·843	1·50
BB'	2576·984	1860·052	716·932	

It may here be stated that the results deduced from experiments performed with different pairs of thermometers were in excellent agreement, and afforded strong evidence of the accuracy of the temperature measurements.

The twin thermometers were connected in the usual manner, *i.e.*, the coil of the first in series with the compensator of the second on one side of the bridge, the compensator of the first and the coil of the second being placed on the opposite side.

For the remaining sides of the bridge, several forms of approximately equal arms were used. All our later experiments were performed with two Pt-Ag coils, wound together on a mica rack and placed in a brass tube containing oil, the tube itself being immersed in a constant temperature tank. Their resistances at 0° C. were

$$S_1 = 1533\cdot618, \quad S_2 = 1533\cdot685.$$

Their resistances could be taken separately, and were determined in ice and also differentially, both at 0° C. and at higher temperatures. Their continued equality with change of temperature was remarkable.

The galvanometer contact with the junction of S_1 and S_2 was made on a Pt-Ag wire connecting their ends and situated near the bridge wire. As both ends of the galvanometer circuit were connected with similarly situated Pt-Ag wires, the magnitude of the thermo-electric effect having its origin in these contacts was diminished. The Pt-Ag wires were further shielded by the massive casting of brass which carried the contact maker. During all standardisations and experiments the current through the bridge battery circuit was maintained at 0·013 ampere.

Fig. 3 shows the general arrangement and the approximate resistance of the various arms is indicated when the thermometers are at 0° C., the resistances being so arranged as to give nearly the maximum sensitiveness for a given current.

The current through the thermometer coils was less than 0·006 ampere; its heating effect was so small that it could be disregarded, both thermometers and, therefore, both blocks of metal being equally affected.

The battery key was of the type described in 'Phil. Trans.,' vol. 184, p. 398, and re-established the galvanometer circuit after the battery one was broken. Hence, the

* The value of δ was determined in the vapour of boiling aniline (184°·13 C.), as the resistance of thermometer AA' in sulphur vapour would have exceeded the total range of our standard marble top box A. The value of δ was of secondary importance, as we were concerned only with the value of $d\theta/dpt$ at various tank temperatures.

position of the galvanometer spot when the battery was disconnected was that due to any thermo-electric currents existing in the bridge and its connections, and thus any movement visible on establishing the battery circuit was attributable to that circuit only. The key, however, presented some novel features. Brass segments were

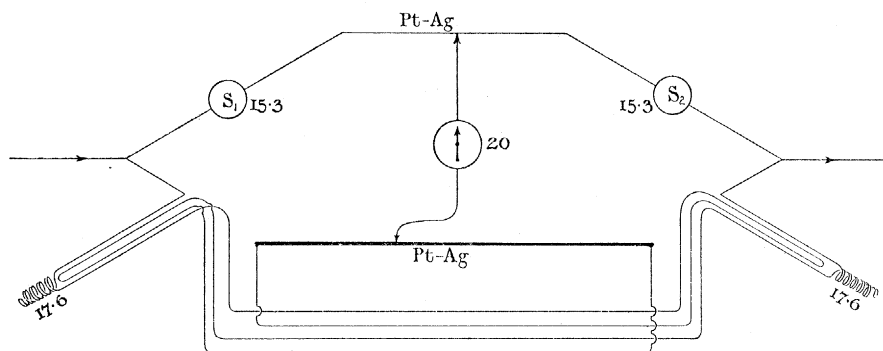


Fig. 3.

fixed on a vertical spindle in such a manner that when the pointer was at 0, the galvanometer circuit alone was complete, when rotated through 120° both galvanometer and battery circuit were established, and on a further rotation through 120° the battery was reversed. The segments were so devised that induced currents during the "makes" and "breaks" would not affect the galvanometer. The whole series of operations could thus be performed very rapidly by one turn of the spindle.

The galvanometer was one of the original Paschen type. Its four coils were wound with wire whose diameters increased with their distance from the centre.

Four coils, each of about 5 ohms and separately adjustable, were used. It was desirable for the present work to obtain a system whose period of oscillation would be small, which would rapidly settle to its final position and yet have great sensitiveness.

For such a purpose it is advisable to use a system whose moment of inertia is reduced as far as possible. The type, constructed by ourselves, consisted of two groups, each containing 18 magnets astatically arranged. The extreme length of the longer magnets was about $1\frac{1}{2}$ mm. The whole system, together with the mirror and the connecting glass fibre, weighed less than 11 mgr. It was suspended by a quartz thread about 17 cm. long and between 3 and 4 μ diameter. The clearance allowed by the ovals in the coils was but a fraction of a millimetre and the faces of the coils were almost in contact, these faces being coated with tinfoil, to promote the damping of the oscillations by electro-magnetic induction. Reckoned on the usual scale, the sensitiveness of this galvanometer could have been easily raised beyond 10^{-10} , but by exterior magnetic control we reduced it until by one reversal of battery a deflection of 1 mm. indicated about $\frac{1}{15,000}^\circ$ Pt as we found that, owing to the wandering of the zero point, a higher degree of sensitiveness detracted from, rather than increased, the accuracy of our observations.

The galvanometer had to be placed at a considerable distance (about 13 m.)

from the tank, as, if nearer, it responded to the flashing on and off of the heating lamps, the changes in the magnetic system of the chronograph, &c. It stood on the top of a massive pillar of masonry which passed through the laboratory floor without contact, and whose foundations were embedded deeply below the base of an underground chamber. The traffic in Cardiff is heavy, but by taking special precautions, the galvanometer in these circumstances was but little affected. We found it necessary, however, carefully to guard the system against convection currents. Every small opening near the suspension was blocked with slips of mica, and the whole galvanometer was enclosed within two separate chambers. Many of the oscillations usually attributed to earth vibrations are, we believe, due to insufficient attention to the effect of convection currents.

As all our temperature measurements were observed in terms of lengths of the bridge wire, it is evident that the accuracy obtainable was dependent upon the accuracy of the calibration of that wire. We have notes of a calibration made some 14 years ago. Before these observations were begun a careful re-calibration was made in terms of the "mean unit" of the marble-top box (A) previously referred to. The d'Arsonal galvanometer used on that occasion, however, was not sufficiently sensitive to enable the determination of the smaller inequalities.

The calibration was made in terms of 3 coils in Box A, of the approximate value of 1, 5, and 10 hundredths of an ohm. Near the conclusion of our present work, a very careful re-calibration was conducted, with the object of ascertaining the accuracy of the earlier one and also of ascertaining if the bridge wire had suffered any alteration through use. The Paschen galvanometer was employed; two separate and independent calibrations were conducted by the two observers and the results were in remarkable agreement.

It appeared that the calibration over the longer intervals on the former occasion was correct, thus showing that the wire had not suffered in the interval.

Each unit of the wire was then expressed in terms of a "mean Box A unit" (the same unit as that used in the standardisation of the thermometers), and a table was formed showing the value of a bridge wire unit at regular intervals, in terms of one Pt degree of each pair of thermometers.

It should here be stated that until the final steps in the reduction of our results, all temperatures are expressed in the platinum scale.

SECTION IV.

Resistance of Heating Coil.

Our methods of reduction demanded a knowledge of R under the actual conditions prevailing during an experiment. As it was impracticable to stir the oil in which the coil was immersed, a wire of small temperature coefficient was chosen to reduce to its smallest limits the correction for the heating effect of the current on the wire.

For preliminary experiments a 10-ohm coil of constantan wire was used, but was replaced in the final form of apparatus by a 20-ohm coil of bare manganin wire, as it was essential to eliminate, as far as possible, sources of thermo-electric forces in the potential circuit.

The diameter of the circle in which the wire was formed was approximately 7 mm. ; the number of turns being 59. The upper end of the wire coil was situated about 20 mm. below the surface of the block ; two straight manganin leads (1 mm. diameter) projecting from the coil terminated at their upper extremities at the junctions with the current and potential leads.

Both potential and current leads were of manganin, the latter being 1 mm. diameter, and to further diminish the heating effect of the current, two leads were connected in parallel. Thus six leads extended up the central quartz tube to a distance of 30 cm. These leads were insulated by perforated mica discs. A solid wad of such discs was fixed between the top of the rack and the junctions to the current and potential leads, in order to diminish the passage for convection currents.

As the resistance of the coil had to be observed *in situ* at each temperature and at frequent intervals, four brass cups, amalgamated inside and containing mercury, were soldered on the current and potential leads outside the apparatus ; plugs enabled us to isolate these circuits, when a resistance had to be taken, from the various connections to battery, &c. Heavy leads from a dial resistance box terminated in a pair of brass cups alongside those above referred to.

If

R be resistance of coil,

r_1 and r_3 ,, ,, ,, current leads,

r_2 and r_4 ,, ,, ,, potential leads from cups to coil,

then, if

$$N_1 = R + r_1 + r_3,$$

$$N_2 = R + r_2 + r_4,$$

$$N_3 = r_1 + r_2,$$

$$N_4 = r_3 + r_4,$$

we have

$$R = \frac{1}{2} \{ (N_1 + N_2) - (N_3 + N_4) \}.$$

As the absolute value of R was required, the resistance of a reference heating coil (of the same construction and about the same value as the one used) was determined in ice by means of the dial box, and then forwarded to the National Physical Laboratory, where its value was determined in international ohms ; on its return we checked our previous determination by the dial box.

This enabled us to reduce our determinations of the resistances of the heating coils used in the work to international ohms.

RESISTANCE OF REFERENCE COIL.

National Physical Laboratory Report.

" COIL Immersed in Unstirred Paraffin Oil cooled to 0° C.

Resistance in international ohms.*	Testing current through resistance.
20·1360	ampere
20·1362	0·025
20·1370	0·050
	0·100

Resistance in legal ohms in terms of our dial box.	Testing current through resistance.
20·2010	ampere
	0·001

Hence, the factor to convert our box readings to international ohms = 0·99678.

As the same ratio arms and plugs in the thousand and hundred dials were used in the determination of both coils, any change in the relative values of the dial box

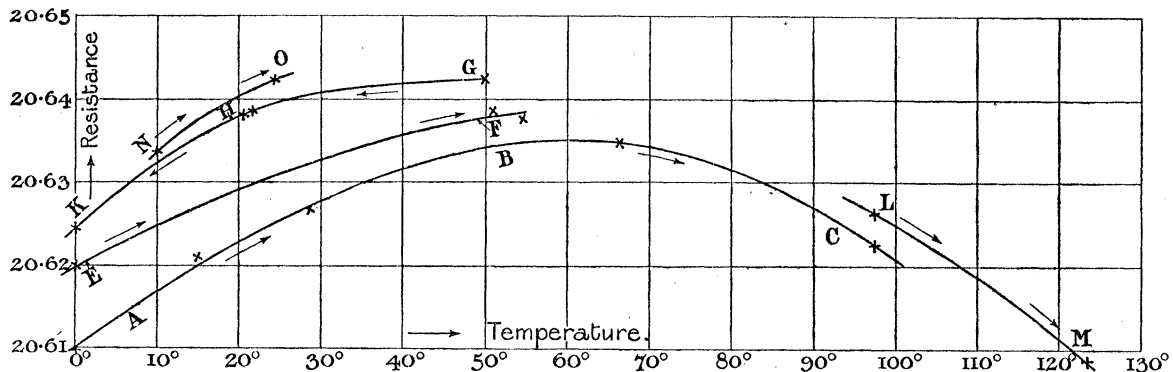


Fig. 4. Variation of resistance of heating coil with temperature and time.

Curve ABC, July 18 to October 26, 1912.

„ EF, December 4 „ December 30, 1912.

„ GHK, January 19 „ February 10, 1913.

„ LM, February 17 „ „ 19, 1913.

„ NO, „ 23 „ March 2, 1913.

since calibration ('Phil. Trans.,' vol. 184, p. 409) would not appreciably affect our results. Fig. 4 shows the variation with temperature of the heating coil and the permanent change by use and exposure to temperatures of about 100° C.

* "Probable error of resistance values is not greater than 2 parts in 100,000."

The value of R so determined requires a small correction, as it includes the entire resistance of the two straight leads, previously mentioned, connecting the upper ends of the coil with the potential junctions.

Of the heat generated in these leads, a portion is lost by radiation, &c., owing to their projecting 24 mm. above the surface of the oil.

The resistance of the leads could not be diminished beyond a certain limit, on account of thermal conduction along them of the heat from the hot oil. A diameter of 1 mm. was decided upon, as the thermal conductivity of a manganin wire of this size would be negligibly small.

A certain amount of heat was developed in these short leads by the current. That generated in the 20 mm. below the surface of the oil would undoubtedly be absorbed by the oil. Of the heat generated in the 24 mm. above the oil-surface, it is probable that about one-half would pass into the block, &c., by conduction and by radiation to the ferrules and quartz tubes.

Taking the actual figures:—Resistance per millimetre of the wire = 0·000642. Hence, resistance of portion above the oil surface = 0·0154 ohm.

On the above assumption only the heat generated in half of this was, in the case of either lead, effective in heating the block. We confess that this is merely an assumption, but, with our knowledge of the actual conditions, it appears to be a reasonable one; moreover an error of 10 per cent. therein would only affect the absolute value of our results by less than 1 part in 10,000.

Change of Resistance due to Change in the Current.

If R' is the resistance of the heating coil when a certain current (defined later) is passing through it and R is the value determined in the usual manner by the dial resistance box, then we define δR by the relation

$$\frac{R'}{R} = 1 + \delta R.$$

The effect of the temperature rise (produced by the heating current) on the resistance of the wire was of course very small in the case of an alloy like manganin; the resulting correction, however, could be determined with considerable accuracy in the following manner (see fig. 5).

A series of observations was made in which the current was measured by the ordinary potentiometer method. Included in the circuit was a 3-ohm coil (W) of bare manganin wire immersed in stirred paraffin oil. It consisted of 4 strands of 0·4 mm. diameter, in parallel, wound on eight projecting mica plates fixed longitudinally on a wooden drum. The passage of the maximum current (0·45 ampere) for intervals of several minutes did not produce any appreciable change in the temperature of the oil.

One observer adjusted the current in the circuit until the potential difference at

the ends of the heating coil R' was balanced against that of a number of cadmium cells, as in the ordinary method of experiment.

The second observer measured the potential difference at the ends of the 3-ohm coil, by means of a Thomson-Varley potentiometer (P), the readings being taken to about 1 part in 50,000, by interpolation by galvanometer swings.

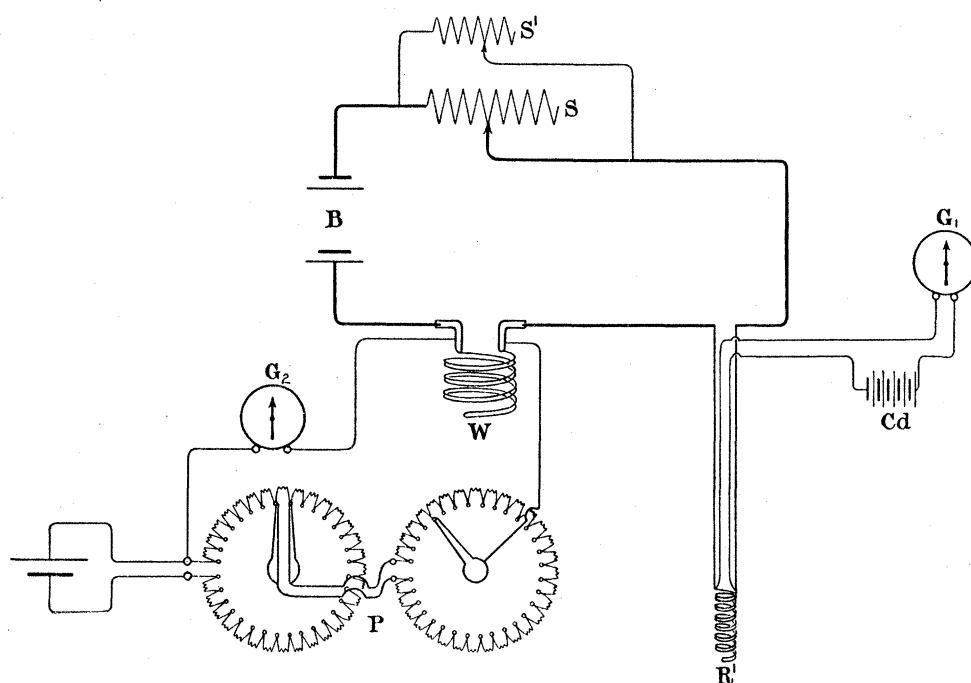


Fig. 5.

