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The Capacity for Heat of Metals at Low Temperatures

E. H. Griffiths and Ezer Griffiths

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The Capacity for Heat of Metals at Low Temperatures.

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

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Introduction.

In two previous papers* accounts have been given of experimental investigations into the variation with temperature of the specific heats of certain metals, the range of temperature covered being, in general, from 0° C. to 100° C., or, in the case of sodium, to nearly 140° C.

The present paper is a further contribution to the same subject, the temperature range being continued down to about $-160°$ C.

As pointed out in the previous papers, determinations of the true specific heats throughout this range are needed to bridge the large gap between Nernst's observations at liquid hydrogen and liquid air temperatures and the observations above referred to at higher temperatures.

For determinations in the vicinity of fixed points at low temperatures the method employed by Nernst is an admirable one and his experimental values carry great weight.

He has given, in the cases of silver and lead, the results of investigations at higher temperatures (*e.g.*, at $-78°$ C.), but these determinations cannot, for several reasons, be regarded as satisfactory. The validity of this conclusion is indicated by the fact that individual values at the same temperature differ by about 4 per cent.

PART I.

Experimental Methods and Results.

(1) *Description of Apparatus.*

Our method of investigation demanded a constant temperature enclosure, and the apparatus described in succeeding pages was designed for this purpose.

We abandoned the use of liquid air on account of the uneconomical nature of the processes that would be involved, and utilised the Joule-Thomson cooling effect in a direct manner.

Fig. 1 is a sectional view of the apparatus. Compressed air† at a pressure of 2000 to 3000 lbs. per square inch entered the interchanger by the pipe A. This interchanger BB was constructed of ordinary solid drawn copper tubing, $\frac{1}{8}''$ bore, coiled in the form of flat spirals. Successive layers of the coil were separated by strips of cardboard and the entire coil was inserted into a length of motor tyre tubing which fitted it closely. From the interchanger coils the air was carried to the valve C, by means of which an observer controlled the flow, excess of air being discharged at the safety valve on the compressor. Although not shown in the figure, a Hook's joint was inserted in the spindle controlling the valve.

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* 'Phil. Trans.,' A, 500, vol. 213, p. 119, 1913; 'Roy. Soc. Proc.,' A, vol. 89, p. 561, 1914.

† Freed from moisture and CO_2.

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After expansion the air circulated through the coil of lead tubing, D, and then back over the surface of the interchanger coils.

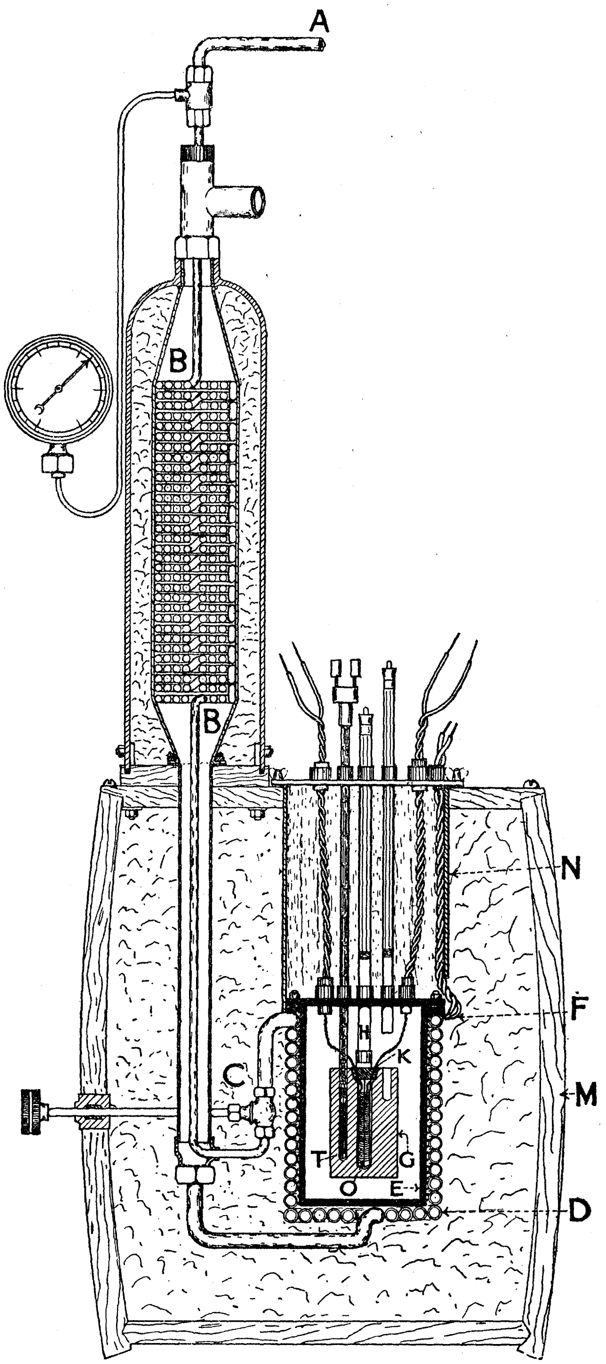

Fig. 1. BB, interchanger coils; C, valve; D, coil piping around enclosure; E, thick copper enclosure; F, insulated copper wire around enclosure; G, metal block; H, supporting tube; K, taper plug closing central hole in block; O, heating coil; T, platinum thermometer; N, cardboard tube to keep slag wool in position.

On the exterior surface of the thick walled copper enclosure, E, was wound a layer of insulated copper wire, F, which served as a resistance thermometer. Variations in

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temperature of the walls of this enclosure were rendered visible by the movements of a galvanometer spot. By controlling the flow of air the oscillations of the spot could be kept within narrow limits and, under normal conditions, the oscillations did not exceed a hundredth of a degree.

The interior of the wooden vessel, M, was packed with slag wool, the passage for the withdrawal of the copper enclosure being kept clear by a cylindrical tube of cardboard, N.

The space between the top of the enclosure and the outer lid was filled by wrapping felt matting around the glass tubes and leads.

The block of metal, G, was suspended within the enclosure by a single glass tube, H.

The central hole contained the heating coil, O, of manganin wire wound on a mica rack and immersed in a light paraffin, usually petrol.

The heating coil was fixed to a short taper plug of copper, K, which closed the central hole. Many such coils and plugs were used in the course of the work, since it was rarely possible to withdraw a plug, after it had once been firmly inserted, without doing considerable damage to the heating coil. The usual resistance for the heating coil was about 26 ohms.

In our preliminary experiments we used many modifications of the above arrangements: *e.g.*, the central hole was but one half the diameter and was closed by a rubber washer pressed down by the lid; the heating coil was of 12 ohms resistance with leads either of manganin or of copper. The defect of this arrangement was that the rubber disintegrated and, with such a volatile liquid as pentane, it was necessary to ensure that no evaporation could take place during the interval (prior to an experiment) that the block was at room temperature.

The platinum thermometer was inserted in the cylindrical hole, T, the annular gap between the stem and the walls being closed by a packing of asbestos thread. The thermometer was connected to a Callendar and Griffiths resistance bridge which was carefully recalibrated during the course of the work.

It may be remarked that, in the preliminary experiments referred to above, a thermometer with a much larger size coil was used. The results obtained were in complete agreement with the values subsequently found by the modified arrangements, using a smaller sized thermometer (Q) the coil of which was constructed of platinum wire of a higher degree of purity.

The same samples of metals were used in this as in the previous work, their dimensions being reduced to the required size by machining.

In the case of sodium, this procedure could not be followed, so another copper sheath was constructed and filled in the manner described below.

(2) *Construction of the Sodium Block.*

The block of sodium was constructed on a different plan* from that described in the

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* We are indebted to Mr. EDGAR A. GRIFFITHS for this design.

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previous work and, as the method is generally applicable to substances of low melting point, a brief description may be of use.

A section of the block complete is shown in fig. 2. The heating element consisted of 300 cm. of double cotton covered manganin wire, No. 36, enclosed in a fine metal tube* of about 1 mm. bore; the total resistance of the coil was about 38 ohms.

The wire was dipped in hot paraffin wax before insertion in the tubing and the insulation resistance between wire and tube was found to be entirely satisfactory.

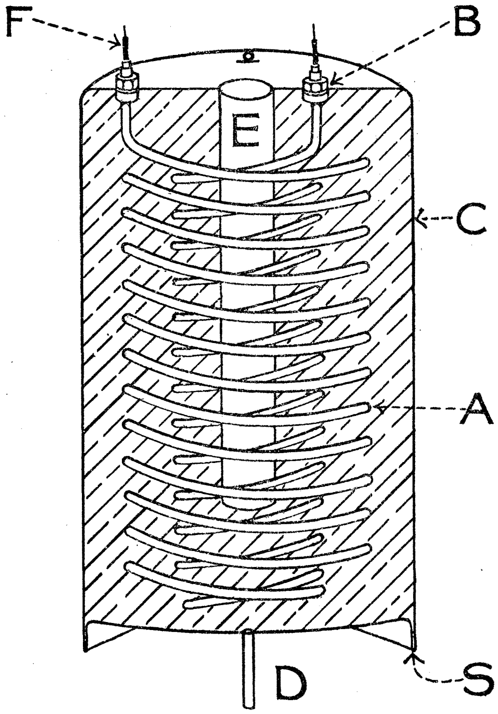

Fig. 2. A, tubing containing insulated manganin wire; B, hollow steel bolts brazed on to tubing to make joint with copper case; C, copper case silver-soldered at S; D, tube used for filling case with sodium, afterwards sealed off; E, copper tube closed at lower end to contain Pt thermometer; F, copper leads to heating coil.

The tubing was wound in the form of a double helix and spaced so as to be distributed as uniformly as possible through the volume of the sodium.

(This would be a point of considerable importance when working with poor conductors of heat.)

The other details of the construction will be understood from the figure.

One further point, however, deserves mention, namely, the soldering on of the bottom of the case after the insertion of the helix.

It was found that hard soldering was absolutely necessary and, since this involved

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* This solid drawn tubing was composed of copper alloyed with a small proportion of brass to strengthen it.

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a fairly high temperature, precautions had to be taken to shield the spiral, otherwise the insulation would have suffered.

This protection was effected by drawing the spiral up compactly against the top with thin wire loops passing out through the bolt holes. The case was fixed in an inverted position in water with about 1 cm. projecting, the ends of the fine tubing being capped with rubber tubing to prevent access of water to the manganin wire.

The spiral, being totally immersed, was thus effectively shielded, while the bottom was soldered on with an oxy-coal gas blowpipe and, when completed, the spiral was released from without and the nuts screwed on to the ends of the tubing.

Filling the case with sodium was effected *in vacuo*, the electrically heated iron vessel containing the sodium being supported by a tripod, the tube from the case projecting up through the bottom of the iron vessel.

After sealing, the sodium was annealed by slow cooling from the molten state.

The block was suspended within the enclosure by two threads, the platinum thermometer being inserted into the central copper tube.

Two experiments near 0° C. were performed by the method described later in this paper, and the resulting mean value of the specific heat, namely, 0·2826 at $-2^\circ{\cdot}5$ C., agrees extremely well with the value at 0° C. for the annealed state, previously obtained,* namely, **0·2829**.

It will be observed that in the present arrangement there were no supporting tubes of quartz; the thermometer was in the centre, while the heating coil was distributed throughout the volume of the metal and had a resistance of about twice that of the coil used previously.

The relative proportions of copper and sodium were very different, as well as the geometrical form of the blocks. When we consider the complete change, both of apparatus and of method, the close correspondence between the results affords a strong proof of the validity of the assumptions underlying both methods.

(3) *Measurement of Mass, Time, Electromotive Force, &c.*

Details concerning the measurement of the above quantities have already been given† and all the precautions there dealt with have been observed.

The method of determining the correction for the heating effect of the current on the resistance of the coil was slightly different from that previously described, insomuch that the temperature of the block, while the electrical supply was on, was maintained constant by lowering the temperature of the enclosure until losses by radiation,‡ &c., balanced the electrical supply for each rate.

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* 'Roy. Soc. Proc.,' A, vol. 89, 1914, p. 567.

† *Loc. cit.*, p. 126.

‡ To save repetition, losses by radiation, convection, and conduction will be referred to as losses by radiation.

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The procedure in other respects was the same as before. The rise in temperature of the wire above the mean temperature of the block is given by the relation

$$0 = 0{\cdot}10n^2,$$

where n is the number of standard cells balanced at the ends of the heating coil.

Thus, from the temperature coefficient of resistance at any temperature, the correction could be calculated.

Our practice of determining the resistance of the heating coil on the completion of an experiment, when the temperature of the block was a few degrees above the surroundings, rendered the correction of small magnitude and in most cases it could be neglected.

In the case of sodium it was found that the increase of resistance due to increase of current was not appreciable.

(4) *Measurement of Temperature.*

The calibration of a platinum thermometer for use at low temperatures presents some difficulty, since the parabolic formula

$$t - pt = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}$$

does not hold true below about −40° C.

At first we endeavoured to approximate to the true scale below 0° C. by means of an expression of the form

$$\mathrm{R} = \mathrm{R}_0\,(1 + \alpha t - \beta t^2 + \gamma t^3),$$

where the constants α, β, and γ are determined by standardisation in liquid oxygen, ice, steam and vapour of boiling sulphur.

Recently, however, HENNING[*] has effected a direct comparison down to liquid air temperature of some platinum thermometers with the hydrogen gas thermometer, and as our standardisations enabled us to utilize the data obtained by HENNING for the purpose of a reduction to the gas scale, we base our calculations on the results obtained in that comparison. He found that thermometers constructed of wires having different values of δ[†] do not give consistent results at low temperatures, their indications differing by as much as half a degree.

If, however, the platinum temperatures pt' and pt deduced from observations with two thermometers are compared at the same true temperature t, then the following relationship holds good

$$pt' - pt = c\,pt\,(pt - 100), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is a constant determined by a comparison of the two thermometers at one temperature, as for example, in a liquid air bath.

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[*] 'Annalen d. Physik,' vol. 4, p. 635, 1913; vol. 10, p. 1064, 1913.

[†] HENNING determined δ by the freezing-point of zinc (419°·40).

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While it was not possible to compare our thermometers with a standard, the observations in liquid oxygen supplied data for calculating c, taking the boiling-point of liquid oxygen on the gas scale as $-182^{\circ}\cdot 97$ C., thus connecting our scale with that of the platinum thermometer which HENNING had calibrated by means of the gas thermometer.

Table I. below summarises some of the fundamental quantities for the various thermometers :—

Column I.—The letters designate the various thermometers.

Column II.—The mean coefficient between 0° C. and 100° C., denoted by α.

Column III.—The constant of the parabolic formula

$$t-pt = \delta\left\{\left(\frac{t}{100}\right)^2 - \frac{t}{100}\right\}$$

as determined by the sulphur point.

Column IV.—Pt (oxygen), the boiling-point of oxygen on the platinum scale.

Column V.—The difference between the boiling-point of oxygen by the gas thermometer and the value deduced from the parabolic formula given above.

Column VI.—The constant c of equation 1, connecting the thermometer with HENNING'S standard.

TABLE I.

I.	II.	III.	IV.	V.	VI.
Thermometer.	$\alpha \times 10^2$.	δ.	Pt (oxygen).	Difference.	$c \times 10^5$.
Q	0·38598	1·514	−192·37	1·56	+0·07
AA	0·38591	1·534	−192·60	1·68	−0·34
AB	0·38899	1·508	−192·63	1·85	−0·39
CD	0·38888	1·501	−192·71	1·99	−0·53

HENNING'S standard platinum thermometer gives a difference of $1^{\circ}\cdot 74$ C. from the gas scale at the oxygen point.

The values of the constant c for the different thermometers examined by him vary from $-0\cdot 68$ to $+0\cdot 11$.

The quantity with which we were most concerned, however, was not the exact

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temperature on the gas scale at which the values of the specific heat were determined, but the value of $\partial(t)/\partial(pt)$ at each temperature.

For this purpose it was more convenient to work with the curve representing the relation between $(t-pt)$ and pt, and in case any revision should be necessary in future, we have inserted below a table of the values of $\partial(t)/\partial(pt)$ used in the reduction of our observations.

TABLE II.

$pt°$.	$t-pt$.	$\partial(t)/\partial(pt)$.
− 20°	0·33	0·980
− 40°	0·78	0·974
− 60°	1·38	0·967
− 80°	2·12	0·960
−100°	2·98	0·952
−120°	4·00	0·944
−140°	5·21	0·934
−160°	6·62	0·924
−180°	8·27	0·912
−190°	9·17	0·906

(5) *Details of the Standardisation of the Thermometers.*

Four thermometers were standardised at the same time; thermometer AA was used in the preliminary experiments, Q in the final determinations, while AB and CD were used in subsidiary work with the ice calorimeter.

At 0° C., 100° C., and 444°·6 C. (boiling-point of sulphur), the standardisations were performed with the customary form of apparatus and the results call for no remark.

For the low temperature point −182°·97 C. (boiling-point of liquid oxygen), a two-litre vacuum flask was filled with commercial liquid oxygen. The thermometer bulbs were well immersed in the liquid and the mouth of the flask lightly stoppered with cotton wool.

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The observations were continued at intervals, as long as the level of the oxygen was sufficient for total immersion of the coils and portion of the stem, with the object of ascertaining how far the constancy was affected by the presence of traces of nitrogen in the liquid oxygen.

Three different values of the battery current were used, and Table III. below summarises one series for thermometer Q, with a battery current giving 0·003 amperes through the wire of the coil.

The quantities in brackets [ ] are the corrections necessary to reduce the resistance to mean box units; temperature of box, 17° C., and barometer 760 mm.

The value of $\frac{\partial p}{\partial t}$ for liquid oxygen was taken as 77 mm. Hg per degree Centigrade.

The abnormally high value of R indicated by the asterisk (*) is probably due to superheating of the liquid and was also shown by another thermometer standardised at the same time.

TABLE III.—Thermometer Q in Oxygen.

Time.	Plugs.	Bridge wire.	Temperature box.	Barometer.	Resistance (after correction).
h. m.			° C.		
Date: October 14th.					
12 32	330·116	3·212 [−0·029]	18·09 [+0·078]	767·41 [−0·526]	332·851
3 21 3 22		5·447 5·510 [−0·043]	18·485 18·49 [−0·109]	766·54 [−0·464]	335·196*
8 43 8 45 8 50		3·209 3·186 3·176 [−0·029]	18·83 18·85 18·85 [+0·138]	765·81 [−0·412]	333·004
Date: October 15th.					
10 37 10 39 10 41 10 43 10 46	330·116	3·430 3·515 3·630 3·593 3·550 [−0·032]	17·97 17·98 17·985 [+0·069]	767·22 [−0·513]	333·184

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(6) *Heat Capacity of Subsidiary Substances.*

The mean values of the specific heats of glass, petrol, alloy, &c., between 0° C. and liquid air temperatures were determined by means of the ice calorimeter.

The arrangement was very simple; a vessel with a central tube was fixed above the calorimeter and the annular space was filled with liquid air.

The substance was suspended in the central tube alongside a platinum thermometer, and when it had settled to an approximately constant temperature it was dropped directly into the calorimeter.

An approximate value of the coefficient of variation of specific heat with temperature was obtained by determining the mean values of the specific heats over another range, usually 0° C. to 80° C., and assuming a linear variation the values given in Table IV. were deduced.

Since the heat capacity of these substances entered only as a small correction, the approximate values were amply sufficient for our purpose.

TABLE IV.

Substance.	Specific heat at 0° C.	Specific heat at − 150° C.
Glass (soft soda).	0·180	0·092
Petrol (density 0·74) . .	0·455	0·358

The calorimeter constant* was taken as 15·486 mgr. mercury per mean calorie.

(7) *Method of Experiment.*

The constant attention necessary to maintain the surrounding enclosure at a fixed temperature imposed considerable strain on the observer attending to this part of the apparatus and precluded the possibility of experiments such as those described in our previous work.

The procedure adopted in the present investigation was as follows:—

The temperature of the enclosure was lowered progressively by utilizing the full supply from the compressor and controlling the flow so as to produce a steady pressure drop through the valve of 120 to 150 atmospheres.

The temperature of the block would fall at a steady rate by radiation to the enclosure walls, and when its temperature had nearly reached the desired point the compressor was stopped.

The temperature of the enclosure would then rise rapidly by conduction from without and soon pass that of the block which, in consequence of the slow transmission of heat by radiation, would lag behind that of the walls.

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* 'Proc. Phys. Soc.,' London, vol. 26, p. 1, 1913.