- R' . Heating coil in metal block.
- W . Manganin coil (about 3 ohm) immersed in oil.
- P . Thomson-Varley potentiometer.
- S and S' . Rheostats to adjust current.
- B . Main storage battery.
- Cd . Standard cells balanced at ends of R' .
- G_1 . High-resistance galvanometer.
- G_2 . Paschen galvanometer.

Observations were taken when the potential difference at the ends of the heating coil was varied in steps from that of three to eight standard cadmium cells. The temperature of the block was maintained approximately constant by cooling with the ether tube.

Calculation of δR .

If ω is the resistance of the 3-ohm coil, W , and the current in the circuit is caused by a potential difference of nE at the ends of the heating coil, and R' is the resistance

of the heating coil for that value of the current, then

$$C = \frac{nE}{R'}.$$

Potential difference at the ends of 3-ohm coil is

$$\frac{nE}{R'} \times \omega.$$

If s_1, s_2, \dots, s_n be the potentiometer readings corresponding to 1, 2, 3, 4, ..., n number of Cd cells balanced at the ends of the heating coil, then

$$s_n = K \cdot \frac{nE}{R'} \times \omega; \text{ where } K \text{ is a constant.}$$

Hence,

$$R' \propto \frac{n}{s_n}.$$

By plotting n^2 horizontally—since the heating effect is proportional to the square of the electromotive force—and the quantity n/s_n vertically, but reduced in such proportion that for $n = 0$ it is unity, we get the relation between δR , the increment of resistance, and n^2 . The resulting points fall (within the limits of experimental error) on the straight line, $\delta R = \kappa n^2$. These observations were repeated when the tank temperatures were 0°C. and 97°C. , and for both the copper and iron blocks.

In the locality of 0°C. the temperature coefficient of manganin is positive, as shown by the relation

$$\text{At } 0^\circ \text{C., } \delta R = 0.0552n^2.$$

About 100°C. manganin has a negative coefficient and it was found on reducing the results that δR was negative.

$$\text{At } 97^\circ \text{C., } \delta R = -0.0586n^2.$$

These equations represent the extremes of δR in our range, for at intermediate temperatures, owing to the locus of R being concave downwards, the factor k was smaller and vanished altogether between 50°C. and 60°C.

It may be pointed out that for the highest rate usually employed, viz., that due to 8 cells, the correction on account of δR amounted to only 3 parts in 10,000, corresponding to a temperature change in the wire of 10°C. As the values of δR at both 0°C. and 97°C. indicated that the rise in temperature of the wire depended on n^2 only and was independent of all other conditions, we could, from the curve giving the relation between temperature and resistance, calculate the relation between δR and n^2 for any temperature within our range.

The value of R was the one directly determined by the dial box when the heating effect was insignificant, the current through the coil being in that case 0.0015 ampere,

SECTION V.

Electromotive Force.

The potential difference at the ends of the heating coil was always balanced against an integral number of standard Weston cells in series. A batch of 25 cells was constructed for use in this investigation, according to the method described by G. A. HULETT ("The Construction of Standard Cells, &c.," 'Physical Review,' Vol. XXXII., 1911).

The glass work was of the usual H form, the platinum leads not being sealed through the glass. The two limbs extended about 15 cm. above the cross tube, and were closed by corks; through these corks passed the electrodes sheathed by capillary tubing, the fine platinum wires projecting 5 mm. beyond the sealed ends.

This mode of construction admits of the cells being directly immersed in water, with the limbs projecting about 7 cm. above the surface.

The water tank containing them was of considerable capacity and well lagged, the temperature rarely varying by one-fifth of a degree Centigrade per day.

The leads from the cells passed to a switchboard across well insulated supports.

The cells were frequently compared by means of a Thomson-Varley potentiometer with two standard Weston cells constructed by Mr. F. E. SMITH of the National Physical Laboratory. (We take this opportunity of thanking Mr. F. E. SMITH for presenting us with these cells.) Table I. gives the values of the cells in terms of the N.P.L. standard. All our results are expressed in terms of these standards.

From an examination of the comparisons at various times during the course of fifteen months, we can find no change greater than that which might be attributed to the experimental errors.

TABLE I.

Temperature 17° C.

The National Physical Laboratory Standards are denoted by symbols BC-1, BC-2.

No. of cell.	E.M.F. in international volts.*	No. of cell.	E.M.F. in international volts.
BC-1	1·0184	10	1·0184
BC-2	1·0184	11	1·0185
1	1·0183	12	1·0184
3	1·0183	13	1·0184
4	1·0183	14	1·0185
5	1·0182	15	1·0183
6	1·0183	16	1·0183
8	1·0183	17	1·0184
9	1·0184		

* The tables used in the reduction of the observations express the E.M.F. of our cells in terms of the standards correct to 1 part in 20,000.

Statement received with Weston normal cells BC-1, BC-2:—

“ E.M.F. = $1\cdot0183_0$ international volts at 20° C.

Temperature coefficient:—

$$E_t = E_{20} - 0\cdot0000406 (t-20) - 0\cdot00000095 (t-20)^2 + 0\cdot00000001 (t-20)^3.”$$

While an experiment was in progress, the current in the heating coil was continually adjusted to keep the balance exact. This was effected by two rheostats in parallel; the shunt being of fairly high resistance. After the preliminary adjustment, the potential balance could be maintained by use of the shunt alone.

The sensibility of the high resistance Thomson galvanometer (7000 ohms) in the standard cell circuit was such that a deflection of 1 mm. on the galvanometer scale corresponded to a change in the potential difference of 1 part in 20,000.

During the course of an experiment, the potential balance could be maintained with great steadiness, the slight oscillations rarely amounting to more than 1 part in 10,000.

SECTION VI.

Minor Corrections for the Thermal Capacity of Accessory Substances.

In order to facilitate transmission of heat from the heating coil to the metal block, the central hole was, as previously stated, filled at low temperatures with boiled paraffin oil, and at higher temperatures with a heavy hydrocarbon.

The quantity of liquid thus inserted varied slightly with different blocks, the average volume being about 7 c.c. It was therefore necessary to ascertain the thermal capacity of the oils and their approximate variation with temperature.

In the construction of the apparatus 15·06 gr. of alloy were used in fixing the quartz tubes to the lid of the copper case first employed, and 8·25 gr. of solder in the second and somewhat heavier lid.

Again, the thermal capacity of the portions of the glass sheaths of the thermometers which entered the block had to be allowed for; the mass thus inserted amounted, when thermometer CD was in use, to 3·1 gr., and, in the case of AA and AA', to 1·67 gr.

Lastly, allowance had to be made for the heat absorbed by the lower ends of the quartz tubes which supported the apparatus. This was a most difficult correction to determine, as it was not possible, *à priori*, to specify what mass of the quartz could be regarded as raised through the same temperature as the copper lid.

1. *Specific Heat of Glass and Oil.*

The mean specific heat of the paraffin oil between 0° C. and 100° C. was determined with a Bunsen's calorimeter, by the introduction of about 2·8 c.c. of oil sealed in a thin glass bulb.

The mercury drawn into the Bunsen was directly determined from the loss in weight of a small capsule ; in the first experiment, 2·7347 gr. of mercury ; in the second experiment, 2·7335 gr. of mercury.

The constant assumed was 15·44 mgr. mercury per calorie.

The resulting value of the mean specific heat for this paraffin was 0·491, its density being 0·813.

The mean specific heat of glass was determined in a similar manner and was found to be 0·194.

The specific heat and temperature variation of the hydrocarbon oil had already been determined ('Phil. Trans.,' vol. 186, p. 338), viz., $S_t = 0·466 + 0·0009t$, its density being 0·865. As both oils were paraffins, the temperature coefficients were assumed to be the same, to a first approximation.

2. *Alloy and Solder.*

The alloy-fixed lid was used only in our earlier experiments and when determining the specific heats of certain metals at 0° C.

The mean specific heat of this alloy over the range 0° C. to 47°·6 C. (its melting point being 97° C.) was also ascertained by the Bunsen calorimeter and was found to be 0·0348.

The soldered lid was used over the range 0° C. to 125° C., hence, both its specific heat and its temperature variations were required.

A block of the sample of solder (3 kgr.) was cast and machined to the same size as the other metal blocks. Its specific heat at 0° C. and 97° C. was determined in our apparatus in the same manner as copper, &c.,

$$S_t = 0·0422 + 0·000038t.$$

On analysis, the composition of the block was found to be 53·7 per cent. tin and 46·0 per cent. lead, with bismuth and antimony as impurities. The density of the solder block was 8·77. The platinum deposit on the ends of the quartz tubes was negligible, the weight of three coats being only 0·0105 gr.

3. *Heat Absorbed by the Supporting Quartz Tubes.*

As previously indicated, two different copper lids were used. The copper alone in the first weighed 51·6 gr. and thin quartz tubes were fixed into its ferrules (which were 15 mm. in depth) by fusible alloy. The copper alone in the second lid weighed 68·5 gr. ; the tubes were of much heavier make and fixed with solder. The masses of the quartz tubes per unit length in the first lid were only three-fifths of those used in the second ; advantage was taken of this difference to determine the effective capacity for heat of that portion of the quartz which might be regarded as rising through the same range as the block of metal.

Two series of experiments with copper at 0° C. were performed under precisely the same conditions, except that the lid with the lighter tubes was employed in the first, and that with the heavier, in the second, series.

From the differences in the capacity for heat resulting from these two series, the difference in the amount which had passed into the quartz tubes could be determined, the capacity of the alloy, solder and copper, being known. Let m_1s_1 and m_2s_2 be the respective quartz capacities. Then, from the experimental results we found

$$m_1s_1 = 1.37; \quad m_2s_2 = 2.28.$$

No doubt, a temperature gradient existed along these tubes, but the value of sm thus obtained gave the "effective" capacity, *i.e.*, the number of calories which flowed into the quartz tubes as the temperature of the block was raised by 1° C.

A comparison of other experiments at 0° C., where the conditions were similarly altered, indicated that the accuracy of this "quartz correction" was sufficient.

4. *Heat Absorbed by the Air Within the Brass Vessel.*

As stated in Section II. we were able to measure the average increase in pressure, and therefore in temperature, of this air during an experiment. The volume being approximately 1500 c.c., the average rise of pressure was 0.7 mm. Hg, indicating an increase of temperature of 0.26° C. The number of calories thus expended equals 0.08.

As the average heat supply during an experiment was about 400 calories, it is evident that this correction would not amount to more than 1 part in 5000; we did not consider, therefore, that the accuracy of our experiments necessitated the inclusion of this correction, especially as it could be only roughly determined.

SECTION VII.

Mass and Density of the Metals.

The masses of the blocks varied from 1 to 4 kgr. The balance used for the larger masses was capable of weighing to 0.01 gr.; masses under 100 gr. were determined by a Verbeek short-beam balance. The method of double weighing was used and a correction was applied for the displaced air.

A calibration of the box weights proved that, relatively, they were correct to a high degree of accuracy; as, however, the absolute values were required, the 2 kilos. (from another box), and the 1 kilo. and 100 gr. from this box were forwarded to the National Physical Laboratory for standardisation. The kilogram and the 100 gr. weights of our box were found to be exact and the correction on the 2 kilos was given as +0.29 gr.

Densities.

The densities of the metals were found by weighing in air and water, the usual precautions being observed. The values were checked by calculation from the dimensions and weight.

SECTION VIII.

Measurement of Time.

The only records made during the course of an experiment were the times of transit of the temperature of the thermometer in the block past bridge-wire divisions, and as these were effected mechanically by the depression of a key, the observer's attention could be concentrated on the transits.

The time-recording arrangements may be briefly described as follows :—

An electrically driven seconds pendulum bob, suspended by an Invar rod, at each swing tilted over an exhausted tube about 2 inches long by $\frac{1}{4}$ -inch diameter, fixed in a frame capable of oscillating about an axis perpendicular to the length of the tube.

As the carriage bearing the tube was unstable about this axis, a slight impulse sent it over from one stop to the other, causing a small mercury pellet to run down the tube and make momentary connection between two platinum wires fused midway into it, thus completing the electro-magnet circuit in the chronograph.

A series of equally spaced dots about 2 cm. apart on the tape indicated seconds, while the marks of the respective observer's keys were recorded on opposite sides of the tape. By counting and measuring the fraction, the times of transit could be obtained to $\frac{1}{20}$ second.

Although the seconds pendulum kept a fairly constant rate—being fitted with a cut-out device to keep its amplitude to a definite limit—the absolute rate was determined for each experiment by comparison with a rated chronometer.*

This comparison of the total time also afforded a check on the accuracy of the reading of the tape, always a somewhat laborious process, the lengths of tape used varying from 20 to 60 metres.

SECTION IX.

Temperature Control of the Baths.

The absolute steadiness of the bath temperature was of prime importance, as our conclusions were based on the assumption that the temperature of the walls surrounding the blocks remained constant throughout an experiment.

* We are indebted to Mr. T. J. Williams, 63, Bute Street, Docks, Cardiff, for the loan of this chronometer, and for kindly checking its rate from time to time.

When the values of the specific heat at 0° C. were required, a special tank of 15 gallons capacity and lagged with asphalt was used. Two screws—protected by strong metal cages—caused a rapid circulation of water through the powdered ice. For work at higher temperatures this tank was replaced by an oil or water bath, of capacity about 20 gallons, the heat being supplied by immersed electric radiator lamps.

Some difficulty was encountered in insulating the 200-volt leads of these lamps when the tank-temperature was above 50° C., owing to the softening of the stretched rubber tubing by continued exposure to hot water. The cement fastening the caps of the lamps frequently broke down and entailed the loss of several experiments.

The most satisfactory method of insulation hitherto tried was by clipping a discarded motor tyre tube over the end of the “radiator” lamp, the leads being separated within the tube by lengths of glass tubing.

The “lux” lamps used for the purposes of fine adjustment, were insulated by fixing glass tubing of slightly larger diameter over their ends, the joint being closed by a short length of rubber tubing well covered with adhesive tape.

Thermostats.

We tried a considerable variety of thermostats which proved defective from one cause or another. The two most satisfactory ones may be briefly described. The first was composed of thin solid-drawn copper piping $\frac{3}{4}$ inch internal diameter and 16 feet long.

This tube was wound into an oval spiral, so as to surround the two brass cases in the tank (see fig. 1). Two glass tubes were soldered into reduction pieces at each end, one terminating in a tap, the other in a U-tube containing mercury. As the method of constructing these soldered joints is both simple and effective, we have given in Appendix III. a brief description of the process.

Another form of thermostat used in a considerable number of determinations consisted of a large branchwork of glass tubes fused together and so distributed as to take the mean temperature of the tank. The thermostat was filled with toluol, which however proved unsatisfactory at high temperatures, and was replaced by commercial aniline, which in every way seems to be a suitable liquid for thermostats. It has a high coefficient of expansion, low viscosity and a high boiling point (184° C.).

We found it necessary to keep the tap closing the thermostat well greased, otherwise slow leakage and consequent drift of temperature took place.*

The motion of the mercury in the U-tube operated a relay, which in turn switched on and off the lamps in the tank. Both the make and the break in the main circuit

* We have some reasons for suspecting that, owing to neglect of this precaution, the temperature of the bath was not maintained with its accustomed steadiness during some of the group of observations about 67° C.

and the relay circuit had a pair of aluminium plates in water as shunts, to diminish sparking.

A considerable fraction of the heat necessary to maintain the tank at the required temperature was given by a constant supply, while the relay operated the fine adjustment.

The intermittent lamps were placed close to the stirrer, and thus the whole arrangement tended to keep the oscillations of the temperature within narrow limits. At some temperatures we had thermometers by which we could detect changes of $\frac{1}{500}^{\circ}$ C., but when the apparatus was working satisfactorily we at no time observed oscillations of this magnitude.