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The safety valve on the compressor was adjusted to blow off at the required pressure (the lower the temperature of the experiment the higher the blowing-off pressure) the engine was then again started and the temperature of the enclosure walls maintained at a steady temperature of about three degrees higher than that of the metal block.

Some time had to elapse before the conditions were sufficiently settled to justify the commencement of an experiment.

The first group of readings consisted of observations of the rate of rise of temperature of the block by radiation, the transits of the temperature being observed across successive equal intervals (usually 0°·04 C.); the time between successive transits being of the order of 50 seconds.

The electrical supply was then switched on and, after allowing a little time for the setting up of a steady gradient, lag, &c., transits every 0°·2 C. were taken.

When the temperature had risen two or three degrees above the surroundings, the electrical supply was switched off and observations of temperature and time continued.

The temperature would rise to a maximum, then fall steadily under the influence of radiation; the rate of cooling being observed in precisely the same manner as the rate of rise before the electrical supply.

If σ is the rate of rise or fall due to radiation for 1° C. difference in temperature between the block and the surroundings;

θ_0 the temperature of the walls of the enclosure;

θ_l the thermometer lag for the rate of electrical supply—the magnitude of this lag being determined by observations of temperature and time after switching off the electrical supply.*

Then assuming NEWTON'S law to be valid for the loss or gain by radiation (an assumption which was fully justified by the experimental results), we have the expression

$$\frac{\partial\theta}{\partial t} = \sigma(\theta - \theta_0), \quad \ldots \ldots \ldots \quad (2)$$

for the rate of rise or fall under the influence of radiation alone.

Hence, plotting $\partial\theta/\partial t$ against θ, the straight line joining the two groups will cut the temperature axis at $\theta = \theta_0$, which determines the temperature of the surroundings.

For the rate of rise under the combined effect of the electrical supply and radiation, we have the equation

$$\frac{\partial\theta}{\partial t} = \frac{(n\mathrm{E})^2}{\mathrm{JR}f(\mathrm{MS}+ms)} + \sigma(\overline{\theta+\theta_l} - \theta_0), \quad \ldots \ldots \quad (3)$$

θ being the apparent temperature.

Plotting the observed rates of rise on the same scale as the radiation observations, it is obvious that the straight line thus obtained should be parallel to the line joining the two groups of radiation observations, since the tangent of the angle made with the θ axis is equal to σ.

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* See p. 151, 'Phil. Trans.,' A, vol. 213, 1913.

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For $\overline{\theta+\theta_l} = \theta_0$ the radiation term vanishes, hence, if $\partial\theta_N/\partial t$ denotes the value of the ordinate at this point,

$$\frac{\partial\theta_N}{\partial t} = \frac{n^2E^2}{JRf(MS+ms)}, \qquad (4)$$

which enables the value of the specific heat to be deduced.

As an illustration of the method, one experiment in the case of zinc at −64° Pt may be quoted.

All temperatures are expressed on the platinum scale, the conversion being effected by the factor $\frac{\partial(t)}{\partial(pt)}$ $(\equiv f)$ in the final reduction.

Table V.

I. Warming up under Radiation.

Temperature.	$\frac{\partial\theta}{\partial t}\times 10^4$.	Temperature.	$\frac{\partial\theta}{\partial t}\times 10^4$.
−66·75	3·87	−66·63	3·81
−66·71	3·84	−66·59	3·77
−66·67	3·99		

II. Electrical Supply on.

Temperature. $(\theta+\theta_l)$.	$\frac{\partial\theta}{\partial t}\times 10^4$.	Temperature. $(\theta+\theta_l)$.	$\frac{\partial\theta}{\partial t}\times 10^4$.
−65·44	35·78	−63·03	33·09
−65·04	35·44	−62·63	32·51
−64·64	34·98	−62·23	32·13
−64·23	34·31	−61·87	31·59
−63·83	34·01	−61·47	31·15
−63·43	33·57		

III. Cooling down by Radiation.

Temperature.	$\frac{\partial\theta}{\partial t}\times 10^4$.	Temperature.	$\frac{\partial\theta}{\partial t}\times 10^4$.
−61·35	2·65	−61·47	2·54
−61·39	2·66	−61·51	2·53
−61·43	2·60		

The data for computing III. in the above table were obtained from the following observations of temperature and time, after switching off the electrical supply :—

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IV. Cooling Curve.

(Time measured from instant of switching off, and temperature difference from the last transit.)

Time.	Temperature difference.	Time.	Temperature difference.
secs.		secs.	
246	+0·120	698	0
331	0·100	786	−0·020
396	0·080	854	−0·040
481	0·060	942	−0·060
545	0·040	1011	−0·080
633	0·020		

If the results of IV. are plotted on sectional paper and the line prolonged to cut the temperature axis for $t = 0$, we obtain the "rise above" after switching off, which quantity is denoted by θ_l in the equations above. In this particular case $\theta_l = 0{\cdot}185°$ C.

Referring to fig. 3, the observations at "A" are the rates of rise by radiation in the above experiment, when the temperature of the block was below that of the surroundings; those at "B" correspond to the rate of cooling under radiation after the block has been heated up above the surroundings by the electrical supply.

In some experiments the electrical supply was switched off; a group of "radiation" observations taken; then the electrical supply continued and the experiment completed in the usual way.

The intermediate group of "radiation" points thus obtained always fell on the straight line joining the extreme groups and justified the application of NEWTON's law for the small temperature differences employed.

The observations distributed about the line "CD" correspond to the period of the electrical supply. It will be observed that, as required by theory, "CD" is parallel within the limits of experimental error to the line "AB."

If desired, the radiation group at "A" could be dispensed with and the line drawn through the mean of group "B" parallel to "CD." Occasionally this plan was adopted when the observations "A" were very irregular on account of the conditions not being sufficiently steady when the observations were commenced.

The point "N" on "AB" corresponds to the temperature at which there is no loss or gain by radiation and "NQ" to $\partial\theta_N / \partial t$ of equation 4.

In the case of several metals, experiments were performed near 0° C. by this method and also by the "intersection" method described in the previous paper, with entire accordance between the results.

(8) *Experimental Results.*

The results obtained in this and the previous investigation are summarised below. Where more than one experiment has been performed at any temperature, the mean

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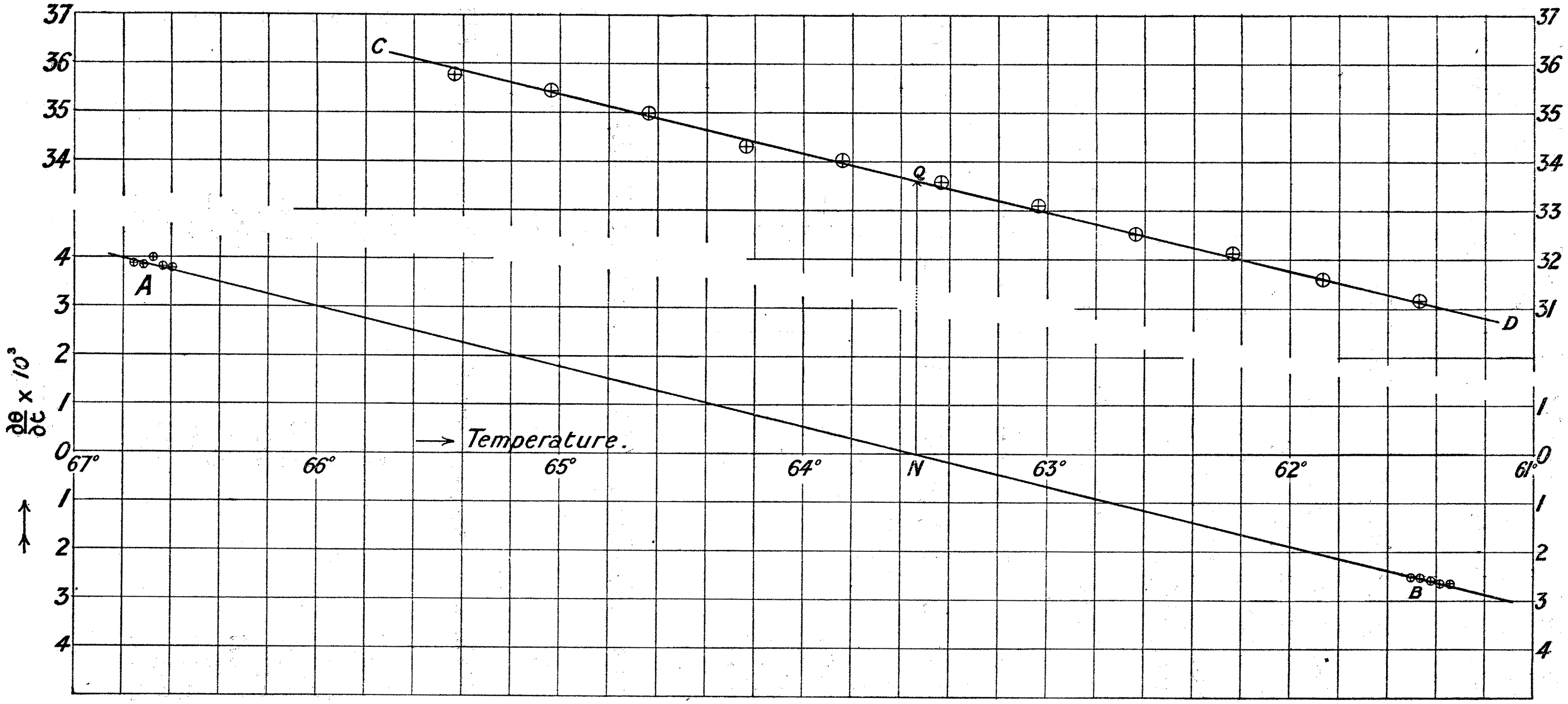

Fig. 3.

Line CD, rate of rise due to electrical supply and radiation; Group A, rate of rise due to radiation when temperature of block below surroundings; Group B, rate of fall due to radiation when temperature of block above surroundings.

Note.—Temperatures are in degree *pt* below 0° C.

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value is given. The atomic heats were plotted on a large scale against absolute temperature and the mean curves drawn through the observations, the lines being prolonged through the experimental values of NERNST* or DEWAR† at very low temperatures.

Explanation of the Tables VI.–XIII.