Another circumstance which perhaps assisted in diminishing the oscillations was the fact that the stirring was sufficiently vigorous to cause a continual vibration of the U-tube of the thermostat and so prevent any adhesion of the mercury to the platinum point which established connection with the relay.

SECTION X.

(1) *The Total Heat Method.*

The metal under examination was cooled to a temperature lower than that of the tank (θ_0) and the fall being observed by means of bridge-wire observations, it was stopped when it had passed below the range of the bridge.

The contact-maker was then set at a certain reading, which, for clearness, we will specify as -9 .* Meanwhile, the "heating" current was adjusted on an auxiliary coil enclosed in a tube containing oil. This auxiliary coil was a duplicate of the coil in the metal block and the change-over from the one to the other could be effected by the depression of a recording key. Before the transference of the current, the temperature of the block rose very slowly by radiation, &c., and could be followed by the gradual approach of the galvanometer spot to its zero mark.

The rate of rise was of the order of $0^{\circ}0,36$ Pt per second, consequently the temperature throughout the block was practically uniform.

The moment the temperature had reached the bridge reading -9 , as indicated by the transit of the spot across its zero mark, the heating current was switched over, the key† at the same time recording the time on the chronograph tape. A slight readjustment of the rheostat was usually required to maintain exact potential balance when the change-over was effected. The contact-maker of the bridge was then set at the next integer, -8 (the temperature interval from -9 to -8 being roughly

* This was the customary starting point.

† The key was so constructed that any time lag between the marking of the tape and the actual switch on was compensated for during the operation of switching off.

$\frac{1}{4}^{\circ}$ Pt), and after slight adjustment* of the galvanometer spot to its zero mark, the galvanometer key was turned so as to re-establish the bridge current (0.013 ampere).

The rise of temperature, as indicated by the movement of the spot, was uniform, and its transit was recorded by a tap on the chronograph key. The cycle of operations was repeated; the transits of the temperature across each bridge-wire reading being recorded in succession until the temperature had risen to +8 bridge-wire reading, when the current was switched over to the auxiliary coil.

After the current had ceased to impart any heat to the metal, the observed temperature continued to rise, on account of excess of heat in the oil, the gradient from the interior to the surface of the metal and the temperature lag of the thermometer.

The metal would, however, after its temperature had risen to a maximum, part with its heat by radiation, &c., only, the resulting fall being slow and regular. This "rise above," as we termed it, could be accurately determined by the following procedure:—

The bridge contact-maker was set above the switching-off point by an amount such that the galvanometer spot moved to near the centre of the scale before the regular cooling began. The galvanometer deflections on reversal of the bridge current were noted, and also (on the chronograph tape) the times of the observations, until the deflections had increased beyond the range of the scale. The value of 1 mm. scale deflection in terms of a bridge-wire unit being known,† the rate of fall in temperature could be determined, and the temperature time-curve P... ABCD could be constructed.

One of the resulting diagrams for the "rise above" is shown in fig. 6.

If P is the point at which the current was switched off, the slope of the line CD, *i.e.*, the rate of uniform cooling, gives the data required for the determination of the horizontal line EG, and thus the temperature which the metal would have attained, in the absence of radiation, &c., can be ascertained.

If GE be produced backwards to meet the temperature ordinate at F, then it will be evident that F falls on DC produced.

Thus PF, the rise due to the residual heat in the block, could be determined at the close of each experiment with considerable accuracy. The value rarely exceeded $0^{\circ}.1$ Pt and could be measured to 1 part in 1000, that is, about 1 in 15,000 of the whole range.

It may be mentioned that the "rises above" for a series of experiments with the same metal under the same conditions were proportional to n^2 , *i.e.*, to the rate of supply.

* The galvanometer system generally required this slight readjustment between each observation of transit in order to maintain the spot on the scale zero when the bridge current was broken. This was effected by the movement of a small subsidiary control magnet on the table by the observer, and about $1\frac{1}{2}$ m. distant from the galvanometer. The changes of zero were chiefly those due to variations in the thermoelectric effects in the circuit, and with considerable attention to shielding the various junctions we succeeded in diminishing such changes to small dimensions, but could not altogether eliminate them.

† Ascertained for each set of experiments.

We may here point out that the two fundamental observations which determined the temperature range were taken when the temperature of the metal was steady and practically uniform, the only change taking place being that due to the very small rate of rise or fall consequent on radiation, &c.

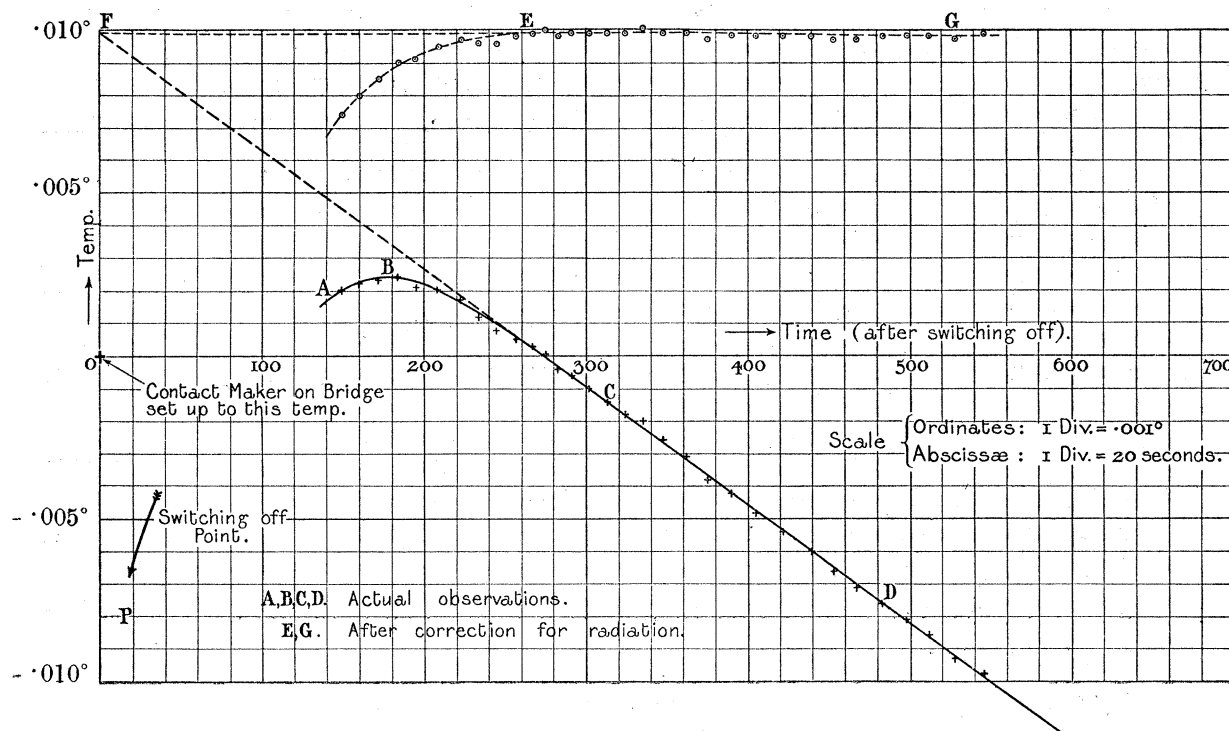


Fig. 6. "Rise above" for Experiment IV., June 2, 1912 (7 standard cells).

We have next to consider any other necessary correction for the effect of radiation during an experiment. When the current was established at -9 bridge-wire reading, the oil had first to rise in temperature, then a gradient established from centre to surface of block and, when the temperature began to rise, the thermometer would undoubtedly lag behind the temperature of the surrounding walls.

For these reasons, the time of rising through the first bridge-wire division would considerably exceed the times of passing over succeeding equal divisions.

It was found that when the temperature had reached the end of the first bridge-wire division, the conditions had become practically steady, as shown by the fact that in subsidiary experiments in which the current was switched off at the end of the first bridge-wire division, the "rise above" was found to be very nearly the same as when the experiments were completed in the customary manner.

We also investigated, with the smaller currents, the curve showing the rate of rise of the thermometer throughout this first interval and it appeared that, during the first half of the time of passing through the interval, the thermometer only rose from -9 to -8.7 bridge-wire. Consequently, this reading -8.7 bridge-wire may be regarded as approximately the mean temperature throughout the time of the first interval.

The temperature ranges above and below θ_0 were so selected that, excluding the first interval, the two ranges were equal and as they were small (about $0\cdot6$ C.), the times over these ranges were so near equality that the losses and gains due to radiation might be neglected.* Hence, the only radiation correction required was that which expressed the heat thus received as the metal rose through the first bridge-wire interval. The true time, however, over that interval was less than the time recorded between the switching on the current and the first transit, owing to the causes of lag above referred to. As this lag was known in terms of temperature, by the "rise above," it was possible to obtain from it an expression involving time.

If

θ_l is the "rise above" in degrees Pt,

t_1 = the average time of rising through 1° Pt when the temperature of the block is rising steadily on account of the heating current,

then $\theta_l \times t_1$ would be the approximate time, at any part of the range, of moving through the "rise above"; this we term the "time lag" = τ .

τ was found to be practically the same for all rates of heating for the same metal. For example, in the case of copper, 36 seconds; of silver, 40 seconds.

Hence, the actual time over the first interval was equal to the observed time diminished by τ .

The rate of rise per second due to radiation alone was obtained by two distinct methods, namely:—

- I. By subsidiary experiments in which rate of rise due to radiation alone over the range -9 to -8 was observed;
- II. From the observations of the transits taken during the actual experiment when the conditions were settled.

For, if

M = mass of the substance,

S = specific heat at θ_0 ,

ms = thermal capacity of oil, copper case, &c.,

σ = rate of rise due to radiation alone for a difference of 1° Pt between the block and the surroundings,

t = time in seconds,

E = E.M.F. of a standard Weston cell,

n = number of cells balanced,

R = resistance at this temperature corrected for heating effect of the current,

* In a previous communication ('Phil. Trans.,' vol. 184, p. 500) it was shown that if t_1 is the time of rising to θ_0 from any temperature below that of the tank, and t_2 is the time from the lower temperature to an equal range above the tank, then the sum of the losses and gains due to radiation, &c., is zero at a time = $2t_1 + \frac{1}{3}(t_2 - 2t_1)$.

In the conditions above indicated, the error due to the assumption that the radiation, &c., was zero at time t_2 was found to be negligible.

then

$$\left(\frac{d\theta}{dt}\right)_{\text{at } \theta'} - \sigma\theta' = \frac{(nE)^2}{JR(MS + ms)}$$

and

$$\left(\frac{d\theta}{dt}\right)_{\text{at } \theta''} - \sigma\theta'' = \frac{(nE)^2}{JR(MS + ms)}$$

Hence

$$\sigma(\theta'' - \theta') = \left(\frac{d\theta}{dt}\right)_{\text{at } \theta''} - \left(\frac{d\theta}{dt}\right)_{\text{at } \theta'}$$

The table below shows the values of σ deduced from the two methods, and their agreement affords strong evidence of the accuracy of the resulting correction.

Metal.	Method I.	Method II.
Silver	0·000078	0·000079
Copper	0·000057	0·000053
Cadmium	0·000093	0·000096

Hence, if θ_1 is the range below θ_0 , corrected for radiation, and θ_2 the range above θ_0 , and θ_i the “rise above” after correction for radiation, then

$$(M \cdot S + ms)(\theta_2 + \theta_1 + \theta_i) = \frac{n^2 E^2 t}{JR}$$

Table II. (p. 148) represents a typical series of experiments by the “total heat” method, the metal being copper at 0° C., and the thermometers AB and CD.

(2) *The Intersection Method.*

The metal having been cooled a considerable distance beyond the limits of the bridge, the current and potential balance were established from five to ten minutes before the temperature came within the bridge range. This preliminary heating up under the normal conditions of the experiment was essential, as it ensured a steady state of gradient, lag, &c., being established before the commencement of the observations. The time of transit of the temperature across each bridge wire division was recorded on the chronograph tape, as in the “total heat” experiments.

The current was switched off and the “rise above” taken in the usual way. Similar experiments over the same range were performed with various values of n (the number of standard cells balanced at the end of the heating coil).

From these observations the value of $\delta\theta/\delta t$ at the centre of each scale unit of the

TABLE II.—“Total Heat” Method.

Copper at 0° C. Thermometers AB, CD.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
				° C.		° C.		
February 24	5	1374·8	109·5	0·0027	0·0355	1·3356	0·09070	+0·02
„ 24	6	965·5	85·5	0·0018	0·0510	1·3519	0·09062	-0·06
„ 25	3	3743·5	231·1	0·0071	0·0141	1·3095	0·09068	0
„ 25	8	557·4	60·1	0·0009	0·0843	1·3863	0·09070	+0·02
„ 25	9	446·8	52·3	0·0006	0·1036	1·4059	0·09073	+0·05
„ 26	4	2125·9	150·5	0·0042	0·0239	1·3224	0·09066	-0·02
„ 28	7	717·8	70·5	0·0012	0·0662	1·3678	0·09064	-0·04
March 10	8	557·6	59·9	0·0009	0·0841	1·3861	0·09073	+0·05
„ 10	9	446·9	52·2	0·0006	0·1039	1·4062	0·09073	+0·05
„ 10	7	718·3	70·3	0·0012	0·0658	1·3674	0·09072	+0·04
„ 11	4	2126·0	150·9	0·0042	0·0241	1·3227	0·09070	+0·02
„ 12	4	2123·8	150·2	0·0042	0·0234	1·3219	0·09060	-0·08
Mean							0·09068 + 0·00016*	
where		M = 3395·80,	R = 20·599,					
		ms = 6·489,	E = 1·01843 (17° C.),					
Column	I. = date of experiment,							
„	II. = n (number of standard cells),							
„	III. = t (seconds),							
„	IV. = time over first interval,							
„	V. = radiation correction on range,							
„	VI. = “rise above” in degrees Pt,							
„	VII. = true range,							
„	VIII. = specific heat,							
„	IX. = percentage difference from mean.							

* The value 0·09068 for S is obtained on the assumption that θ_0 coincides with 0 bridge-wire reading; if, however, the balancing point was at +0·1 bridge wire reading, and the range from -9 to +8 bridge wire, then, on account of radiation gain, the above value of S requires a correction of +0·00005.

At the time these experiments were made we did not realise the importance of this correction and, consequently, did not determine the balancing point on the bridge with sufficient care (see p. 151).

In our rough notes made at the time we have values ranging from +0·1 to +0·4 bridge wire.

Applying the “intersection method” (see Section X. (2)) to the above experiments, omitting the first two or three transits in each case, we find from the calculated value of θ_N that the balancing point should be at +0·33 bridge wire. If we assume this value, the correction on S is +0·00016.

Hence

$$S = 0\cdot09084.$$

bridge-wire division could be calculated, and also $\tan \phi$, the slope of the resulting straight line obtained by plotting $d\theta/dt$ against θ .

If there were no losses or gains by radiation, the resulting lines would be horizontal.

As the rate of rise due to radiation depends solely on the difference of temperature between the metal and the surroundings, the lines representing the observed values of $\delta\theta/\delta t$ for the various rates of electrical supply have all the same inclination to the horizontal, within the limits of experimental error.

The equation of the line representing an experiment, where n standard cells are balanced at the ends of the heating coil, is seen to be

$$\frac{\delta\theta}{\delta t} + \sigma(\theta + \theta_l - \theta_0) = \frac{n^2 E^2}{JR(MS + ms)},$$

where

$\delta\theta/\delta t$ is the observed rate of rise,

θ is the temperature indicated by the thermometer,

θ_0 is the temperature of surrounding envelope,

θ_l is the lag of the observed temperature for the particular rate behind the temperature of the "radiating" surface.

(The determination of this lag is discussed below.)

Hence, by dividing throughout by n^2 , we have

$$\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t} + \frac{\sigma}{n^2}(\theta + \theta_l - \theta_0) = \frac{E^2}{JR(MS + ms)}.$$

The right-hand side would represent the rate of rise due to the electrical supply with a potential difference of one standard cell.

Hence, if we can determine the particular value of $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ at the temperature which we denote by θ_N , when the second term of the equation vanishes, we have the rate of rise due to the electrical supply only.

Plotting $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ against the observed temperature due to the various values of n , we obtain a series of straight lines whose tangents vary inversely as n^2 .

Now, for each experiment thus plotted, there is a certain point on the line where $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ represents $\frac{E^2}{JR(MS + ms)}$ alone, and this would correspond to the temperature θ_N at which there are no losses or gains by radiation, *i.e.*, when the mean temperature of the surface subject to radiation is coincident with the temperature of the surroundings. As the co-ordinates of this point are the same for all rates, the lines would intersect at one point if either the observed θ was the actual temperature of the "radiating" surface, or the lag was constant for all.

The dotted lines in fig. 7 represent a typical case—that of copper at 0° C. with thermometer AA.

It will be noticed that the lines representing the higher rates of supply are markedly to the left of those obtained from the lesser values of n , indicating that the “lag” increases with the rate of supply, as might be expected.

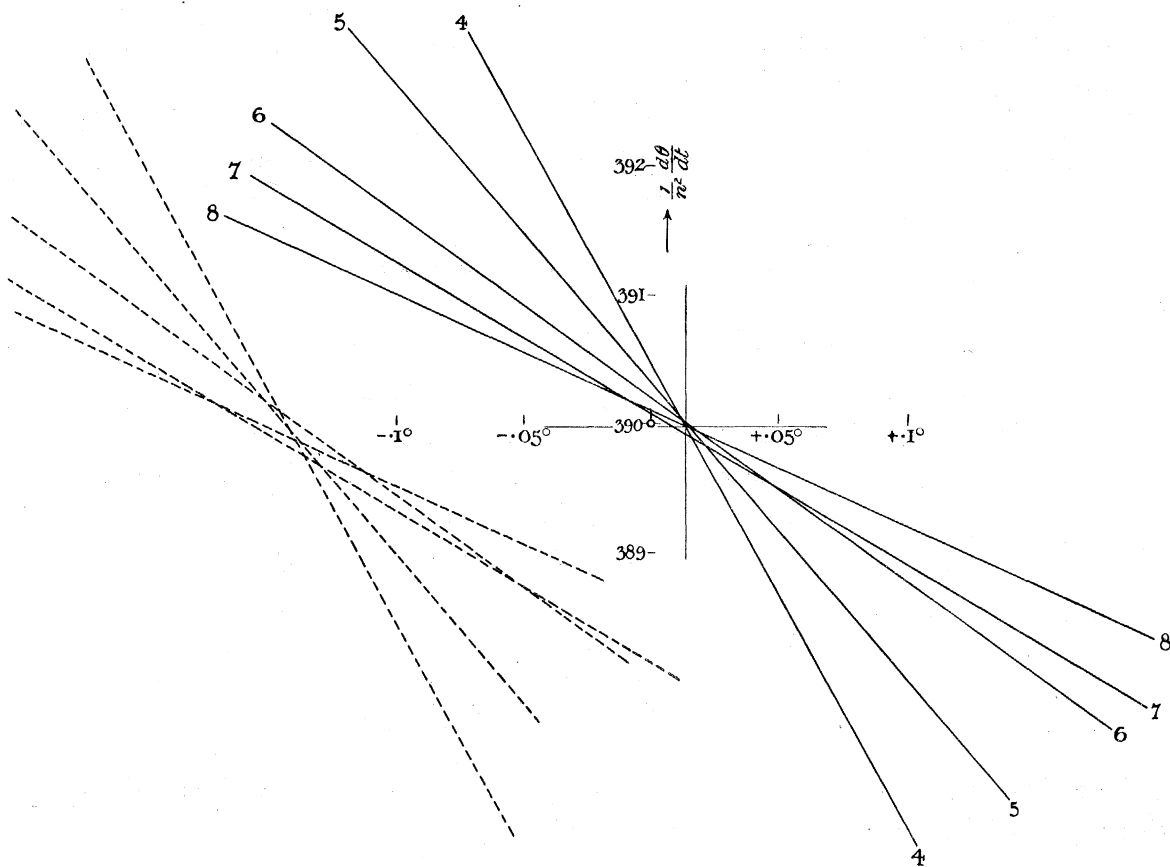


Fig. 7.

A study of the “total heat” experiments led us to the conclusion that the “rise above” was intimately connected with this “lag.” Although the entire “rise above” on switching off could not be solely due to thermometer lag, yet, as a first approximation, it represents the superior limit.

Hence, by shifting each line parallel to itself to the right by the value of θ_i determined at the close of the experiment, we obtained the figure shown in full lines, the result, of course, being the same as if $\frac{1}{n^2} \cdot \frac{\partial \theta}{\partial t}$ had been plotted against $\theta + \theta_i$.

Owing to observational errors, the lines do not intersect in a single point, but enclose a small area. In cases where a really satisfactory series of observations has been obtained, however, the area of the triangle (when three experiments are considered) is vanishingly small even when the results are plotted on such a scale

that 1 cm. vertically represents a change of 1 in 2000 in $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ and there are many instances where the ordinates of the vertices do not differ from the mean by more than 1 part in 5000.

This, in our opinion, is the strongest evidence in support of the assumption that the "rise above" is practically equal to the "lag" to the degree of accuracy to which the horizontal scale is required. We may state here that when plotting the results, we used a scale such that 5 cm. abscissæ represented $0^{\circ}\cdot 1$ Pt, the vertical scale, of course, being considerably greater, enabling the fifth figure in the value of $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ to be determined. In our earlier reductions, we ascertained the mean ordinate by reading the ordinates of all the points of intersection; for example, for 4 values of n , we obtained 6 intersections. In cases, however, where the angle ϕ resulting from two experiments differed but by a small amount, as in the case of $n = 7$ and $n = 8$, a slight error in the inclination of either line might cause a large displacement in the point of intersection. We therefore adopted a method of reduction* which enabled us to calculate the co-ordinates of the point such that, measured along the ordinate passing through this point, the sum of the moments of inertia of the points of intersection of the several lines with this ordinate is a minimum about this point. Or, stated otherwise:—The point so calculated gives, by the method of least squares, the most probable value of the ordinate of the point of intersection of all the lines (for a typical example see p. 157).

A large number of determinations of the specific heats of Cu at 0° C. were made by both the "total heat" and the "intersection" methods (see Section XI.).

The correspondence between the final results obtained was remarkably close (the differences in no case exceeding 1 in 1000), and indicated the validity of both methods. Having satisfied ourselves on this point, we adopted the latter method for all our remaining experiments, as it avoided the following cause of difficulty and delay which was unavoidable in the former.

The removal of our metal block and its replacement by another was a lengthy business, requiring considerable care, as all the soldered joints in the various electrical circuits had to be separated and remade, the brass case removed and opened, &c.

It was not possible to complete the operation in less than several hours, and the temperature of the tank necessarily suffered some alteration in the process. On re-establishing the system, small consequential changes in the balancing point on the bridge might have occurred, or, at all events, the absence of any such changes had to be ascertained. Thus, it was necessary to allow time for the newly inserted block to settle to the tank temperature, and, as its approach to that temperature was slow and asymptotic, at least a day or two had to elapse before the "zero" point could be ascertained with certainty. The importance of this matter is indicated by the fact

* For this suggestion we are indebted to Mr. G. M. CLARKE, M.A.

that an error of 0·1 bridge-wire division ($= 0^{\circ}\cdot007$ Pt) in the estimation of the zero point would affect conclusions derived from an experiment of average length by the total heat method by (in the case of Cu, for example) 5 parts in 9000. In our earlier "total heat" experiments we had not realized the importance of this zero reading, and this no doubt is the cause of certain discrepancies.

The position of the zero point was, however, of little importance when the intersection method was adopted, for so long as the temperature of the reference block remained unchanged, the effect of any alteration in the zero point was self-eliminated.

The method of reduction is shown by one example, namely, that of copper at 0° C., with thermometers AA, BB.

The only reason which has guided us in the selection of this out of the 48 similar groups, is that it happens to be first of the groups given in Table XI. The large amount of arithmetic involved in the reduction of our observations is well illustrated by this example.

Explanation of Tables.

n = number of standard cells balanced on heating coil.

Column I., bridge readings.—The successive points on bridge wire across which transits were taken.

Column II. (t).—Times of transit from chronograph tape.

Column III. (δt).—Interval between successive transits. (If transits observed every $1\frac{1}{2}$ bridge wire, as in Experiment IV., then δt for 1 bridge wire calculated.)

Column IV. ($\delta\theta$).—Value in Pt degree of bridge-wire division corresponding to δt .

Column V. $\left(\frac{\delta\theta}{\delta t} \times 10^7\right)$.

Column VI. (θ).—Temperature at mid-point of $\delta\theta$, measured from centre of bridge wire.

Column VII.—The letters denote the values of $\delta\theta/\delta t$ taken in pairs, for the purpose of obtaining the slope of the line.

Column VIII.—Change in $\delta\theta/\delta t$ for equal intervals of temperature.

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TABLE III.—Experiment I., June 3, 1912. Number Standard Cells, 5.

I.	II.	III.	IV.	V.	VI.		VII.	VIII.
Bridge readings.	t .	δt .	$\delta\theta \times 10^2$.	$\frac{\delta\theta}{\delta t} \times 10^7$.	θ .			$\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}}$.
-9.5	215.25							
8.5	286.90	71.65	7.2820	10163	-0.657	A		
7.5	359.45	72.55	7.2845	10041	-0.584	B	A - A'	357
6.5	432.20	72.75	7.2882	10018	-0.511	C		
5.5	504.95	72.75	7.2901	10021	-0.438	D	B - B'	381
4.5	578.75	73.80	7.2874	9875	-0.365	E		
3.5	652.75	74.00	7.2742	9830	-0.292	F	C - C'	357
2.5	726.55	73.80	7.2736	9994	-0.219	G		
1.5	801.20	74.65	7.2902	9766	-0.146	H	D - D'	353
0.5	875.60	74.40	7.2958	9806	-0.073	A'		
+0.5	951.15	75.55	7.2978	9660	0	B'	E - E'	311
1.5	1026.70	75.55	7.2990	9661	+0.073	C'		
2.5	1102.20	75.50	7.3018	9668	+0.146	D'	F - F'	304
3.5	1178.80	76.60	7.3230	9563	+0.219	E'		
4.5	1255.90	77.10	7.3422	9526	+0.292	F'	G - G'	413
5.5	1332.50	76.60	7.3390	9581	+0.365	G'		
6.5	1409.90	77.40	7.3106	9446	+0.438	H'	H - H'	320
Mean . . .				9789 at $-0^{\circ}110$ C.		Mean . . .		350 for difference of $0^{\circ}584$ C.

TABLE IV.—Experiment II., June 1, 1912. Number Standard Cells, 4.

I.	II.	III.	IV.	V.	VI.		VII.	VIII.
Bridge readings.	t .	δt .	$\delta\theta \times 10^2$.	$\frac{\delta\theta}{\delta t} \times 10^7$.	θ .			$\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}}$.
-9.5	0.75							
-8.5	111.30	110.55	7.2820	6587	-0.657	A		
-7.5	222.00	110.70	7.2845	6580	-0.584	B	A - A'	372
-6.5	334.00	112.00	7.2882	6507	-0.511	C		
-5.5	447.10	113.10	7.2901	6446	-0.438	D	B - B'	327
4.5	561.50	114.40	7.2874	6370	-0.365	E		
3.5	675.20	113.70	7.2742	6398	-0.292	F	C - C'	337
2.5	789.75	114.55	7.2736	6350	-0.219	G		
1.5	906.10	116.35	7.2902	6266	-0.146	H	D - D'	361
0.5	1023.50	117.40	7.2958	6214	-0.073	A'		
+0.5	1140.20	116.70	7.2978	6253	0	B'	E - E'	280
1.5	1258.50	118.30	7.2990	6170	+0.073	C'		
2.5	1378.50	120.00	7.3018	6085	+0.146	D'	F - F'	332
3.5	1498.75	120.25	7.3230	6090	+0.219	E'		
4.5	1619.80	121.05	7.3422	6065	+0.292	F'	G - G'	329
5.5	1741.70	121.90	7.3390	6021	+0.365	G'		
6.5	1864.00	122.30	7.3106	5978	+0.438	H'	H - H'	288
Mean . . .				6290 at $-0^{\circ}110$ C.		Mean . . .		328 for difference of $0^{\circ}584$ C.

TABLE V.—Experiment III., June 2, 1912. Number Standard Cells, 6.

I.	II.	III.	IV.	V.	VI.		VII.	VIII.
Bridge readings.	t .	δt .	$\delta\theta \times 10^2$.	$\frac{\delta\theta}{\delta t} \times 10^7$.	θ .			$\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}}$.
-9.5	151.65							
-8.5	202.00	50.35	7.2820	14463	-0.657	A		
-7.5	252.90	50.90	7.2845	14311	-0.584	B	A - A'	513
-6.5	303.90	51.00	7.2882	14291	-0.511	C		
-5.5	354.80	50.90	7.2901	14322	-0.438	D	B - B'	358
-4.5	406.40	51.60	7.2874	14123	-0.365	E		
-3.5	457.90	51.50	7.2742	14125	-0.292	F	C - C'	348
-2.5	509.20	51.30	7.2736	14178	-0.219	G		
-1.5	561.00	51.80	7.2902	14074	-0.146	H	D - D'	427
-0.5	613.30	52.30	7.2958	13950	-0.073	A'		
0.5	665.60	52.30	7.2978	13954	0	B'	E - E'	148
1.5	717.95	52.35	7.2990	13943	+0.073	C'		
2.5	770.50	52.55	7.3018	13895	+0.146	D'	F - F'	337
3.5	822.90	52.40	7.3230	13975	+0.219	E'		
4.5	876.15	53.25	7.3422	13788	+0.292	F'	G - G'	344
5.5	929.20	53.05	7.3390	13834	+0.365	G'		
6.5	982.30	53.10	7.3106	13768	+0.438	H'	H - H'	306
Mean . . .				14062 at $-0^{\circ}110$ C.		Mean . . .		348 for difference of $0^{\circ}584$ C.

TABLE VI.—Experiment IV., June 2, 1912. Number Standard Cells, 7.

I.	II.	III.	IV.	V.	VI.		VII.	VIII.
Bridge readings.	t .	δt .	$\delta\theta \times 10^2$.	$\frac{\delta\theta}{\delta t} \times 10^7$.	θ .			$\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}}$.
-9.5	75.55							
-8.5	112.75	37.20	7.2820	19575	-0.657	A		
-7.5	150.50	37.75	7.2845	19297	-0.584	B	A - A'	526
-6.5	188.00	37.50	7.2882	19435	-0.511	C		
-5.5	225.70	37.70	7.2901	19337	-0.438	D	B - B'	292
-4.5	263.70	38.00	7.2874	19177	-0.365	E		
-3.5	301.55	37.85	7.2742	19219	-0.292	F	C - C'	278
-2.5	339.55	38.00	7.2736	19141	-0.219	G		
-1.5	377.70	38.15	7.2902	19109	-0.146	H	D - D'	469
0.5	416.00	38.30	7.2958	19049	-0.073	A'		
+0.5	454.40	38.40	7.2978	19005	0	B'	E - E'	255
1.5	492.50	38.10	7.2990	19157	+0.073	C'		
2.5	531.20	38.70	7.3018	18868	+0.146	D'	F - F'	295
3.5	569.90	38.70	7.3230	18923	+0.219	E'		
4.5	608.70	38.80	7.3422	18923	+0.292	F'	G - G'	275
5.5	647.60	39.90	7.3390	18866	+0.365	G'		
6.5	686.65	39.05	7.3106	18721	+0.438	H'	H - H'	388
Mean . . .				19113 at $-0^{\circ}110$ C.		Mean . . .		347 for difference of $0^{\circ}584$ C.