Column I.—The absolute temperature, T.
Column II.—The specific heat at this temperature.
Column III.—The atomic heat under constant pressure, which is denoted by C_p.
Column IV.—Value of C_p at this temperature, as read from the smoothed curve.
Column V.—Difference, Column III. minus Column IV.

TABLE VI.—Aluminium. (Atomic Weight: 27·1.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
158·7	0·1709	4·63	4·62	+0·01
191·5	0·1867	5·06	5·06	—
273·1	0·2096	5·68	5·68	—
301·5	0·2147	5·82	5·82	—
324·1	0·2184	5·92	5·92	—
370·6	0·2248	6·09	6·09	—

TABLE VII.—Iron. (Atomic Weight: 55·85.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
140·3	0·0770	4·30	4·29	+0·01
214·3	0·0967	5·40	5·40	—
267·0	0·1044	5·83	5·82	+0·01
273·1	0·1045	5·84	5·86	−0·02
274·0	0·1045	5·84	5·87	−0·03
283·1	0·1060	5·92	5·93	−0·01
294·1	0·1077	6·02	6·00	+0·02
297·6	0·1080	6·03	6·02	+0·01
323·4	0·1105	6·17	6·16	+0·01
339·4	0·1112	6·21	6·23	−0·02
370·6	0·1137	6·35	6·35	—

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* Berlin, 'Sitz. Ber.,' p. 262, 1910; pp. 306, 316, 494, 1911; p. 1160, 1912.

† 'Roy. Soc. Proc.,' A, vol. 89, p. 158, 1913.

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TABLE VIII.—Copper. (Atomic Weight: 63·57.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
138	0·07766	4·94	4·92	+0·02
149·5	0·07942	5·05	5·05	—
171·4	0·08235	5·23	5·23	—
204·9	0·08593	5·46	5·46	—
273·1	0·09088	5·78	5·78	—
301·6	0·09230	5·87	5·87	—
336·7	0·09365	5·95	5·96	−0·01
340·5	0·09387	5·97	5·97	—
370·5	0·09521	6·05	6·04	+0·01

TABLE IX.—Zinc. (Atomic Weight: 65·37.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
145·5	0·08421	5·50	5·50	—
211·1	0·08898	5·82	5·82	—
273·1	0·09176	6·00	6·01	−0·01
294·6	0·09265	6·06	6·06	—
323·6	0·09412	6·15	6·14	+0·01
370·5	0·09521	6·22	6·22	—
396·5	0·09570	6·26	6·26	—

TABLE X.—Silver. (Atomic Weight: 107·88.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
158·1	0·05210	5·62	5·62	—
187·4	0·05362	5·78	5·78	—
273·1	0·05560	6·00	6·00	—
301·5	0·05613	6·05	6·05	—
340·5	0·05680	6·13	6·13	—
370·6	0·05737	6·19	6·19	—

TABLE XI.—Cadmium. (Atomic Weight: 112·4.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
108·3	0·04907	5·52	5·52	—
181·8	0·05287	5·94	5·94	—
273·1	0·05475	6·15	6·17	−0·02
301·5	0·05554	6·24	6·24	—
327·6	0·05616	6·31	6·31	—
370·8	0·05714	6·42	6·42	—

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TABLE XII.—Lead. (Atomic Weight: 207·1.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
118·6	0·02867	5·94	5·93	+0·01
166·3	0·02903	6·01	6·02	−0·01
254·4	0·02989	6·19	6·22	−0·03
273·1	0·03020	6·25	6·26	−0·01
301·5	0·03053	6·32	6·33	−0·01
324·1	0·03073	6·36	6·38	−0·02
340·5	0·03102	6·42	6·41	+0·01
370·6	0·03127	6·48	6·48	—

TABLE XIII.—Sodium. (Atomic Weight: 23.)

I.	II.	III.	IV.	V.
T.	Specific heat.	C_p (experimental).	C_p (curve).	Difference.
		Annealed.		
123·3	0·2466	5·67	5·67	—
155·2	0·2586	5·95	5·93	+0·02
179·3	0·2619	6·02	6·06	−0·04
210·5	0·2707	6·23	6·23	—
270·6	0·2826	6·51	6·51	—
273·1	0·2829	6·51	6·52	−0·01
305·9	0·2910	6·69	6·69	—
322·4	0·2952	6·79	6·79	—
340·9	0·3019	6·94	6·94	—
352·2	0·3083	7·09	7·09	—
358·7	0·3171	7·29	7·28	+0·01
363·1	0·3209	7·38	7·39	−0·01
368·6	0·3258	7·49	7·49	—
		Molten State.		
373·9	0·3234	7·44	7·44	—
376·2	0·3232	7·43	7·43	—
390·1	0·3217	7·40	7·40	—
400·6	0·3205	7·37	7·37	—
411·6	0·3189	7·34	7·34	—

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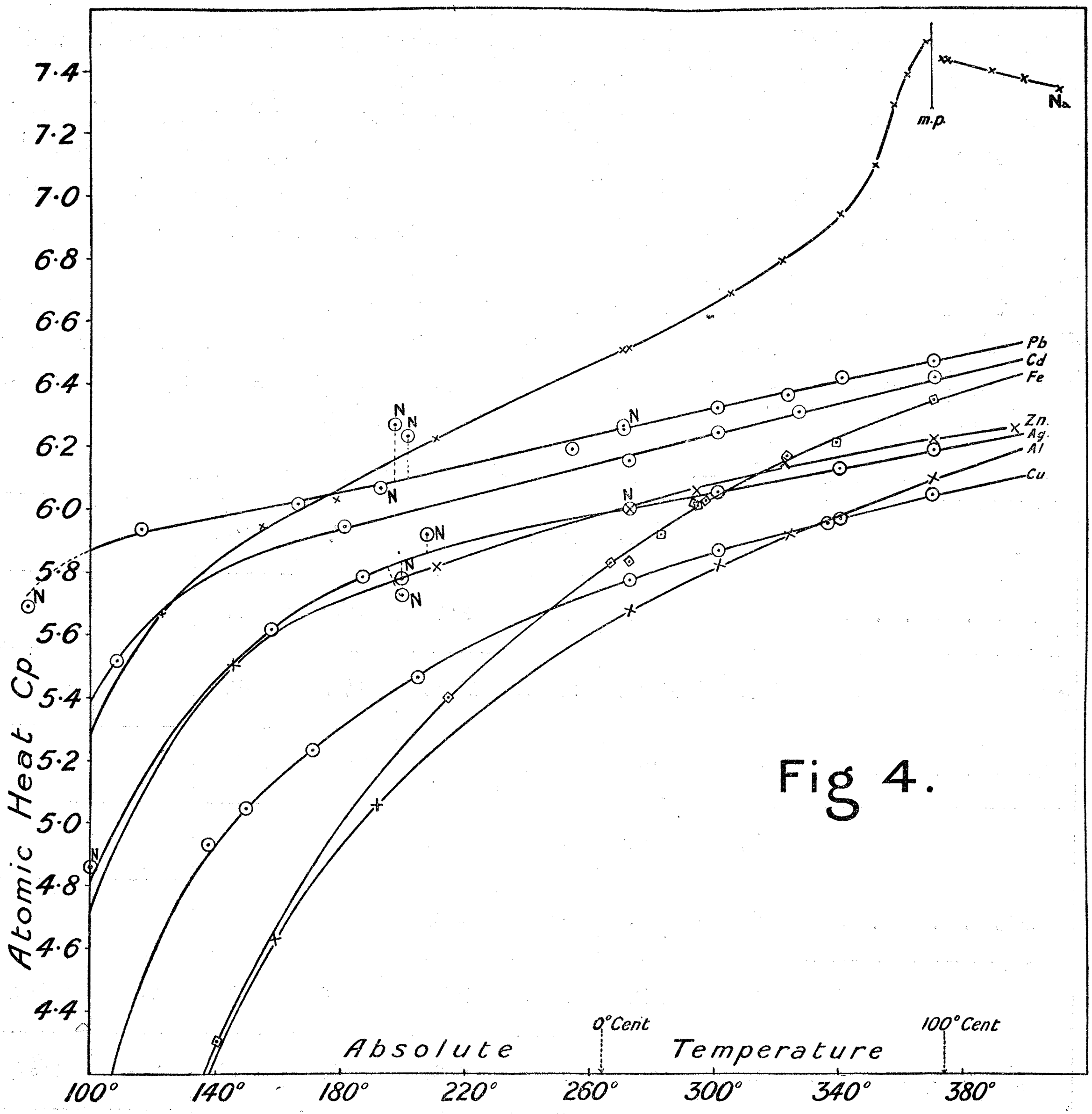
In Part II., where the various theoretical formulæ are examined, to avoid confusion between experimental errors and systematic divergences, the values from the mean curves will be taken as the basis of comparison.

Fig. 4 exhibits the results graphically over the temperature range which we have investigated.



The letter N denotes the observations of Nernst in the case of silver and of lead.

(9) Nernst's *Method.*

The work of Nernst at low temperatures has already been referred to and since some of his results are quoted below, it is desirable to indicate briefly the method by which they have been obtained.

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The block of metal under examination was suspended in an exhausted glass vessel immersed in liquid air or hydrogen. The heat was supplied electrically by a platinum wire which also served as a resistance thermometer. It was essential that the vacuum should be extremely high, since no correction was applied for losses or gains by radiation, &c., and for this reason his values at the lowest temperatures should be the most reliable.

In the cases of silver and lead NERNST has also recorded observations at the temperatures of solid CO_2 and ice by the same method.

In fig. 4 these values are indicated by the letter N, and it will be observed that in both cases the smoothed curves through our observations are in general accordance with NERNST'S *mean* values, though his individual observations show marked discrepancies.

For the same two metals at liquid air temperatures, the mean of several values at closely adjacent temperatures is given in Table XIV.

In the lead group the values are not very concordant, some of the observations differ from the smoothed curve by more than 3 per cent.; the probable error, however, is much less than this. Lead, from our own experience, appears to be a metal with which it is difficult to obtain concordant results.

TABLE XIV.—NERNST'S Values at Low Temperatures.

Al	T.	32°·4.	35°·1.	83°.	86°.	88°·3.		
	C_p	0·25	0·33	2·41	2·52	2·62		
Cu	T.	23°·5.	27°·7.	33°·4.	87°.	88°.		
	C_p	0·22	0·32	0·54	3·33	3·38		
Zn*	T.	40°.	60°.	80°.				
	C_p	1·77	3·15	4·09				
Ag	T.	35°.	39°·1.	44°·2.	52°·6.	65°.	77°.	85°·3.
	C_p	1·58	1·90	2·36	2·85	3·74	4·07	4·37
Pb	T.	23°.	28°·3.	37°·3.	80°.			
	C_p	2·96	3·92	4·41	5·69			

* In the case of zinc the actual figures are not recorded, and the above figures have been obtained from the curves given in the paper.