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TABLE VII.—Experiment V., June 2, 1912. Number Standard Cells, 8.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Bridge readings.	t .	$\frac{3}{2}\delta t \times 10^2$.	$\delta\theta \times 10^2$.	$\frac{\delta\theta}{\delta t} \times 10^7$.	θ .		$\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}}$.
-9.0	86.20						
7.5	129.50	43.30	7.2826	25228	-0.602	A	
6.0	172.80	43.30	7.2890	25250	-0.493	B	A - A'
4.5	216.60	43.80	7.2892	24963	-0.383	C	
3.0	260.10	43.50	7.2718	25075	-0.274	D	B - B'
1.5	303.85	43.75	7.2875	24985	-0.164	E	
0	347.70	43.85	7.2964	24959	-0.055	A'	C - C'
+1.5	391.70	44.00	7.2985	24882	+0.055	B'	
3.0	436.25	44.55	7.3034	24591	+0.164	C'	D - D'
4.5	480.45	44.20	7.3400	24909	+0.274	D'	
6.0	569.50	44.65	7.3320	24631	+0.383	E'	E - E'
			Mean . . .	24947 at +0°.110 C.		Mean . . .	306 for difference of 0°.547 C.

In Experiment I., 5 cells, $\frac{\delta\theta_A}{\delta t_A} - \frac{\delta\theta_{A'}}{\delta t_{A'}} / \theta_A - \theta_{A'} = 350/0.584 = 59.9 \times 10^{-7}$ for 0°.1 C.

„ II., 4 „ „ „ „ = 382/0.584 = 56.2 „ „ „

„ III., 6 „ „ „ „ = 348/0.584 = 59.6 „ „ „

„ IV., 7 „ „ „ „ = 347/0.584 = 59.4 „ „ „

„ V., 8 „ „ „ „ = 306/0.547 = 55.9 „ „ „

Hence mean difference for change of 0°.1 Pt = 58×10^{-7} .

Reducing the mean $\delta\theta/\delta t$ in each experiment from -0°.110 C. to 0° C. by this mean tangent and then calculating the values at -0°.1 C. and +0°.1 C., we obtain the following results:—

Experiment No.	n .	$\frac{\delta\theta}{\delta t}$ at 0° C.	$\frac{\delta\theta}{\delta t}$ at -0°.1 C.	$\frac{\delta\theta}{\delta t}$ at +0°.1 C.	$\frac{1}{n^2} \left(\frac{\delta\theta}{\delta t} \right)_{-0°.1 \text{ C.}} \times 10^9$.	$\frac{1}{n^2} \left(\frac{\delta\theta}{\delta t} \right)_{+0°.1 \text{ C.}} \times 10^9$.
I.	5	9725	9783	9667	39132	38668
II.	4	6226	6284	6168	39275	38550
III.	6	13998	14056	13940	39044	38722
IV.	7	19049	19107	18991	38994	38757
V.	8	24883	24941	24825	38970	38789

Two corrections are necessary to make the values of $\left(\frac{1}{n^2} \frac{\delta\theta}{\delta t}\right)$ comparable—

- (1) The change in resistance by change of current ;
- (2) The departure of the mean E.M.F. of the group of standard cells used from the standards.

The correction to $\frac{1}{n^2} \frac{\delta\theta}{\delta t}$ for these is designated by Cd cell and δR , the experimental results are now arranged in order of n .

Experiment No.	n .	Cd cell.	δR .	$\frac{1}{n^2} \left(\frac{\delta\theta}{\delta t}\right)_{\text{at } -0^{\circ}1 \text{ C.}} \times 10^9$.	$\frac{1}{n^2} \left(\frac{\delta\theta}{\delta t}\right)_{\text{at } +0^{\circ}1 \text{ C.}} \times 10^9$.
II.	4	+10	+ 3	39288	38563
I.	5	+10	+ 5	39147	38683
III.	6	+ 9	+ 7	39060	38773
IV.	7	+ 6	+10	39010	38773
V.	8	+ 5	+13	38988	38807

Before proceeding with the next step—the determination of the mean point of intersection either graphically or by calculation—we require the value of the “rise above” in each experiment.

As an example of the method, we quote that of Experiment IV., June 2, 1912. Number standard cells, 7.

Contact maker of bridge set up $0^{\circ}088$ Pt beyond switching-off point.

TABLE VIII.

Time (from instant of switching off).	Millimetre scale deflection.	$\theta \times 10^3$.	θ after radiation correction $\times 10^3$.	Time (from instant of switching off).	Millimetre scale deflection.	$\theta \times 10^3$.	θ after radiation correction $\times 10^3$.
149	27	2.0	7.4	324	- 24	-1.8	9.9
160	30	2.2	8.0	335	- 28	-2.0	10.1
172	32	2.3	8.5	348	- 35	-2.6	9.9
184	33	2.4	9.0	362	- 43	-3.1	9.9
195	29	2.1	9.1	375	- 52	-3.8	9.7
209	27	2.0	9.5	390	- 58	-4.2	9.8
223	23	1.7	9.7	405	- 66	-4.8	9.8
234	17	1.2	9.6	422	- 74	-5.4	9.8
245	11	0.8	9.6	439	- 82	-6.0	9.8
257	9	0.6	9.8	453	- 91	-6.6	9.7
267	4	0.3	9.9	467	- 97	-7.1	9.7
275	1	0.1	10.0	483	-104	-7.6	9.8
283	- 5	-0.4	9.8	498	-111	-8.1	9.8
291	- 8	-0.6	9.9	512	-118	-8.6	9.8
302	-14	-1.0	9.9	528	-128	-9.3	9.7
313	-19	-1.4	9.9	546	-135	-9.8	9.9

Hence

$$\text{“Total rise above”} = 0\cdot088 + 0\cdot0099 = 0^{\circ}\cdot0979 \text{ C.}$$

The figure on p. 145 represents the above data.*

TABLE IX.—Calculation of the Co-ordinates of the “Most Probable Common Point of Intersection.”

Experiment No.	n .	$\left(\frac{1}{n^2} \frac{d\theta}{dt}\right)_{-0^{\circ}\cdot1 \text{ C.}} \times 10^9$.	$\frac{1}{n^2} \left(\frac{d\theta}{dt}\right)_{+0^{\circ}\cdot1 \text{ C.}} \times 10^9$.	Shift $\times 10$.	Equation of line after shift applied.
II.	4	39288	38563	0·334	$y = 39046 - 362x$
I.	5	39147	38683	0·512	$y = 39034 - 232x$
III.	6	39060	38773	0·729	$y = 39021 - 144x$
IV.	7	39010	38773	0·979	$y = 39008 - 118x$
V.	8	38988	38807	1·254	$y = 39011 - 91x$

$$\text{Equation of mean line } y = 39024 - 189x. \quad (1)$$

Multiplying each term by the coefficient of x in the same equation

$$\begin{aligned} 362y + 131044x &= 141346, \\ 232y + 53824x &= 90559, \\ 144y + 20736x &= 56190, \\ 118y + 13924x &= 46029, \\ 91y + 8281x &= 35500, \end{aligned}$$

Mean

$$y + 240x = 39031. \quad (2)$$

Solving equations (1) and (2) for x and y we have the co-ordinates of the required point

$$\begin{aligned} x &= +0\cdot137, \\ y &= 38998. \end{aligned}$$

Expressing x and y in absolute measure we have

$$\begin{cases} x \times 0\cdot1 = \text{degrees Pt,} \\ y \times 10^{-9} = \frac{1}{n^2} \frac{\partial \theta}{\partial t}. \end{cases}$$

Hence

$$\begin{aligned} \theta_N &= +0^{\circ}\cdot0137 \text{ Pt,} \\ \frac{1}{n^2} \frac{\partial \theta_N}{\partial t} &= 38998 \times 10^{-9}. \end{aligned}$$

* This figure indicates how the “rise above corrected” can be obtained more simply by the prolongation of a straight line.

A small uncertainty in the value of θ_N has but little effect on $\frac{1}{n^2} \frac{\partial \theta_N}{\partial t}$; for example, an error of 0.1 in x would only produce an error of 1 in 2000 in the above value of y .

A correction of -3 has to be applied to y for the clock rate, which was a losing one of 0.05 sec. per 1000.

The distribution of the results of the individual experiments about the "most probable point of intersection" may be determined by solving the equation of each line for its intersection point with the ordinate through $x = +0.137$.

TABLE X

I.	II.	III.	IV.	V.	VI.
Experiment No.	n .	y (mean).	y (calculated).	Difference.	(Difference) ² .
II.	4	} 38995 {	38993	-2	4
I.	5		38999	+4	16
III.	6		38998	+3	9
IV.	7		38989	-6	36
V.	8		38996	+1	1
				Total . . .	66

$$\text{Probable observational error} = \pm \frac{2}{3} \sqrt{\frac{\Sigma (\text{difference})^2}{\text{No. experiments} - 1}} = \pm 3.$$

$$\text{Coefficient of variation per cent.} = \pm 0.01.$$

In Tables XI. to XVIII., pp. 161 to 169, we give the value of y (calculated) for each group in Column VII.; the error per cent. (Column VIII.) being the coefficient of variation obtained as above.

Fig. 7, p. 150, represents the above group of experiments; the most probable point of intersection obtained by calculation is shown by a large cross.

Attention may be drawn to the fact that no "smoothed curves" have been used in the above reduction.

Reduction to Specific Heat.

$$[ms + MS] \frac{1}{n^2} \frac{d\theta_N}{dt} = \frac{E^2}{JRf}.$$

M = mass copper block + case = 3392.37 grms.,

ms = thermal capacity of oil, quartz, glass and solder = 4.898,

R = resistance of coil = 20.599,

E = E.M.F. standard cell at 15° C. = 1.01848,

$f = d(\theta)/d(\text{Pt})$ at 0° C. = 0.98480.

Hence

$$S = 0.09094.$$

NOTE. $f = \partial(\theta)/\partial(\text{Pt})$. The values of $\partial\theta/\partial\text{Pt}$ at temperature θ are obtained from CHAPPUIS and HARKER'S tables, 'Phil. Trans.,' vol. 194, p. 114. Assuming $\delta = 1.54$.

SECTION XI.

Experimental Results. Preliminary Experiments.

A considerable number of preliminary experiments were performed with a view of testing the apparatus employed and deciding on the most suitable conditions. Some were carried out with a constantan heating coil of 10 ohms resistance, which was replaced by a manganin coil of wider section and greater resistance.

A large number of experiments were performed with silvered vacuum vessels interposed between the metal blocks and the brass cases. The results obtained with different rates of energy supply were discordant. The faster the rate of rise, the lower the value found for the resulting specific heat. These differences were roughly proportional to the duration of the heating; the range being practically the same in all.

The source of this error we traced to the effect of radiation, &c., on the inner walls of the vacuum vessel. This surface received heat by radiation from the block and as it parted with the heat but slowly, its temperature rose with that of the block to an extent dependent on the rate of increase of temperature of the metal.

After the removal of the vacuum vessels, the loss or gain by radiation was dependent on $\theta - \theta_0$ only, as the surrounding walls were now those washed by the tank water and remained at a constant temperature. Our anxiety to minimize loss or gain of heat from external sources by the interposition of these flasks had led us, when designing the apparatus, to regard the insertion of the non-conducting walls as important; this precaution, however, was a cause of much loss of time and labour.

Explanation of the Tables.

Column I.—The temperature at which experiments were performed.

During our experiments at 0° C. we changed both thermometers and lids ; we have, therefore, in this column indicated the thermometers and lid used.

Letters AA and AA', indicate the thermometers referred to in Section III.

Letters L₁, the lighter, and L₂, the heavier lid (see Section VI.).

Where no indication is given, the thermometer used was AA', and lid, L₂.

Column II.—The dates on which the series were performed is given to indicate the results obtained on repetition after lapse of time.

Column III.—The number of transits denotes the number of observations of $\delta\theta/\delta t$ obtained during the experiment.

Column IV.—No. Cd Cells.—The number of standard Weston cells in series, whose E.M.F. was balanced at the ends of the heating coil.

Column V. "Rise Above."—This was determined at the close of each experiment.

The line representing an experiment was shifted horizontally by this amount.

Column VI. Tangents (Abscissæ 0°·1 Pt).—The slope of the line $\frac{1}{n^2} \cdot \frac{\delta\theta}{\delta t}$ with temperature θ as abscissa.

Absolute value = number in Column $\times 10^{-9}$.

Column VII.—The points of intersection of the lines of various rates with the ordinate through θ_N (see p. 158).

Absolute value = number in Column $\times 10^{-9}$.

Column VIII.—The probable observational error per cent. of the group.

Column IX.—The data required for the reduction. It will be noticed that the mass of the metal block has in some cases changed during the course of the experiment, owing to certain alterations such as enlarging holes, &c., which were found necessary.

ms denotes the capacity for heat of copper case and the group of subsidiary substances, or of the latter only when the block itself is copper.

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TABLE XI.—Copper.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$.	Error per cent.	
° C. 0 AA L ₁	1/6/12 3/6/12 2/6/12 2/6/12	16 16 16 16	4 5 6 7 8	0·033 0·051 0·073 0·098 0·125	362 232 144 118 91	38993 38999 38998 38989 38996 <hr/> 38995	0·01	R = 20·599 E = 1·01848 (15° C.) M = 3392·37 <i>ms</i> = 4·898 S = 0·09094
0 AA' L ₂	25/7/12 23/7/12 24/7/12 25/7/12 23/7/12 24/7/12	16 16 16 16 10 10	5 6 6 7 8 8	0·039 0·057 0·057 0·075 0·097 0·098	237 165 165 121 93 93	38755 38754 38743 38737 38711 mean of two <hr/> 38741	0·03	R = 20·609 E = 1·01838 (18° C.) M = 3409·18 <i>ms</i> = 5·577 S = 0·09079
0 AA' L ₂	3/12/12 3/12/12 3/12/12 3/12/12	16 16 16 12	4 5 6 7	0·037 0·058 0·081 0·107	449 244 169 124	38631 38682 38654 38642 <hr/> 38652	0·05	R = 20·620 E = 1·01842 (17° C.) M = 3409·05 <i>ms</i> = 5·533 S = 0·09098
0 AA' L ₁	5/12/12	16 16 12 10 6	5 6 7 4 4	0·059 0·085 0·114 0·040 0·040	235 164 120 367 367	39052 38964 38931 38969 mean of two <hr/> 38979	0·08	R = 20·620 E = 1·01842 (17° C.) M = 3409·05 <i>ms</i> = 4·789 S = 0·09088
28·42	2/8/12	16 16 10	6 7 8	0·053 0·071 0·091	189 138 105	37916 37877 37846 <hr/> 37880	0·06	R = 20·627 E = 1·01847 (15° C.) M = 3409·18 <i>ms</i> = 5·819 S = 0·09230
63·5	1/9/12	Set of three experiments of little value owing to leakage of tank-heating circuit affecting galvanometer.				36763		S = 0·09365
67·32	13/9/12 13/9/12 16/9/12 16/9/12 13/9/12 13/9/12	20 20 20 10 13 13	4 6 7 8 7 8	0·027 0·064 0·086 0·110 0·084 0·114	427 191 139 108 139 108	36632 36655 36630 mean 7 36629 mean 8 <hr/> 36636	0·02	R = 20·635 E = 1·0185 (14°·5 C.) M = 3409·10 <i>ms</i> = 6·313 S = 0·09387
97·4	11/10/12	16 16 12 8	5 6 7 8	0·042 0·057 0·077 0·103	330 229 151 100	35802 35774 35825 35783 <hr/> 35796	0·04	R = 20·621 E = 1·01840 (17°·5 C.) M = 3409·05 <i>ms</i> = 6·598 S = 0·09520

TABLE XII.—Aluminium.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$.	Error per cent.	
° C. 0 AA L ₁	30/6/12	19 19 12	6 7 8	0·111 0·148 0·191	244 178 137	54722 54747 54720 54730	0·02	R = 20·599 E = 1·01845 (16° C.) M = 954·342 <i>ms</i> = 23·478 S = 0·20937
0 AA' L ₂	14/7/12 19/7/12 20/7/12 21/7/12	19 19 12 12 19 19 13 13 19 13 21	6 7 8 8 7 6 7 7 5 8 6	0·076 0·102 0·131 0·130 0·102 0·077 0·102 0·102 0·054 0·130 0·077	243 177 137 137 177 243 177 177 349 137 243	54022 54005 54041 54139 54144 54080 54144 54143 54108 54095 54114 54094	0·07	R = 20·610 E = 1·01838 (18° C.) M = 954·342 <i>ms</i> = 25·764 S = 0·20957
28·35	6/8/12	19 12 12 19	6 7 7 5	0·075 0·100 0·100 0·053	239 188 188 344	52345 52344 52350 52353 52348	0·02	R = 20·627 E = 1·01845 (16° C.) M = 954·342 <i>ms</i> = 26·207 S = 0·21471
51	25/1/13 25/1/13 26/1/13	18 12 9 18 18 12 18	6 7 8 5 6 7 5	0·073 0·100 0·130 0·056 0·073 0·100 0·056	254 187 143 366 254 187 366	51058 51076 51006 51140 51039 51130 50989 51064	0·04	R = 20·643 E = 1·01842 (16°·7 C.) M = 954·00 <i>ms</i> = 26·772 S = 0·21842
97·48	23/10/12	18 18 12 9 13 10	4 5 6 7 6 7	0·034 0·052 0·073 0·101 0·073 0·101	670 431 299 220 299 220	48936 48939 48973 48828 48959 49018 48942	0·08	R = 20·621 E = 1·01838 (18° C.) M = 954·00 <i>ms</i> = 27·632 S = 0·22482

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TABLE XIII.—Iron (Ingot).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$.	Error per cent.	
° C. 0	24/11/12 24/11/12 25/11/12	12 16 16 20 18	7 6 5 6 4	0·112 0·083 0·057 0·083 0·037	131 175 377 175 397	38405 38370 38402 38339 38354 38374	0·05	R = 20·620 E = 1·0184 (17°·5 C.) M = 2798·67 <i>ms</i> = 25·767 S = 0·1045
0	12/2/13	17 18 18	5 6 7	0·026 0·046 0·062	257 177 131	38502 38525 38494 38507	0·03	R = 20·625 E = 1·0184 (17°·5 C.) M = 2781·22 <i>ms</i> = 25·727 S = 0·1046
10	23/2/13	18 18 18	7 6 5	0·059 0·044 0·032	128 173 251	37958 37980 37959 37966	0·02	R = 20·634 E = 1·01854 (13° C.) M = 2781·22 <i>ms</i> = 25·889 S = 0·1059
9·9	24/2/13	18 18 10 12	5 6 7 8	0·032 0·047 0·060 0·081	257 177 131 100	37948 37807 37923 37938 37904	0·11	All same as 23/2/13 S = 0·1061
20·5	31/1/13 31/1/13 1/2/13	17 12 38 12	6 7 4 8	0·040 0·056 0·018 0·074	171 126 379 96	37157 37168 37176 37182 37171	0·06	R = 20·638 E = 1·01843 (16°·5 C.) M = 2781·22 <i>ms</i> = 20·638 S = 0·1078
21·5	4/2/13 4/2/13 4/2/13	12 17 18	7 5 6	0·060 0·029 0·042	149 287 269	37170 37159 37192 37174	0·03	Constants same as for 20°·5 C S = 0·1077

TABLE XIII. (continued).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$.	Error per cent.	
° C. 24·5	2/3/13	18	6	0·045	213	37067	0·02	R = 20·642 E = 1·0185 (15° C.) M = 2781·22 <i>ms</i> = 26·231
		18	5	0·028	307	37073		
		18	7	0·055	156	37080		
						37073		S = 0·1080
50·3	19/1/13	18	7	0·057	128	35705	0·03	R = 20·643 E = 1·0184 (16° C.) M = 2798·67 <i>ms</i> = 26·938
		18	6	0·042	175	35729		
		18	5	0·029	254	35701		
						35712		S = 0·1105
66·3	7/12/12	18	4	0·029	756	35363	0·24	R = 20·635 E = 1·0184 (17° C.) M = 2798·67 <i>ms</i> = 27·299
		18	5	0·048	483	35167		
		18	6	0·065	339	35410		
						35313		S = 0·1112
97·5	29/10/12	16	4	0·027	883	34248	0·02	R = 20·622 E = 1·01838 (18° C.) M = 2798·67 <i>ms</i> = 27·798
		16	5	0·037	565	34226		
		16	6	0·051	395	34238		
		12	7	0·069	289	34243		
						34239		S = 0·1137

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TABLE XIV.—Zinc.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n_2} \frac{d\theta_N}{dt}$.	Error per cent.	
0	27/11/12 27/11/12 27/11/12 27/11/12 28/11/12	16 12 10 16 12	5 6 7 4 7	0·062 0·090 0·120 0·040 0·120	300 209 154 471 154	47389 47314 47367 47307 47271 <hr/> 47330	0·07	R = 20·620 E = 1·0184 (17° C.) M = 2538·40 <i>ms</i> = 25·644 S = 0·09150
0	9/2/13	18 18 18	7 6 5	0·075 0·056 0·039	143 195 281	47219 47170 47209 <hr/> 47199	0·04	R = 20·624 E = 1·0184 (17° C.) M = 2538·4 <i>ms</i> = 25·582 S = 0·09180
21·5	6/2/13	37 18 12 9	5 6 7 8	0·039 0·055 0·075 0·099	295 205 149 116	46335 46383 46348 46330 <hr/> 46349	0·03	R = 20·638 E = 1·0184 (16° C.) M = 2538·4 <i>ms</i> = 26·231 S = 0·09265
50·5	22/1/13	18 18 12 18 18 14	6 7 8 5 7 8	0·055 0·077 0·100 0·038 0·077 0·100	205 150 115 295 190 145	45210 45149 45196 45194 45215 45224 <hr/> 45198	0·04	R = 20·643 E = 1·0184 (16° C.) M = 2538·40 <i>ms</i> = 26·756 S = 0·09412
97·4	21/10/12 21/10/12 21/10/12 21/10/12 21/10/12	17 18 20 12 8 12	4 5 4 6 7 6	0·029 0·038 0·029 0·055 0·074 0·055	599 382 599 265 194 265	43944 43982 43926 43980 43947 43876 <hr/> 43942	0·06	R = 20·621 E = 1·01836 (18° C.) M = 2538·40 <i>ms</i> = 27·607 S = 0·09534
97·4	16/2/13	17 18 18	5 6 7	0·039 0·055 0·073	606 420 308	44064 44105 44055 <hr/> 44076	0·05	R = 20·6266 E = 1·0185 (14°·5 C.) M = 2538·40 <i>ms</i> = 27·488 S = 0·09507
123·4	18/2/13	18 18 18 12	6 5 7 8	0·051 0·038 0·070 0·088	505 725 370 283	43401 43446 43582 43305 <hr/> 43434	0·18	R = 20·609 E = 1·0185 (13·5° C.) M = 2538·40 <i>ms</i> = 27·886 S = 0·09570

TABLE XV.—Silver.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$	Error per cent.	
° C. 0 AA L ₁	27/5/12	18 18 8	4 6 8	0·048 0·106 0·183	496 220 124	52897 52926 52887 52903	0·02	R = 20·599 E = 1·0185 (14° C.) M = 3733·10 <i>ms</i> = 23·443 S = 0·05560
28·4	3/8/12	19 19 12	5 6 7	0·054 0·078 0·102	339 235 172	51302 51273 51304 51293	0·02	R = 20·627 E = 1·0184 (16° C.) M = 3733·10 <i>ms</i> = 26·188 S = 0·05613
67·41	18/9/12 19/9/12 20/9/12 21/9/12	18 18 12 9 9 12 18 20 10 10 10 10	4 6 7 8 8 7 6 6 8 8 7 7	0·042 0·092 0·123 0·158 0·159 0·122 0·090 0·090 0·159 0·159 0·123 0·123	613 272 201 153 153 201 273 273 153 153 201 201	50001 50005 50017 49908 49986 50145 50024 49963 50016 50013 50054 50009 50011	0·07	R = 20·635 E = 1·01848 (15° C.) M = 3733·10 <i>ms</i> = 27·056 S = 0·05680
97·4	13/10/12	18 12 18 18	6 7 5 4	0·082 0·111 0·057 0·037	307 227 442 692	49098 48970 48991 49018 49019	0·07	R = 20·621 E = 1·0184 (18° C.) M = 3733·10 <i>ms</i> = 27·564 S = 0·05737

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TABLE XVI.—Cadmium.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$	Error per cent.	
° C. 0 AA L ₁	12/5/12	19 19 10	4 6 8	0·053 0·117 0·202	595 266 149	63811 63852* 63795 63819*	0·03	R = 20·599 E = 1·0185 (15° C.) M = 3070·71 <i>ms</i> = 23·325 S = 0·05468
28·4	8/8/12	19 12 14 19	6 7 7 5	0·080 0·107 0·107 0·058	284 209 209 410	61560 61526 61529 61533 61537	0·02	R = 20·627 E = 1·01847 (15° C.) M = 3070·71 <i>ms</i> = 26·054 S = 0·05554
54·5	29/12/12 30/12/12	18 12 8 18 17 10	5 6 7 3 4 7	0·058 0·082 0·113 0·019 0·036 0·113	415 289 213 115 648 213	60193 60254 60214 (mean) 60226 60229 60223	0·02	R = 20·638 E = 1·0184 (17° C.) M = 3070·71 <i>ms</i> = 26·718 S = 0·05616
97·64	16/10/12	18 18 16 11 13	4 5 5 6 6	0·036 0·061 0·061 0·085 0·085	784 502 491 349 349	58408 58483 58303 58413 58404 58402	0·07	R = 20·621 E = 1·01836 (18°·5 C.) M = 3070·71 <i>ms</i> = 27·437 S = 0·05714

* Omitting 6 cell experiments on the date 12/5/12, we have from other two experiments

$$S = 0\cdot05475.$$

TABLE XVII.—Tin.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	
Tem- perature tank.	Date.	No. transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_n}{dt}$.	Error per cent.		
° C.	17/5/12	18	5	0·085	466	75254	0·05	R = 20·599 E = 1·01851 (14° C.) M = 2591·49 <i>ms</i> = 23·434	
		18	4	0·055	728	75209			
		14	5	0·085	466	75309			
	19/5/12	8	6	0·123	323	75166			
		8	6	0·122	323	75186			
		7	6	0·122	323	75136			
	0	20/5/12	9	7	0·162	237			75250
		21/5/12	19	4	0·056	728			75126
	AA		9	8	0·216	182			75240
			14	5	0·086	466			75225
	L ₁	22/5/12	9	8	0·216	182			75134
			9	7	0·163	237			75240
			9	8	0·217	182			75105
		26/5/12	9	8	0·216	182			75233
									75201
28·4	9/8/12	12	7	0·118	235	72122 (mean)	0·02	R = 20·627 E = 1·0185 (16° C.) M = 2591·49 <i>ms</i> = 26·169	
		12	6	0·087	318	72081			
		19	5	0·062	459	72107			
		14	7	0·118	235				
						72103			
53·9	2/1/13	16	4	0·038	793	70292 (mean)	0·01	R = 20·638 E = 1·0184 (17°·5 C.) M = 2591·49 <i>ms</i> = 26·798	
		17	4	0·038	793	70308 („)			
		18	5	0·059	508	70296 („)			
	3/1/13	12	6	0·089	352	70317			
		9	7	0·120	258				
		13	6	0·089	352				
		18	5	0·059	508				
					70303				
97·6	19/10/12	10	5	0·065	541	67819	0·09	R = 20·621 E = 1·01836 (18°·6 C.) M = 2591·49 <i>ms</i> = 27·580	
		12	5	0·065	541	67809			
	20/10/12	9	6	0·088	375	67704			
		10	6	0·088	375	67603			
		18	4	0·042	844	67645			
					67716				

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TABLE XVIII.—Lead.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Temperature tank.	Date.	No. of transits.	No. Cd cells, <i>n</i> .	Rise above ° Pt.	Tangents (abscissæ 0°·1 C.).	$\frac{1}{n^2} \frac{d\theta_N}{dt}$.	Error per cent.	
° C.	20/6/12	18 12 12 9 9 9	4 5 5 6 6 7	0·062 0·093 0·094 0·135 0·132 0·178	813 521 521 355 362 266	84253 84462 84294 84577 84461 84504	0·09	R = 20·599 E = 1·0184 (16° C.) M = 4016·56 <i>ms</i> = 23·442 S = 0·03020
0	23/6/12 23/6/12 29/6/12 29/6/12	8 18 12 8	7 3 7 8	0·175 0·034 0·176 0·229	266 1443 291 222	84324 84550 84406 84579		
						84441		
28·38	5/8/12	19 12 19 19	5 6 4 5	0·060 0·074 0·038 0·052	508 371 835 508	81440 81231 81334 81238	0·08	R = 20·627 E = 1·0184 (16° C.) M = 4016·56 <i>ms</i> = 26·148 S = 0·03053
51	23/12/12	17 18 18 12 20 12	5 4 3 6 5 6	0·065 0·041 0·026 0·093 0·065 0·093	553 949 161 280 553 280	80008 (mean) 80118 79838 79808 (mean)	0·19	R = 20·639 E = 1·01841 (17° C.) M = 4016·56 <i>ms</i> = 26·786 S = 0·03073
						79938		
57	13/12/12	18 18	3 4	0·020 0·037	151 931	Intersection of the two lines.		R = 20·638 E = 1·01840 (17·5° C.) M = 4016·56 <i>ms</i> = 26·743 S = 0·03078
						79710		
67·4	22/9/12	18 12 18 18 20 20 13	5 6 4 5 5 4 6	0·070 0·105 0·045 0·070 0·070 0·045 0·105	562 390 879 562 562 879 390	78743 78681 78561 78515 78579 78715 78603	0·07	R = 20·635 E = 1·01846 (15·5° C.) M = 4016·56 <i>ms</i> = 27·056 S = 0·03102
						78629		
97·45	15/10/12	18 18 12 9 10 13	3 4 5 6 6 5	0·025 0·044 0·067 0·097 0·097 0·067	177 990 633 441 441 633	77252 77532 77632 76991 77298 77448	0·19	R = 20·621 E = 1·01838 (18° C.) M = 4016·56 <i>ms</i> = 27·587 S = 0·03127
						77358		

SECTION XII.

Summary of Results. Copper.

The validity of our methods was rigorously tested by the determinations of the specific heat of copper at 0° C.

We have already, in the previous sections, discussed the various changes made during the course of these experiments, and the table below summarises the results.

TABLE XIX.

Method.	No. of experiments.	Observed error per cent.	Remarks.	Specific heat.
“Total heat”	12	0·03	Thermometers AB, CD (see Table II.)	0·09084
“Total heat”	3	0·03	Thermometers AA, BB.	0·09095
“Intersection method” . .	4	0·05	Thermometers AA', BB'; heavy lid; December 3, 1912	0·09098
“Intersection method” . .	5	0·08	Thermometers AA', BB'; light lid; December 5, 1912	0·09088
“Intersection method” . .	6	0·03	Thermometers AA', BB'; heavy lid; July 23–25	0·09079
“Intersection method” . .	5	0·01	Thermometers AA, BB; light lid; June 3	0·09094
“Intersection method” . .	12	0·04	Thermometers AB, CD. Intersection method applied to 1st group	0·09081

Giving equal weight to each group, we have

$$S_0 = 0\cdot09088 \pm 0\cdot000047, \text{ i.e., probable error} = 0\cdot05 \text{ per cent.}$$

In Tables XX. to XXVII. we summarise our final conclusions.

Messrs. Johnson and Matthey state that the previous treatment of all the metals, except copper and iron, was as follows:—

“The cylinders in every instance were cast, and then allowed to cool, subsequently being turned in a lathe, they were not annealed.”

The data supplied by the manufacturers indicate that the physical condition of the iron is probably distinct from that of the other metals, and this may to some extent account for the marked difference in the rate of change of its S and θ curve over the range 0°C. to 100°C. , as compared with the remaining curves.

We are desirous of maintaining the iron in its present condition until we have investigated its behaviour at low temperatures, but we hope eventually to ascertain the effect of careful annealing on this specimen.