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For iron, cadmium, and sodium, which NERNST has not investigated, the mean values obtained by DEWAR over the range from liquid nitrogen to liquid hydrogen have been utilized for the purpose of extending the curves to low temperatures.

Whilst DEWAR's method is of great use for obtaining comparative values, especially of organic substances and poor heat conductors, it cannot, when applied to metals, claim to be capable of giving *absolute values* with the same precision as the electrical methods, and it is noticeable that DEWAR used a mass of only 1 gr. of lead as compared with 400 gr. by NERNST and 2200 gr. in the investigation recorded in this paper.

Moreover it should be remembered that, where the curvature is marked, the mean value over a range may depart appreciably from the real value at the mid point; and, for this reason also, values obtained by an electrical method are to be preferred.

DEWAR's Mean Values at 50° C. Absolute.

C_p	Fe, 0·98	Cd, 3·46	Na, 3·50

(10) *Discussion of the Results.*

The question of the variation of atomic heat with temperature has recently received a considerable amount of attention, chiefly on account of its bearing on PLANCK's "quantum" theory.

The theoretical formulæ are concerned with C_v (the atomic heat at constant volume), while the quantity experimentally investigated is C_p, the atomic heat when the solid is free to expand with temperature.

It is necessary to know the values of the compressibility and expansion coefficients, in order to apply the well-known thermodynamical relation

$$C_p - C_v = a^2 \epsilon v t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where a is the coefficient of cubical expansion, ϵ is the coefficient of volumetric elasticity, v is the reciprocal of the density, and t the absolute temperature.

The values of ϵ[*] obtained by RICHARDS have been assumed, but, on account of lack of data, we have been compelled to disregard the variation of the compressibilities with temperature.

The coefficient of expansion of metals decreases with temperature, as shown by the work of FIZEAU, DORSEY,[†] AYRES,[‡] and others.

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[*] 'Journ. Chem. Soc.,' 1911.

[†] 'Phy. Rev.,' vol. xxv., p. 97, 1907.

[‡] 'Phy. Rev.,' vol. xx., p. 38, 1905.

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With the exception of sodium, the smoothed curves have been drawn through the experimental results of DORSEY and of AYRES in the range 0° C. to −180° C., and the curves extrapolated in order to deduce the value of $\alpha\epsilon v\int_0^t \alpha\,dt$ at various temperatures.

For sodium the value 0·000224, determined by us in some preliminary experiments by a new method, has been utilized.

This method, which will be described in a later paper, did not indicate any marked change in the coefficient over the range 0° C. to 95° C.

For low temperature a coefficient of decrease of the same order as that of cadmium was assumed, a procedure which is justified by the fact that the coefficient of expansion is proportional to the atomic heat, as shown by GRUNEISEN, and at low temperature the atomic heat curves of sodium and cadmium are similar.

NERNST and LINDEMANN* adopt a different procedure, basing their method on GRUNEISEN'S observation that the coefficient of expansion is proportional to the atomic heat; they obtain the approximate relation

$$C_p - C_v = C_p^2 TA. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where A is a constant characteristic of the substance which can be deduced from measurements of the compressibility and coefficient of expansion made at one temperature.

In the cases of Al, Ag, Pb, and Cu the values so obtained are compared with the values calculated by means of equation (5), which are utilized in all subsequent comparisons of theory and experiment in this paper.

It is shown in Part II. of this paper that no one of the theoretical formulæ hitherto published is capable of representing the atomic heat-temperature curves over the entire range. Since data based on the experimental observations are necessary to test any theory, we summarise below the values, at convenient intervals of temperature, of the atomic heat read from curves which we believe represent the most probable paths through the observations of NERNST at liquid air and hydrogen temperatures; of DEWAR at 50° C. abs. and through our own numbers† from 100° C. abs. to 400° C. abs.

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* 'La Théorie du Rayonnement et les Quanta,' p. 265, 1912.

† *Vide* Tables VI. to XIV. and fig. 4.

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Table XV.

Column I.—Absolute temperature.

Column II.—Atomic heat C_p, from the smoothed curves.

Column III.—Difference between the atomic heat when the metal is free to expand and the hypothetical value at constant volume.

For Al, Cu, Ag, and Pb the values deduced from equation (5) are given under (1) and those from equation (6) under (2).

I.	II.	III.		I.	II.	III.		I.	II.	III.	
T.	C_p.	$C_p - C_v$.		T.	C_p.	$C_p - C_v$.		T.	C_p.	$C_p - C_v$.	
		(1.)	(2.)			(1.)	(2.)			(1.)	(2.)
					Aluminium.						
32·4°	0·25			120°	3·74	0·05	0·05	300°	5·81	0·24	0·21
35·1	0·33			160	4·64	0·08	0·08	320	5·90	0·26	0·23
50	0·91			200	5·14	0·12	0·11	340	5·98	0·29	0·26
80	2·27	0·01	0·01	230	5·40	0·15	0·14	360	6·05	0·31	0·28
100	3·08	0·03	0·03	250	5·54	0·17	0·16	380	6·13	0·34	0·30
					Iron.						
50°	0·98			170°	4·85	0·03		290°	5·98	0·09	
70	1·86			190	5·13	0·04		310	6·09	0·10	
90	2·74			210	5·36	0·04		330	6·19	0·12	
110	3·47	0·01		230	5·54	0·06		350	6·28	0·13	
130	4·05	0·01		250	5·70	0·07		370	6·35	0·15	
150	4·50	0·02		270	5·85	0·08		390	6·41	0·17	
					Copper.						
23·5°	0·22			150°	5·05	0·04	0·06	290°	5·83	0·15	0·14
27·7	0·32			170	5·23	0·06	0·07	310	5·89	0·16	0·15
50	1·32			190	5·37	0·07	0·08	330	5·95	0·18	0·16
70	2·43		0·01	210	5·50	0·08	0·09	350	5·99	0·20	0·17
90	3·48		0·02	230	5·61	0·10	0·10	370	6·04	0·22	0·18
110	4·31	0·02	0·03	250	5·70	0·11	0·11	390	6·09	0·23	0·19
130	4·78	0·03	0·05	270	5·77	0·13	0·13				
					Zinc.						
30°	0·94			160°	5·61	0·09		290°	6·05	0·23	
50	2·54			190	5·75	0·12		310	6·10	0·25	
80	4·09	0·01		210	5·82	0·14		330	6·15	0·28	
100	4·72	0·03		230	5·88	0·16		350	6·19	0·30	
120	5·15	0·05		250	5·95	0·18		370	6·22	0·33	
140	5·44	0·07		270	5·99	0·20		390	6·25	0·36	

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TABLE XV. (continued).

I.	II.	III.		I.	II.	III.		I.	II.	III.	
T.	C_p.	$C_p - C_v$.		T.	C_p.	$C_p - C_v$.		T.	C_p.	$C_p - C_v$.	
		(1.)	(2.)			(1.)	(2.)			(1.)	(2.)
Silver.											
35°	1·58			150°	5·55	0·08	0·11	280°	6·02	0·21	0·25
40	1·99		0·01	180	5·75	0·11	0·15	300	6·05	0·23	0·27
60	3·32	0·01	0·02	200	5·83	0·13	0·17	320	6·09	0·25	0·29
80	4·24	0·02	0·04	220	5·90	0·15	0·19	340	6·12	0·27	0·31
100	4·83	0·04	0·06	240	5·94	0·17	0·21	360	6·17	0·30	0·34
130	5·33	0·06	0·09	260	5·98	0·19	0·23	380	6·21	0·32	0·36
Cadmium.											
50°	3·46	0·02		180°	5·93	0·15		300°	6·24	0·32	
70	4·58	0·04		200	5·99	0·18		320	6·29	0·35	
100	5·37	0·07		220	6·04	0·20		340	6·33	0·38	
120	5·65	0·08		240	6·09	0·23		360	6·39	0·42	
140	5·79	0·11		260	6·14	0·26		380	6·44	0·45	
160	5·87	0·13		280	6·19	0·29					
Lead.											
23°	2·96	0·01	0·01	140°	5·97	0·15	0·14	280°	6·28	0·35	0·34
28	3·58	0·01	0·01	160	6·01	0·17	0·17	300	6·32	0·39	0·37
37	4·50	0·02	0·02	180	6·05	0·20	0·19	320	6·37	0·43	0·40
50	5·14	0·04	0·04	200	6·10	0·23	0·22	340	6·41	0·47	0·43
80	5·72	0·07	0·07	220	6·14	0·26	0·25	360	6·45	0·51	0·46
100	5·87	0·10	0·09	240	6·18	0·29	0·28	380	6·49	0·55	0·49
120	5·93	0·12	0·11	260	6·23	0·32	0·31				
Sodium (Annealed).*											
50°	3·50	0·04		180°	6·06	0·22		330°	6·85	0·48	
70	4·43	0·07		210	6·22	0·27		350	7·05	0·51	
90	5·04	0·09		240	6·36	0·32		360	7·33	0·53	
120	5·62	0·13		270	6·50	0·37		368	7·48	0·55	
150	5·90	0·17		300	6·66	0·43					

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* The changes in the atomic heat consequent on variations in the heat treatment will be considered in a later paper.

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PART II.

COMPARISON OF THE EXPERIMENTAL RESULTS WITH THOSE DEDUCED FROM FORMULÆ BASED ON THE "QUANTUM" THEORY.

(1) *Theoretical Formulæ for* C_v.

In order to appreciate the limitations of the various theoretical formulæ which have been given to represent the variation of atomic heat with temperature, it is necessary to review briefly the fundamental assumptions on which they are based.

(*a*) EINSTEIN'S *Theory.*—EINSTEIN* was the first to show that if we regard the atoms of solid substances as charged with electricity and oscillating about fixed positions, we may consider them as equivalent to a number of PLANCK'S resonators.