TABLE XX.—Copper.

Weight, 3392 grms. Density, 8.922.

Temperature	0°C.	$28^\circ \cdot 42 \text{C.}$	$63^\circ \cdot 52 \text{C.}$	$67^\circ \cdot 32 \text{C.}$	$97^\circ \cdot 4 \text{C.}$
S (experimental value)	0.09088	0.09230	0.09365 ?	0.09387	0.09521
Difference from curve per cent.	0	+0.09	-0.13	-0.07	0

$$S_t = 0.09088 (1 + 0.0005341t - 0.00000048t^2).$$

This copper was electrolytically deposited.

Mr. C. T. HEYCOCK writes as follows:—

“Cu = 99.95 per cent. Remaining 0.05 per cent. consists of Pb, Fe, and a very little SiO_2 . You will be correct in stating that it is of high purity.”

TABLE XXI.—Aluminium.

Weight, 954 grms. Density, 2.704.

Temperature	0°C.	$28^\circ \cdot 35 \text{C.}$	$51^\circ \cdot 0 \text{C.}$	$97^\circ \cdot 48 \text{C.}$
S (experimental value).	0.20957	0.21471	0.21842	0.22482
Difference from curve per cent.	0	0	0	0

$$S_t = 0.20957 (1 + 0.0009161t - 0.0000017t^2).$$

Messrs. Johnson and Matthey state:—

“Aluminium we have reason to believe to be exceptionally pure, say 99.90 per cent., with traces of iron.”

With the exception of one group of three at 0°C. , these experiments were extremely satisfactory, so much so that the fifth figure appears to have some real significance. The perfect agreement of the experimental and the curve values is very noticeable.

TABLE XXII.—Iron (Ingot).

Weight, 2798 grms. Density, 7·858.

Temperature	0° C.	10°·0 C. and 9°·9 C. (mean)	20°·5 C.	21°·5 C.	24°·5 C.	50°·3 C.	66°·3 C.	97°·5 C.
S (experimental value)	0·1045	0·1060	0·1078	0·1077	0·1080	0·1105	0·1112?	0·1137
Difference from curve per cent. }	0	0	+0·22	+0·10	0	-0·22	-0·99	+0·10

$$S_t = 0\cdot1045 (1 + 0\cdot001520t - 0\cdot00000617t^2).$$

This specimen was obtained from the American Rolling Mill Company, who state:—

“Material rolled from an ingot into a billet (4 inches by 4 inches), on ‘Blooming Mill’; billet forged into round section at blacksmith’s shop. Same had no further annealing nor additional heat treatment, other than when rolled and forged.”

Specimen turned down to size in laboratory workshop.

“Sample from which material was taken and forged shows following analysis:—

“ S = 0·021 per cent.	Cu = 0·040 per cent.
“ P = 0·005 ”	O = 0·015 ”
“ C = 0·012 ”	N = 0·0026 ”
“ Mn = 0·036 ”	H = 0·0005 ”

“ Silicon, trace; Fe (by diff.), 99·87.”

Our sincere thanks are due to the American Rolling Mill Company, Middletown, Ohio, U.S.A., for presenting us with this sample.

TABLE XXIII.—Zinc.

Weight, 2538 grms. Density, 7·141.

Temperature	0° C.	21°·5 C.	50°·5 C.	97°·4 C.	123°·4 C.
S (experimental value)	0·09176	0·09265	0·09412	0·09521	0·09570
Difference from curve per cent.	0	-0·14	+0·19	-0·01	+0·08

$$S_t = 0\cdot09176 (1 + 0\cdot0005605t - 0\cdot00000178t^2).$$

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Messrs. Johnson and Matthey state :—

“ Approximately, 99·95 per cent. Zn.”

The agreement between the results on repetition at the same temperature was less satisfactory than usual, the extreme difference from the adopted value at 0° C. being 0·3 per cent. (see Table XIV.).

TABLE XXIV.—Silver.

Weight, 3733 grms. Density, 10·456.

Temperature	0° C.	28°·41 C.	67°·40 C.	97°·44 C.
S (experimental value)	0·05560	0·05613	0·05680	0·05737
Difference from curve per cent.	0	0	−0·07	+0·07

$$S_t = 0\cdot05560 (1 + 0\cdot0003396t - 0\cdot000000141t^2).$$

Messrs. Johnson and Matthey state :—

“ Better than 999·9 fine.”

At 0° C. two series of experiments by “ total heat ” method were performed—

With thermometers AB, CD, ten experiments ; probable error,

$$\pm 0\cdot05 \text{ per cent. ; } S = 0\cdot05551.$$

With thermometers AA, BB, six experiments ; probable error,

$$\pm 0\cdot04 \text{ per cent. ; } S = 0\cdot05575.$$

TABLE XXV.—Cadmium.

Weight, 3070 grms. Density, 8·652.

Temperature	0° C.	28°·34 C.	54·5° C.	97°·64 C.
S (experimental value)	0·05475	0·05554	0·05616	0·05714
Difference from curve per cent.	0	0·02	−0·04	0

$$S_t = 0\cdot05475 (1 + 0\cdot000520t - 0\cdot000000725t^2).$$

Messrs. Johnson and Matthey state:—

“Fully 99·75 per cent. pure, with very ‘slight traces of iron and zinc.’”

Series of four total heat experiments at 0° C., with probable error of $\pm 0\cdot08$ per cent. gave $S = 0\cdot05468$.

TABLE XXVI.—Tin.

Weight, 2591 grms. Density, 7·292.

Temperature	0° C.	28°·4 C.	53°·9 C.	97°·6 C.
S (experimental value)	0·05363	0·05465	0·05549	0·05690
Difference from curve per cent.	0	+0·02	-0·02	+0·02

$$S_t = 0\cdot05363 (1 + 0\cdot0006704t - 0\cdot000000458t^2).$$

Messrs. Johnson and Matthey state:—

“Probably analyse to 99·80 per cent., with trifling quantities of arsenic, lead, and iron.”

TABLE XXVII.—Lead.

Weight, 4016 grms. Density, 11·341.

Temperature	0° C.	28°·38 C.	51°·0 C.	67°·4 C.	97°·45 C.
S (experimental value)	0·030196	0·03053	0·03073	0·03102	0·03127
Difference from curve per cent.	0	0	-0·16	+0·19	-0·03

$$S_t = 0\cdot030196 (1 + 0\cdot000400t - 0\cdot00000036t^2).$$

Messrs. Johnson and Matthey state:—

“Approximate to 99·90 per cent., with inappreciable traces of arsenic and bismuth.”

The “probable error” of the various groups with this metal is higher than in the case of other metals. This is probably an effect of the low conductivity of lead and the consequent steepness of the thermal gradient within the cylinder.

Fig. 8 represents the increments in specific heat over the range 0° C. to 100° C., on the assumption that the specific heat at 0° C. for each metal is represented by unity.

We had hoped to present curves showing the actual values of the specific heat over this range, but the scale required was so large, that we found that, if reduced to the size necessary for reproduction, they were of little value.

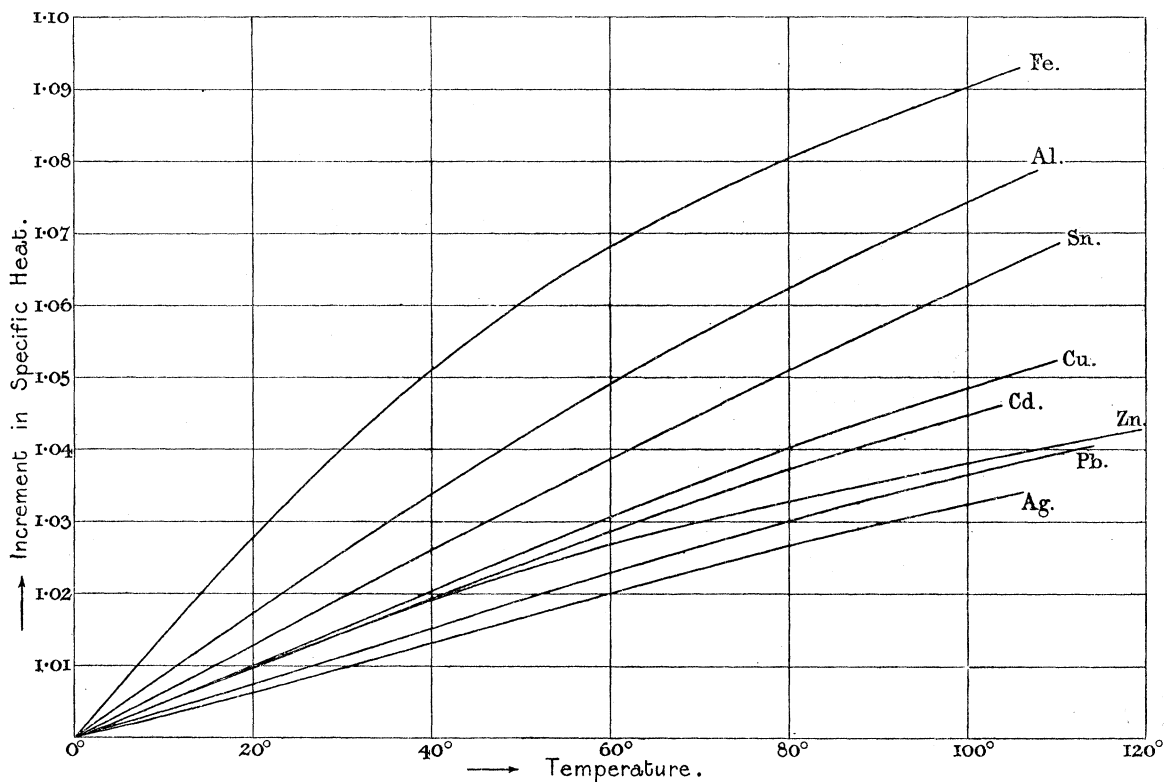


Fig. 8. Variation with temperature.
(Assuming specific heat at 0° C. as unity.)

A noticeable decrease in the increment of the specific heat of zinc is observable at temperatures above 50° C., which may have some connection with its change in physical properties, as zinc becomes malleable about 120° C. For this reason we pushed our examination of this metal up to a temperature of 123° C.

Our thanks are due to the Court of the University of Wales for a grant towards the purchase of the specimens of metals.

We are greatly indebted to Mr. EDGAR A. GRIFFITHS, of this College, for his help in the construction of apparatus and in the conduct of the experiments.

SECTION XIII.

Discussion of the Results of NERNST'S Observations at Low Temperatures.

[After the preceding paper was written, it was suggested to us that we should discuss the relation between our experiments over the range 0° C to 100° C. and those of NERNST at lower temperatures. We feel, however, that a discussion of this kind would carry more weight after the completion of our own work at temperatures below 0° C.

From the brief description of the method published* by NERNST, it is impossible to estimate the magnitude of any errors arising from the neglect of the loss or gain by radiation, &c. It must be remembered that boiling liquid air is not at a steady temperature and therefore the metal block suspended within the envelope could not settle to the temperature of the surroundings; hence, observations of the temperature after switching off the heating current, afford little information concerning losses or gain by radiation.

NERNST'S experiments, however, had one great advantage over those of other observers at lower temperatures, inasmuch as the ranges of temperature employed were small, *e.g.*, 2.7° C. When we consider the curvature of the specific heat curve, it is evident that changes of temperature of the order of 100° C. and upwards can give little accurate information as to the value at the centre of such ranges. Two metals, only, appear to have been examined by NERNST, namely, lead and silver. For lead he obtained the values of the atomic heat given in column II. below; column III. gives the values calculated from the modified EINSTEIN'S formula

$$(A) \quad C = 3R \frac{e^{-\frac{\alpha}{T}} \left(\frac{\alpha}{T}\right)^2}{\left(e^{-\frac{\alpha}{T}} - 1\right)^2} + bT^{3/2},$$

where R is the gas constant, equal to 1.985 gr.-calories.

For lead

$$\alpha = 58, \quad b = 7.8 \times 10^{-5}.$$

In column IV. we give values obtained by extrapolation of the parabolic formula representing the locus of our specific heat curve 0° C. to 100° C., (see p. 174 *supra*).

ATOMIC HEAT.—Lead.

I.	II.	III.	IV.
Absolute temperature.	NERNST'S observed value.	Calculated from formula (A).	Calculated from GRIFFITHS' parabolic formula.
62	5.63	5.58	5.62
66	5.68	5.63	5.64
79	5.69	5.75	5.68
93	5.76	5.84	5.73
Mean . . 75	5.69	5.70	5.67

* 'Journal de Physique,' tome ix., 1910, p. 721.

It will be seen that for the purpose of representing the experimental results, there is little to choose between the two formulæ, the greatest difference from our parabolic formula being less than 1 per cent. which NERNST states to be the probable experimental error in his observations.

The greatest divergence between NERNST'S results and the modified EINSTEIN'S formula amounts to 1·4 per cent., and it must be remembered that the empirical term $bT^{3/2}$ in that formula was added as a consequence of these experimental numbers.

Thus it appears that, in the case of lead, the simple parabolic formula holds over the range 62° C. to 373° C. absolute.

In the case of silver, NERNST records five observations (column II., *infra*).

ATOMIC HEAT.—Silver.

I.	II.	III.	IV.
Absolute temperature.	NERNST'S observed value.	Calculated from formula (A).	Calculated from GRIFFITHS' parabolic formula.
64	3·72	3·61	—
84	4·43	4·44	—
86	4·40	4·50	—
200	5·73	5·78	5·84
208	5·92	5·81	5·86

If we consider the group about 200° C., we have the following results :—

At 204° C. absolute—

Mean observed value	5·83
Calculated (EINSTEIN'S modified formula)	5·80
(GRIFFITHS' parabolic formula)	5·84

Here, again, the conclusions of the different observers are in close agreement.

At the still lower temperatures, the decrease in the observed values is so marked that, assuming the validity of NERNST'S values, the parabolic formula cannot possibly hold good, and we can only conclude that some marked change takes place in the nature of the curve below 200° C. absolute.

We hope to investigate the values of the capacity for heat of silver at some intermediate points in the large gap between the groups determined by NERNST.

In conclusion, it is notable that, with the exception of three observations upon silver taken at closely adjacent temperatures, all the values obtained by NERNST fall (within the margin of probable experimental error) upon the loci of the parabolas which express our experimental results at higher temperatures.]

APPENDIX I.

The hypothesis of DULONG and PETIT has undoubtedly been of great service to chemists; nevertheless, it is acknowledged that, at best, it is but approximately true and that whatever value of the constant is assumed, the number of exceptions at ordinary temperatures, especially in the case of elements of small atomic weights, entitles us to regard it as an indication of a probability rather than as a valid generalization.

Let us consider the values it would yield, at 0° C., if we apply it to the metals whose specific heats we have dealt with in this communication, arranged in order of their atomic weights, assuming that

$$\text{Atomic weight} \times \text{specific heat} = 6.25.$$

TABLE XXVIII.

I.	II.	III.	IV.
Element.	$\frac{6.25}{\text{atomic weight}}$	Our value at 0° C.	Column II. - Column III.
Al	0.2306	0.2096	+0.02100
Fe	0.1119	0.1045	+0.00740
Cu	0.09832	0.09088	+0.00744
Zn	0.09561	0.09176	+0.00385
Ag	0.05794	0.05560	+0.00234
Cd	0.05560	0.05475	+0.00085
Sn	0.05252	0.05363	-0.00111
Pb	0.03018	0.03020	-0.00002

The increase in the numbers in column IV., as the atomic weights diminish, is very noticeable.

If we plot the experimental values (column III., *supra*) as ordinates and the atomic weights as abscissæ, the points lie very evenly about a smooth curve of an exponential type; Cu being rather low, Zn rather high, and Sn decidedly high.

In order to obtain an expression for the curve, assume (column III.) the following values:—

$$\text{Al} = 0.2096; \quad \text{mean of Cu and Zn} = 0.09132; \quad \text{and} \quad \text{Pb} = 0.03020.$$

Then the curve drawn through these three points will be found to follow closely a mean path through the above experimental values.

The expression for this curve is

$$S = 4.804 \times \alpha^{-0.95},$$

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TABLE XXIX.—(The elements arranged in the order of their atomic weights.)

I.	II.	III.	Observer and data indicating how values in Column III. were obtained.	I.
Element.	$S = 4 \cdot 804 \times a^{-0.95}$.	S , experimental values at 0° C.		Element.
H	4.804	2.402	JOLY, at constant volume	H
He	1.290	0.762	Deduced from (1) $C_p - C_v = \frac{R}{J}$; (2) $\frac{C_p}{C_v} = 1.652$	He
Li	0.763	0.778	BERNINI, 0° to 19° = 0.837; 0° to 100° = 1.093	Li
B	0.492	0.251	Mean of values deduced from KOPP and MOISSAN and GAUTIER (amorphous)	B
C	0.453	0.113	As diamond, WEBER, at 11°	C
N	0.391	0.175	PIER, at constant volume	N
O	0.344	0.170	HOLBORN and AUSTIN (Reichsanstalt) $C_p = 0.2320$; $\gamma = 1.400$ (Lummer)	O
Na	0.244	0.291?	BERNINI, at 10° = 0.297; at 128° = 0.333	Na
Mg	0.232	0.234	VOIGT, 18° to 99° = 0.246; STÜCKER at 225° = 0.281	Mg
Al	0.2092	0.2096	GRIFFITHS'	Al
Si	0.201	0.177?	WEBER, at 57° = 0.183; at 232° = 0.203 (Cryst.)	Si
P	0.184	0.188	(Yellow), REGNAULT, -78° to +10° = 0.17; KOPP 13° to 36° = 0.202	P
Cl	0.162	0.0859?	STRECKER gives $C_p = 0.1155$ over 16° to 343° and $\gamma = 1.322$; C_p reduced to 0°	Cl
K	0.148	0.167?	Data uncertain. SCHÜZ, 0.166 at -27°; REGNAULT, 0.165 at -39°	K
A	0.145	0.0738	DITTENBERGER, $C_p = 0.123$; NIEMEYER, $\gamma = 1.667$	A
Fe	0.1052	0.1047	GRIFFITHS'	Fe
Ni	0.1003	0.1004	BEHN, -186° to +18° = 0.086; +18° to +100° = 0.109; TILDEN at 0° = 0.1007	Ni
Co	0.1000	0.099	TILDEN, -182° to +15° = 0.082; +15° to 100° = 0.103; 15° to 630° = 0.123	Co
Cu	0.0929	0.0909	GRIFFITHS'	Cu
Zn	0.0905	0.0917	"	Zn
As	0.0795	0.0778	BETTENDORFF (Cryst.), 21° to 68° = 0.0830; amorphous, 21° to 65° = 0.076	As
Kr	0.0723	0.0359	$C_p - C_v = \frac{R}{J}$; $\frac{C_p}{C_v} = 1.666$	Kr
Pd	0.0569	0.057	BEHN, -186° to +18° = 0.053; 18° to 100° = 0.059	Pd
Ag	0.0563	0.0556	GRIFFITHS'	Ag
Cd	0.0541	0.0547	"	Cd
Sn	0.0512	0.0536	"	Sn
Sb	0.0508	0.0499	GAEDE, 17° to 92° = 0.0508; temperature coefficient from NACCARI, = 0.000016	Sb
Cs	0.0462	0.0482	ECKARDT and GRAEFE, at 13°	Cs
Pt	0.0319	0.0314	BEHN, -186° to +18° = 0.0293; +18° to 100° = 0.0324	Pt
Hg	0.0313	{ 0.0335 liquid 0.0314 solid }	Liquid by BARNES; for solid see WATSON	Hg
Tl	0.0307	0.0308	SCHMITZ, -192° to +20° = 0.0300; 20° to +100° = 0.0326	Tl
Pb	0.0303	0.0302	GRIFFITHS'	Pb
Bi	0.0302	0.0300	GIEBE, -186° = 0.0284; WATERMAN +22° to 100° = 0.0304	Bi
U	0.0265	0.0274?	BLÜMCHÉ, at 49° (0° to 98°). Assume decrease like Pb	U

Hence, if $\alpha = 1$, we obtain $S = 4.804$, that is, just twice the value found by JOLY for the specific heat of hydrogen at constant volume.

We have endeavoured to ascertain how nearly the values obtained from this expression are in harmony with the conclusions of other observers in the case of elements not included in our list. It is difficult, however, in regard to the majority of the elements, to consider any conclusion thus arrived at as decisive. The determinations in the case of the rarer elements have been made with such small quantities that the results are open to suspicion, and, but few investigators have so arranged their temperature ranges as to include 0°C . Where values of S for different values of θ have been given, we have, on the assumption that the changes are of a linear order, deduced the probable values at 0°C ., and in Table XXIX., p. 179, we have indicated the authority and the temperature ranges from which those values were deduced. Where no data for such a reduction can be found, we have inserted any values which fall near 0°C ., together with the mid-temperature and the experimental range. For example, Cs 13°C . (ECKARDT, 0°C . to 26°C .). We have given all the information we have

TABLE XXX.

Column I.		Column II.			
	Per cent. differences.		Per cent. differences.		
H	0	He	+15.0		
Li	+2.0	N	-10.0?		
O	-1.2	Cl	+6.0		
Mg	+0.9	Na	+16.0?		
Al	0	K	+11.0?		
P	+2.2	Sn	+4.6		
A	+1.9	Cs	+4.0?		
Fe	-0.5		Column III.		
Ni	0				
Co	-1.0				
Cu	-2.2				
Zn	+1.3				
As	-2.3				
Kr	-0.7				
Pd	0				
Ag	-1.2				
Cd	+1.1				
Sb	-1.6				
Pt	-1.6				
Tl	+0.3				
Pb	-0.3				
Bi	-0.6				
U	+3.0?				
			Calculated.	Experimental values.	
		B	0.492	0.251	
		C	0.452	0.113	
		Si	0.201	0.177	
		Hg	0.0313	0.0335 (liquid) 0.0314 (solid)	
Sum of per cent. differences	} = -0.5				

been able to gather, concerning the specific heats of the elements, which appeared to us to carry sufficient weight to render the deduced values of any service in such an enquiry; many of those included should, for the reasons given in the introduction to this paper, be regarded as rough approximations only. No element has been omitted in connection with which any satisfactory evidence concerning the specific heat at 0°C . was obtainable.

In column I. of Table XXX., p. 180, we enumerate those elements in which the agreement between the calculated and the experimental values may be regarded as close (*i.e.*, within 3 per cent.), and we have in each case indicated the percentage difference and its sign.

In column II. we place those in which the differences vary from 3 to 16 per cent., including some in which the probable error may be of like dimensions; in column III., those experimental results which differ so greatly from the calculated as to exclude the possibility of agreement. In the case of gases, the experimental values are multiplied by 2.

Remarks on Columns.

Column I.—The sum of the differences (-0.5) and the distribution of the signs show that the experimental values are very evenly distributed about the locus of the curve.

Column II.—The experimental values of N, Na, and K do not appear to be sufficiently established to lend much weight to the results.

The experimental value of the specific heat of tin at 0°C ., as compared with that of other metals examined by us, is high. It is a significant fact that tin, at temperatures below 0°C ., tends to revert into the grey powder form.

[Since the above was written, we have made determinations of the specific heat of sodium at 0°C . Two different samples were used, and the results were in close agreement, giving the value 0.2863 for the specific heat.

The few experiments at higher temperatures (50°C .) indicate that the increase in specific heat with temperature is considerably greater in the case of sodium than in the other metals examined by us, and is of the order of 0.11 per cent. per 1°C .

In this connection it should be remembered that sodium has the lowest melting-point of all the metals considered in the above table.]

Column III.—Two curious coincidences present themselves. The calculated value of C is almost exactly four times that of the diamond.

The mean experimental value for amorphous B is closely half of the calculated one.

It has been shown (see, for example, Al and Pb *supra*) that the rate of change of $\delta S/\delta\theta$ as θ changes, varies markedly for different elements; hence, any relation such as that denoted by the equation $S = 4.804 \times \alpha^{-0.96}$, which holds true for any given temperature, cannot be valid at other temperatures. There are, therefore, serious difficulties in the way of accepting any definite connection between "S" and " α " at an arbitrary

temperature such as 0° C., although it is probable that a large majority of elements are in a stable condition at that temperature.

It is, however, evident that the curve $S^* = 4.804 \times a^{-0.95}$ yields throughout the whole range of atomic weights values of S (of $2S$ in the case of gases) which, in the large majority of cases, are within 2 per cent. of the most probable values.

We prefer to postpone any expression of our views on this matter until we are able to ascertain the results of our experiments at low temperatures.

The Relation between S and θ .

The curves given in fig. 8 show that the curvature from 0° C. to 100° C. is far more marked in the case of Fe and Al than in any of the remaining metals, with, perhaps, the exception of Zn at the higher temperatures. If we produce backwards the parabolas which have been found to represent the mean paths over the above range, it is found that the curves of Al and Fe (if they continue of the same character) must cross those of the remaining metals before the temperature falls to absolute zero.

If we venture to extrapolate, in order to ascertain the values of S given by the respective parabolic equations at -273° C., we obtain the numbers given in column II., Table XXXI.

TABLE XXXI.

Element.	S at -273° C.	Atomic heat at -273° C.
Al	0.1306	3.540
Fe	0.0131	0.730
Cu	0.07438	4.728
Zn†	0.06554	4.294
Ag	0.04986	5.378
Cd	0.04402	4.948
Sn	0.04199	4.997
Pb	0.02186	4.527
Mean of all but Al and Fe . . .		= 4.813

It appears possible that the values of the specific heats of the last six metals may continue to follow the parabolic paths as the temperature falls to -273° C., for an

* The expression, atomic heat = $4.804 \times a^{0.05}$, is obviously an alternative manner of expressing the same relation.

† In the case of Zn, the equation is deduced from values found from 0° C. to 50.5° C., for reasons given.

exceedingly small error in their coefficients over the range 0°C. to 100°C. would account for considerable discrepancies in the values of their Atomic Heats at absolute zero, the more especially as the resulting values of S are multiplied by factors ranging from 63 to 200.

Experimental errors, however, could not account for such divergent results as those given by Al and Fe, hence either the atomic-heat curves of these two metals undergo change at low temperatures, or their values at absolute zero must be lower than that of the others in the above list.

If we assume the continuity of the paths of the six metals above referred to and deduce their respective specific heats at -273°C. from the mean atomic heat ($4\cdot813$), and for the other two points on the parabola employ the values at 0°C. and 100°C. , we obtain the following equations (t being expressed in the absolute scale)*:—

$$\text{Cu} \dots S = 0\cdot0758 (1 + 0\cdot0008352t - 0\cdot00000039t^2),$$

$$\text{Zn} \dots S = 0\cdot07374 (1 + 0\cdot0011155t - 0\cdot000000807t^2),$$

$$\text{Ag} \dots S = 0\cdot0447 (1 + 0\cdot00122t - 0\cdot00000122t^2),$$

$$\text{Cd} \dots S = 0\cdot0429 (1 + 0\cdot0013356t - 0\cdot000001186t^2),$$

$$\text{Sn} \dots S = 0\cdot0405 (1 + 0\cdot0014514t - 0\cdot0000009665t^2),$$

$$\text{Pb} \dots S = 0\cdot02327 (1 + 0\cdot001544t - 0\cdot00000166t^2).$$

If the values of S at the various temperatures at which it was determined by us are now deduced from these equations, it will be found that the differences between the experimental and the calculated values are very small, in no instance exceeding 0·3 per cent., and in most cases much less.

The remarkable approximation between the hypothetical value of the atomic heat at 0°C. ($4\cdot804$) of a body with atomic weight 1, and the likewise hypothetical value of the atomic heat of this group of metals at absolute zero ($4\cdot813$), is probably a coincidence, but may possibly be of some significance.

APPENDIX II.

An inspection of the atomic heats of the metals investigated by us indicates that those of low melting-points have high atomic heats. This is true throughout the range 0°C. to 100°C. , if the values at any given temperature within that range are

* Many equations of an exponential nature, and also of the forms suggested by Professor PERRY ('Phil. Trans.,' vol. 194, pp. 250–255) have been investigated, but none of them fitted the experimental results so closely as the parabola.

considered. It thus appears as if there was some relation between the temperature of the melting-points and the atomic heats.

In fig. 9 the atomic heats at 50° C. have been plotted as ordinates, and the melting-points as abscissæ.

This temperature was selected for comparison as the most reliable data given by other observers have been obtained over temperature ranges including 50° C. as a mean.

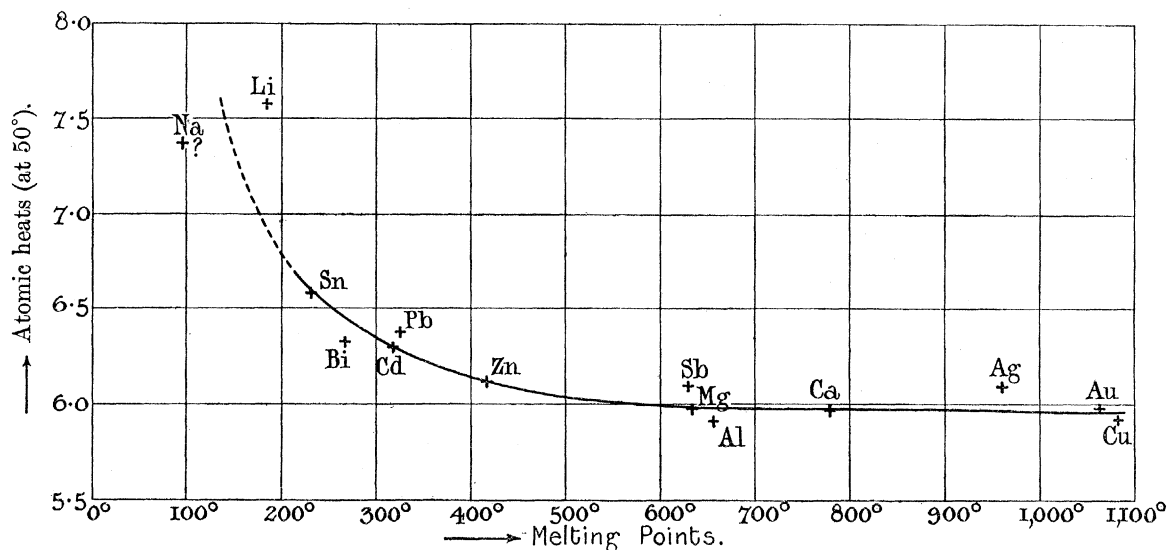


Fig. 9.

[Determinations made by us since the communication of this paper to the Society give the value of the atomic heat of sodium at 50° C. as 7.01, in place of the value 7.37 shown in the diagram, this latter number having been based on the values of NORDMEYER and BERNOUILLI between -185° C. and $+20^{\circ}$ C. (5.38), and BERNINI's at $+10^{\circ}$ C (6.83) and $+128^{\circ}$ C. (7.66).]

APPENDIX III.

Soldering Glass to Metal.

The process is identical for glass, quartz and, no doubt, for porcelain.

The end of the glass or quartz tube is painted with a solution of platinum chloride in a volatile oil. (Solution is sold under the trade name of Liquid Platinum, No. 1.)

The coating is very gently heated at first, and the temperature slowly increased, until all the volatile matter has been driven off and a brilliant film of platinum obtained. The higher the temperature to which the tube is raised, the better the adherence of the film. The tube should glow with a dull red light, before being

allowed to cool. If a thick film is desired, additional coatings can be given. Care should be taken to prevent contamination by flame-gases; if this occurs the surface should be brightened by means of ordinary metal polish.

The next step is to "tin" the surface, and this requires care. The tube is gently heated and rubbed with a lump of resin; the solder melted on with a clean soldering iron which should be only sufficiently hot to just melt the solder. With care the entire platinised surface may be coated with an irregular coating of solder. Vigorous rubbing of the surface with the soldering iron should be avoided, as it would probably tear the film away from the glass.

The tube is then ready to be soldered into the metal ferrule which should be "tinned" on the inside.