On this theory each atom is regarded as possessing three degrees of freedom, and consequently the total vibrational energy of an atom is three times that of a linear oscillator. From these considerations he deduces the expression

$$C_v = 3R \frac{\left(\frac{h}{k}\frac{\nu}{T}\right)^2 e^{\frac{h}{k}\frac{\nu}{T}}}{\left(e^{\frac{h}{k}\frac{\nu}{T}}-1\right)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

for the atomic heat of any elementary substance, where

R is the gas constant, 1·9876,
h is the quantum constant, $7{\cdot}10 \times 10^{-27}$ erg sec,†
k, BOLTZMANN'S constant, $1{\cdot}47 \times 10^{-16}$ erg,
T, the absolute temperature,
ν, the monochromatic frequency of vibration—a constant characteristic of the substance.

In the case of salts, the quantity ν is the frequency found by means of the *reststrahlen*, but, in the case of the metals, it cannot be obtained directly. EINSTEIN showed that if the elastic forces which maintain the atoms in their equilibrium position are the same as those which oppose a diminution of volume when the solid is compressed, and if we assume that these forces are due to the mutual action of adjacent atoms spaced in the form of a lattice, then

$$\nu = 2{\cdot}54 \times 10^7 \times \frac{V^{1/6}}{m^{1/2}k^{1/2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where V is the atomic volume,
m is the atomic weight,
k is the coefficient of compressibility.

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* 'Ann. d. Phys.,' vol. 22, pp. 180, 800, 1907.

† 'Ann. d. Phys.,' vol. 38, p. 41, 1912.

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Magnus found that while formula (7) accounted qualitatively for the decrease in atomic heat with temperature, it gave a too rapid decrease with temperature to represent accurately the form of the experimental line.

(*b*) Nernst *and* Lindemann.*—Nernst† at first endeavoured to effect a better agreement between the formula and his experimental results by the addition of an empirical term‡ of the form $bT^{3/2}$ to equation (7).

In a later memoir Nernst and Lindemann showed that the expression

$$C_v = \frac{3R}{2}\left[\frac{\left(\frac{\beta\nu}{T}\right)^2 e^{\frac{\beta\nu}{T}}}{\left(e^{\frac{\beta\nu}{T}}-1\right)^2}+\frac{\left(\frac{\beta\nu}{2T}\right)^2 e^{\frac{\beta\nu}{2T}}}{\left(e^{\frac{\beta\nu}{2T}}-1\right)^2}\right], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where $h/k = \beta$, more nearly expressed the experimental results than (7).

Here again ν, in the case of salts, is the frequency found by means of the *reststrahlen*, but in no case has an infra red band been observed whose frequency is $\frac{1}{2}\nu$.

Lindemann suggested another method for the indirect determination of ν.

He assumed that fusion was produced when the amplitude of the atomic vibrations became of the same order of magnitude as the distance between adjacent atoms, and thus obtained the expression

$$\nu = 2{\cdot}12 \times 10^{12}\sqrt{\frac{T_s}{mV^{2/3}}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where T_s is the absolute temperature of the melting-point,

V, the atomic volume,

m, the atomic weight.

Expression (9) is empirical, but appears to have been a step in the right direction, as it takes into account more than one frequency, although Nernst was of opinion that the second term represented potential energy.

It is difficult to conceive the atoms in solids, such as metals, as executing monochromatic vibrations; the wide range over which absorption takes place indicates that the vibrations are more complex and, were it possible to apply Fourier's theorem, we should expect frequencies distributed over a continuous spectrum.

(*c*) Debye's *Theory.*§—Debye has attempted the solution of the problem when the atomic vibrations are not regarded as monochromatic. He considers the possible vibrations of the substance as a whole, and proceeds on the supposition that the heat vibrations depend on the elastic forces in such a way that the longest heat waves are

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* Berlin, 'Sitz. Ber.,' p. 494, 1911.

† 'Journal de Physique,' vol. 9, p. 721, 1910.

‡ Einstein had indicated that such a term was necessary to complete the expression on account of the difference between C_p and C_v.

§ 'Annalen d. Physik,' vol. 39, p. 789, 1912.

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identical with elastic vibrations. By applying the classical theory of elasticity to the vibrations of a homogeneous isotropic sphere in the case where the pressures on the surface vanish,* DEBYE determined the number of characteristic types of vibrations up to or below a given frequency ν, and obtained the result that

$$z = \nu^3 v \mathrm{F}, \quad \ldots \ldots \quad (11)$$

where

z is the number of sets of "standing waves" as in the analogous problem in "radiation,"

v, the volume of the sphere,

F, a quantity calculated from the elastic constants and given by

$$\mathrm{F} = \frac{4\pi}{3}\left[\left(\frac{1}{a_1}\right)^3 + 2\left(\frac{1}{a_2}\right)^3\right], \quad \ldots \ldots \quad (12)$$

where

a_1 is the velocity of dilatational waves,

a_2 ,, ,, torsional waves.

Lord RAYLEIGH† has shown that a coupled system of N mass points with 3N degrees of freedom may be regarded as giving rise to 3N types of vibrations.

Taking the N atoms in unit mass of a solid as such a system, DEBYE ascribes to each of these types of vibration the mean energy $\frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}}-1}$ of a linear oscillator.

The next assumption is the characteristic one of the entire theory. He applies equation (11) deduced for a continuous medium in which an infinite number of vibrations is possible to the system of N atoms in which only 3N vibrations are possible.

Since the form of the body considered has no influence on the result expressed in equation (11) for unit volume, we have

$$z_m = 3\mathrm{N} = \nu_m{}^3 \mathrm{F}, \quad \ldots \ldots \quad (13)$$

where ν_m is the limit frequency.

And the number of "standing waves" in the interval $d\nu$ denoted by dz is given by

$$dz = 3\nu^2 \mathrm{F}\, d\nu. \quad \ldots \ldots \quad (14)$$

Hence the total energy of the N atoms is

$$\mathrm{E}_{\mathrm{N}} = \frac{9\mathrm{N}}{\nu_m{}^3}\int_0^{\nu_m} \frac{h\nu}{e^{\frac{h\nu}{k\mathrm{T}}}-1} \cdot \nu^2\, d\nu, \quad \ldots \ldots \quad (15)$$

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* A condition which is regarded as corresponding to the case of a sphere in thermal equilibrium with the outer surroundings, since no energy crosses the surface.

† "Theory of Sound," vol. 1, p. 129, 1877.

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from which the following expression is obtained for the atomic heat in which for simplicity ν_m is inserted as ν and β for h/k as before,

$$C_v = 3R\left[\frac{4\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 - \frac{3\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}}-1} - 12\frac{\beta\nu}{T}\sum_{n=1}^{n=\infty} e^{-\frac{n\beta\nu}{T}}\left(\frac{1}{n\frac{\beta\nu}{T}} + \frac{3}{n^2\left(\frac{\beta\nu}{T}\right)^2} + \frac{6}{n^3\left(\frac{\beta\nu}{T}\right)^3} + \frac{6}{n^4\left(\frac{\beta\nu}{T}\right)^4}\right)\right] \quad . \quad . \quad (16)$$

The great point of difference between the theory of EINSTEIN and that of DEBYE lies in the fact that the latter takes into account all frequencies from 0 to ν_m.

The distribution of the different frequencies given by equation (14) appears to be capable of deduction from different standpoints, as shown by the researches* of BORN and V. KÀRMÀN.

CALLENDAR has drawn our attention to one important difficulty of the quantum theory which is mentioned by EINSTEIN, namely, that for large values of $e^{\beta\nu/T}$, but a small proportion of the atoms could have even one quantum. When $\beta\nu/T = 3$ (as for iron at T = 130° C. abs., but one molecule in twenty could have a single quantum. Even at 100° C. it would be only one in three. PLANCK has endeavoured to avoid this by a more recent and artificial proof which has not received much support.

Before proceeding to consider the other theories of specific heat, we will briefly compare the experimental results with the formulæ based on PLANCK'S "quantum" theory. DEBYE'S equation (16) is acknowledged, for the representation of the facts at low temperature, to be superior to the formulæ of EINSTEIN and of NERNST and LINDEMANN, but we find that no single value of the limit frequency will make the formula fit the experimental results over the complete range.

It is at very low temperatures that the assumption made by DEBYE, namely, that the vibrations whose frequency is greater than ν_m are negligible, can best be justified, since at such temperatures the slow heat vibrations would be the most important. Hence, in the following comparison, the value of ν_m is so chosen that DEBYE'S equation fits the results over the lowest portion of the range.

It is of but little use to calculate the appropriate values of ν_m from the elastic constants of the metals, since these constants are considerably influenced by the nature of the previous heat treatment and by the temperature.

The values calculated from the elastic constants are in accordance with those required by the atomic heat results, as will be shown subsequently.

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* 'Phys. Zeitschr.,' vol. 14, pp. 15 and 65, 1913.

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TABLE XVI.

(2) *Comparison of* DEBYE'S *Formula with the Experimental Results when the Limit Frequency inserted is such that the Locus coincides with the Atomic Heat Curve over the Lowest Portion of the Temperature Range.*

T.	C_p (obs.).	C_p (calc.).	Difference.	T.	C_p (obs.).	C_p (calc.).	Difference.
Aluminium, $\beta\nu = 394$.							
32·4°	0·25	0·25	—	200°	5·14	5·06	0·08
35·1	0·33	0·31	0·02	250	5·54	5·45	0·09
80	2·27	2·26	0·01	300	5·81	5·72	0·09
100	3·08	3·08	—	340	5·98	5·87	0·11
120	3·74	3·72	0·02	380	6·13	5·99	0·14
Iron, $\beta\nu = 385$.							
50°	0·98	0·92	0·06	210°	5·36	5·10	0·26
70	1·86	1·86	—	250	5·70	5·38	0·32
90	2·74	2·75	−0·01	310	6·09	5·63	0·46
110	3·47	3·46	+0·01	350	6·28	5·74	0·54
150	4·50	4·40	0·10	390	6·41	5·85	0·56
Copper, $\beta\nu = 325$.							
27·7°	0·32	0·28	0·04	190°	5·37	5·23	0·14
50	1·32	1·34	−0·02	250	5·70	5·60	0·09
70	2·43	2·46	−0·03	290	5·83	5·75	0·08
90	3·48	3·35	0·13	350	5·99	5·91	0·09
130	4·78	4·47	0·31	390	6·09	5·99	0·10
Zinc, $\beta\nu = 230$.							
30°	0·94	0·91	0·03	190°	5·75	5·67	0·08
50	2·54	2·50	0·04	250	5·95	5·90	0·05
80	4·08	4·08	—	310	6·10	6·06	0·04
100	4·72	4·68	0·04	350	6·19	6·14	0·05
140	5·44	5·29	0·15	390	6·25	6·21	0·04
Silver, $\beta\nu = 215$.							
40°	1·99	1·93	0·06	240°	5·94	5·91	0·03
60	3·32	3·39	−0·07	280	6·02	6·00	0·02
100	4·83	4·82	0·01	300	6·05	6·05	—
150	5·55	5·47	0·08	340	6·12	6·12	—
200	5·83	5·76	0·07	380	6·21	6·19	0·02

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TABLE XVI. (continued).

T.	C_p (obs.).	C_p (calc.).	Difference.	T.	C_p (obs.).	C_p (calc.).	Difference.
			Cadmium, $\beta\nu = 168$.				
50°	3·46	3·60	−0·14	260°	6·14	6·10	0·04
70	4·58	4·58	—	300	6·24	6·19	0·05
100	5·37	5·26	0·11	340	6·33	6·27	0·06
140	5·79	5·66	0·13	380	6·44	6·36	0·08
200	5·99	5·94	0·05				
			Lead, $\beta\nu = 92$.				
23°	2·96	3·01	−0·05	160°	6·01	6·03	−0·02
28	3·58	3·68	−0·10	200	6·10	6·10	—
37	4·50	4·48	0·02	240	6·18	6·21	−0·03
80	5·72	5·66	0·06	300	6·32	6·32	—
120	5·93	5·91	0·02	360	6·45	6·46	−0·01
			Sodium, $\beta\nu = 180$.				
50°	3·50	3·41	0·09	250°	6·41	6·14	0·27
70	4·43	4·43	—	290	6·60	6·26	0·34
90	5·04	5·01	0·03	330	6·85	6·35	0·50
130	5·74	5·57	0·17	350	7·06	6·40	0·66
190	6·12	5·94	0·18	365	7·43	6·44	0·99

In the table below the values of ν_m, which have been obtained from the atomic heat formulæ, are compared with the values deduced by DEBYE from the elastic constants of the metals.

$\nu_m \times 10^{-12}$.

Metal.	Al.	Fe.	Cu.	Ag.	Cd.	Pb.
ν_m (atomic heat) . . .	8·2	8·0	6·7	4·5	3·5	1·9
ν_m (elastic constants) .	8·3	9·7	6·8	4·4	3·5	1·5

Attention may be drawn to some of the conspicuous features shown by the above comparisons.

In the first place it will be observed that, with the possible exception of lead, the calculated values are too low at the higher temperatures; also that the departure is most pronounced where the curvature is greatest; in copper for example, at 130° C. abs. and in zinc at 150° C. abs.

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Much weight should not be attached to the fact that the calculated values are slightly higher than the observed ones in the case of lead at about 200° C. abs., since there is an uncertainty in the value of $C_p - C_v$, due to lack of knowledge of the variation in the coefficient of compressibility with temperature. At 80° C. abs., the calculated value for this metal is also too low.

Only for the metals iron and sodium does the difference between the observed and the calculated values increase considerably with the temperature.

The divergence in the case of iron must, to some extent, be associated with its ferromagnetic properties.

From the work of WEISS and BECK* it appears that about 5 per cent. of the specific heat of iron at room temperature is due to the potential energy of demagnetization of an internal field which, according to the theory advanced by WEISS, exists in ferromagnetic bodies. The magnitude of this term increases rapidly in the neighbourhood of the temperature at which spontaneous magnetization disappears (about 750° C.), amounting there to nearly 40 per cent. of the total.

In the case of sodium, as the melting point is approached, molecular changes† take place and the theories of EINSTEIN and DEBYE are not sufficient.

(3) *Comparison of the Experimental Results with the Formulæ of* EINSTEIN, NERNST *and* LINDEMANN *and* DEBYE, *when the Frequencies Inserted give Coincidence at a Temperature of about* 125° C. *abs.*

If, instead of requiring the formulæ to fit the experimental curves at the lowest temperatures, we take as basis of comparison the range of temperature through which our investigation extends, we find that there is a closer approximation of the theoretical values to the experimental results, and it is notable that the various formulæ give results in fair agreement among themselves over this range.

In the comparison below, values of the frequencies have been chosen to bring the calculated values into coincidence with the experimental values at about 125° C. abs., which, on the average, was the lowest point to which we carried our experiments.

It will be observed that, generally, near the boiling-point of liquid hydrogen, EINSTEIN'S formula gives values which are too low; from NERNST and LINDEMANN'S the values are too high; while DEBYE'S formula gives values which are in fair agreement for Al, Ag, Zn, and Pb, and, in the other metals, agrees with the experimental values better than either EINSTEIN'S or NERNST and LINDEMANN'S. At liquid air temperatures all three formulæ give values which are too high.

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* 'Journ. de Phys.,' col. 7, p. 249, 1908.

† A. E. OXLEY ('Proc. Cam. Phil. Soc.,' vol. XVII., p. 450, 1914), has suggested that a magnetic energy term similar to that of WEISS and BECK could explain abnormally high values of the specific heat near the melting point.

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TABLE XVII.

Comparison of the Experimental Results with the Formulæ of EINSTEIN, NERNST *and* LINDEMANN *and* DEBYE.

Column I.—T, absolute temperature.
Column II.—C_p, from the smoothed curves previously referred to.
Column III.—C_p, calculated value from EINSTEIN'S formula (E.).
Column IV.—C_p, calculated value from NERNST and LINDEMANN'S formula (N. & L.).
Column V.—C_p, calculated value from DEBYE'S formula (D.).
The values of $\beta\nu$ are given at the top of the columns.

T.	C_p (obs.).	C_p (E.).	C_p (N. and L.).	C_p (D.).
Aluminium.		$\beta\nu = 292$.	$\beta\nu = 385$.	$\beta\nu_m = 385$.
35°	0·33	0·12	0·37	0·35
80	2·27	2·18	2·46	2·35
140	4·26	4·26	4·26	4·28
200	5·14	5·12	5·10	5·10
250	5·53	5·49	5·47	5·47
300	5·81	5·75	5·74	5·74
380	6·13	6·02	6·01	6·01
Copper.		$\beta\nu = 222$.	$\beta\nu = 285$.	$\beta\nu_m = 286$.
33·4°	0·54	0·36	0·82	0·71
88	3·38	3·60	3·74	3·70
120	4·58	4·52	4·58	4·57
200	5·44	5·46	5·47	5·47
280	5·80	5·78	5·80	5·80
360	6·02	5·96	6·01	6·01
Zinc.		$\beta\nu = 160$.	$\beta\nu = 210$.	$\beta\nu_m = 210$.
30°	0·95	0·84	1·30	1·13
80	4·09	4·33	4·33	4·33
130	5·31	5·32	5·31	5·31
200	5·78	5·76	5·77	5·77
280	6·02	6·00	6·01	6·00
360	6·21	6·19	6·19	6·19

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TABLE XVII. (continued).

T.	C_p (obs.).	C_p (E.).	C_p (N. and L.).	C_p (D.).
Silver.		$\beta\nu = 157.$	$\beta\nu = 207.$	$\beta\nu_m = 207.$
35°	1·58	1·40	1·80	1·64
85	4·42	4·56	4·53	4·53
120	5·20	5·23	5·21	5·21
200	5·84	5·73	5·78	5·78
280	6·01	6·01	6·01	6·01
360	6·16	6·16	6·16	6·15
Cadmium.		$\beta\nu = 112.$	$\beta\nu = 143.$	$\beta\nu_m = 144.$
50°	3·46	4·02	4·10	4·10
115	5·60	5·59	5·60	5·60
160	5·87	5·85	5·86	5·86
200	5·99	5·97	5·99	5·99
360	6·39	6·33	6·34	6·34
Lead.		$\beta\nu = 68.$	$\beta\nu = 92.$	$\beta\nu = 94.$
23°	2·96	3·03	3·06	2·94
80	5·72	5·75	5·65	5·64
120	5·93	5·93	5·91	5·91
200	6·10	6·13	6·13	6·13
280	6·28	6·28	6·28	6·28
360	6·45	6·45	6·45	6·45
Sodium.		$\beta\nu = 119.$	$\beta\nu = 152.$	$\beta\nu_m = 152.$
50°	3·50	3·87	3·98	3·95
120	5·62	5·62	5·64	5·64
200	6·17	6·02	6·04	6·02
320	6·78	6·36	6·36	6·36
360	7·32	6·43	6·43	6·43
Iron.		$\beta\nu = 286.$	$\beta\nu = 376.$	$\beta\nu_m = 376.$
50°	0·98	0·65	1·10	0·98
140	4·28	4·28	4·29	4·29
220	5·45	5·24	5·21	5·21
300	6·03	5·62	5·61	5·61
380	6·37	5·82	5·82	5·82

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TABLE XVIII.

(4) *Comparison of Frequencies obtained by Calculation from the Physical Constants with the Values assumed in the above Tables.*

Frequencies $\times 10^{-12}$.

Metal.	EINSTEIN'S formulæ.		NERNST and LINDEMANN'S formulæ.		DEBYE'S formulæ.	
	Specific heat.	Calculated.	Specific heat.	Calculated.	Specific heat.	Calculated.
Al	6·1	6·7	8·0	5·8	8·0	8·3
Cu	4·6	5·7	5·9	5·1	5·9	6·8
Zn	3·3	3·7	4·4	3·3	4·4	6·5
Ag	3·3	4·1	4·3	3·3	4·3	4·4
Cd	2·3	2·7	3·0	2·1	3·0	3·5
Pb	1·4	1·9	1·9	1·4	1·9	1·5

The above comparison of the frequencies shows that the values obtained from the specific heat equations are in fair agreement with those calculated from the elastic constants and that the limit frequency ν_m of DEBYE is comparable with the monochromatic frequency of EINSTEIN.

It was found that no progressive change with temperature in the value of the frequency assumed would bring the results into better agreement in all cases.*

The work of ROSENHAIN and HUMFREY† and others give considerable support to the view that a cast metal consists of an agglomeration of crystals cemented together by an amorphous modification and that the elastic constants are intimately connected with this intercrystalline film. Now the glassy or amorphous forms of quartz, benzophenone, and betol possess higher specific heats than the corresponding crystalline forms.

The presence of an amorphous modification would make the problem a more complex one than is taken into consideration in the preceding theories, since a single value of the frequency or the limit frequency would not suffice for the representation of the thermal agitation of the two different forms.

It seems probable, however, that the proportion of an amorphous form present under ordinary conditions is very small.

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* EUCKEN ('Verh. d. D. Phy. Ges.,' 15, p. 571, 1913) has calculated the probable frequency values at low temperatures, taking into account the change in the elastic constants with temperature, but the values so obtained were not in agreement with the atomic heat curves.

† 'Journ. Inst. Metals,' p. 653, Part II., 1913.

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If the assumptions underlying the theoretical equations are valid, then we must conclude that other energy than that required for the three degrees of freedom ascribed to the atom is necessary to account for the atomic heat.

JEANS* has shown that if the atoms in a crystal do not rotate, then they must be kept in their direction by couples under whose influence they could carry out vibrations.

It is possible that at the higher temperatures the energy associated with these vibrations contributes to the specific heat, but hitherto no quantitative expression has been given which would enable this hypothesis to be verified.

(5) *Theories of Atomic Heat which are not Based on the Quantum Theory.*

CALLENDAR has proposed a different theory† of radiation; according to his view, equipartition of energy is not possible in full radiation, because the higher frequencies are being continually degraded by the Doppler effect in isothermal emission under equilibrium conditions. The formula‡ obtained for the representation of the atomic heat is applicable, at present, only to those substances possessing a single frequency and further hypotheses are necessary before it can be applied to the metals.

Prof. CALLENDAR has very kindly permitted us to include the following brief summary of his views in our paper.

CALLENDAR'S THEORY OF SPECIFIC HEAT.

"The total heat E+PV per gramme atom of an isotropic substance, all the atoms of which have the same frequency ν, should be of the form $E+PV = 3RT(1+z)e^{-z}$ (where $z = b\nu/T$) when the substance is in equilibrium with full radiation in which the partial pressure p per unit range of frequency is given by RAYLEIGH'S formula,

$$p\,d\nu = C\nu^2 Te^{-z}\,d\nu.$$

In this case the latent heat of emission or absorption per unit range and volume (in order to agree with WIEN'S displacement law and the Doppler effect in isothermal emission), must be of the form ('Phil. Mag.,' May, 1914, p. 874),

$$T(dp/dT)_\nu = C\nu^2 T(1+z)e^{-z},$$

which agrees better with experiments on radiation than PLANCK'S formula, and has the advantage of being consistent with the classical thermodynamics.

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* 'La Théorie du Rayonnement et les Quanta,' p. 63, 1912.

† 'Phil. Mag.,' May, 1914.

‡ 'Phil. Mag.,' October, 1913.

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The atomic heat, *as measured experimentally* for a solid or liquid in equilibrium with full radiation at a negligible external pressure, is of the form (Curve I., dotted)

$$d(\mathrm{E}+\mathrm{PV})/d\mathrm{T} = 3\mathrm{R}\,(1+z+z^2)\,e^{-z},$$

which gives good agreement in the case of rock salt and sylvin, when the *reststrahlen* frequencies are inserted, in the neighbourhood of the temperature given by $z = 2{\cdot}732$, which corresponds to the maximum of the radiation curve plotted on a frequency base.

In the case of an actual solid, it is impossible that all the molecules should simultaneously have the same frequency. Observation shows that the absorption and emission bands widen considerably with increase of density, so that rock salt, for instance, is opaque over a region extending approximately from 20 to 130 microns, the mean wave-length of the *reststrahlen*, according to RUBENS, being 51·2 microns. Below a certain limit of frequency the substance again becomes transparent. It would appear that resonance generally extends with diminishing amplitude for an equal *interval* of frequency on either side of the mean, and may be represented by supposing that the number of molecules having frequencies included in a given interval is the same for equal intervals on either side of the natural frequency.

In the case of rock salt the probable distribution of frequencies can be approximately inferred from the absorption band and the dispersion formula, and is equivalent to a uniform distribution through a range of a little more than an octave on either side of the mean. The effect of this distribution on the specific heat is shown by the full Curve II., which represents the actual variation of the specific heat of rock salt as closely as can be expected from liquid hydrogen to the ordinary temperature. It will be seen that the agreement would be improved by adopting a slightly lower value for the mean frequency, and a smaller range of resonance. It is evident that the method employed by RUBENS must give too small a value for the wave-length if the resonance is not perfectly sharp, and it is possible that the value 55 microns deduced from the specific heat at $z = 2{\cdot}732$ may be more accurate for the mean wave-length.

The simple theory above sketched could not be expected to apply except in the case of an isotropic substance possessing a single absorption band. The specific heats of quartz, ice, and benzol show a different type of curve, No. III., as shown for quartz, on a reduced scale of temperature (1/6). Such a curve can be fairly represented by assuming two absorption bands, one agreeing with the position indicated by the *reststrahlen*, wave-length 8·85 microns for quartz, and the other about two octaves lower. From our knowledge of absorption spectra it is extremely likely that most substances possess two or more bands of different intensities, and it is possible that the variation of specific heat could be consistently represented if we had all the required data. But a hypothetical selection of frequencies and intensities, though illustrating the possibility of the theory, would not serve as an experimental verification.

It seems fairly certain that the curves often differ in type, and cannot possibly be

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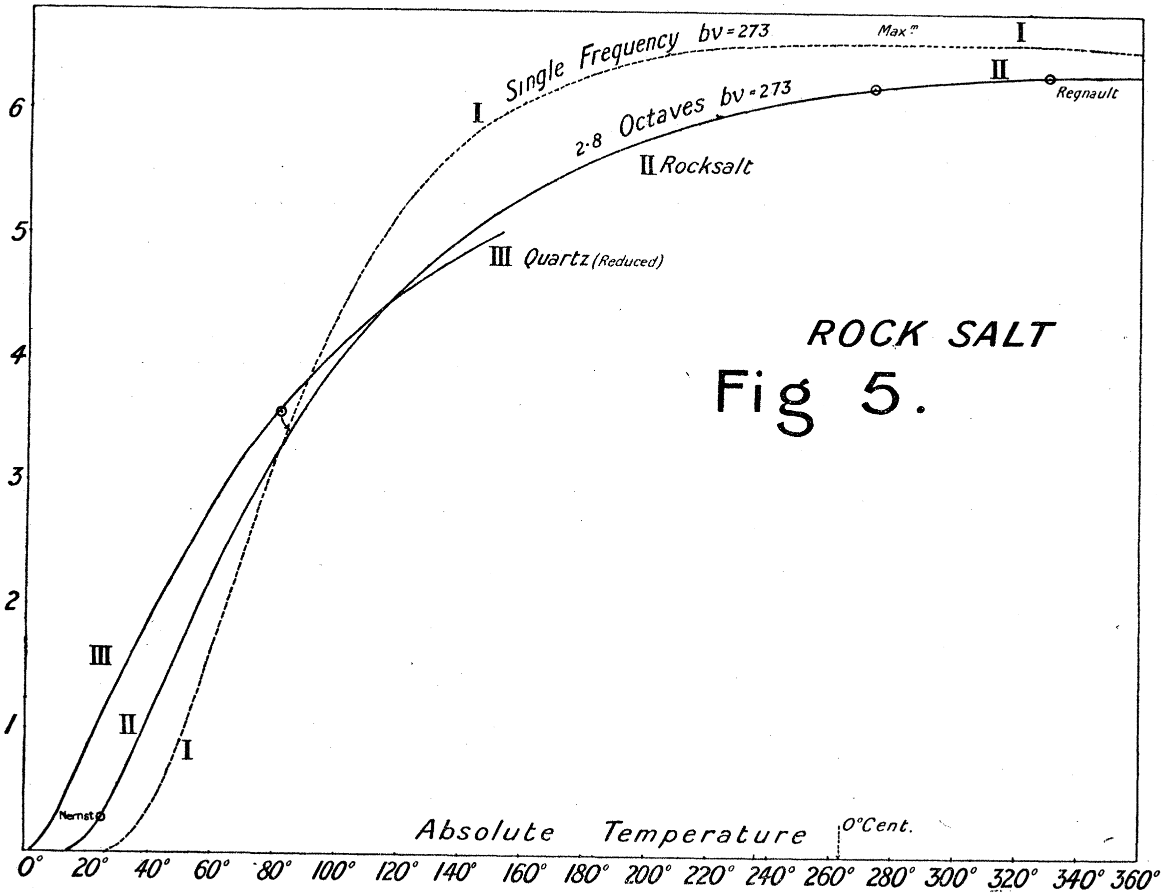
represented by a single parameter (frequency or characteristic temperature) as in Debye's theory, even with the assistance of the correction from constant volume to constant pressure. In a special class, like the metals, the variations of type are not so great, but there is here endless room for speculation with regard to the appropriate frequencies, and if these fail, the magnetons and electrons can be invoked. There are, no doubt, relations between the specific heats and the optical, electrical, and mechanical properties of substances, but qualitative agreement may be obtained on so many different and mutually contradictory hypotheses that very little stress can be laid on such agreement as a verification of any particular hypothesis unless every step in the argument can be proved and tested by independent experimental evidence."



ROCK SALT

Fig 5.

Walker,* in a note to a paper entitled "A Suggestion as to the Origin of Black Body Radiation," states that, by similar reasoning to that of Einstein and Nernst, he found that if the radiation function varied as

$$\theta^5\left(\frac{\lambda\theta}{\lambda^2\theta^2+\alpha^2}\right)^4$$

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* 'Roy. Soc. Proc.,' A, vol. 89, p. 398, 1914.

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the typical term in the expression for the atomic heat varies as

$$\left(\frac{\theta^2}{\theta^2+\theta_0{}^2}\right)^4\left\{1+\frac{8\theta_0{}^2}{\theta^2+\theta_0{}^2}\right\},$$

where θ_0 is some definite temperature.

We have been unable to find any value of θ_0 which would reconcile the locus of this curve with our data.

Summary.

1. In Part I. a description is given of a new method of maintaining an enclosure at any required temperature from that of the room down to about −165° C., by a direct application of the Joule-Thomson cooling effect on expansion of air.

2. Specific heat determinations have been made at various points in the above range for Al, Cu, Zn, Ag, Cd, Pb, Fe, and Na, and data obtained for these metals which determine the *loci* of the atomic heat temperature curves from about 120° C. abs. to 400° C. abs.

3. It is shown that in the case of silver and lead there is no difference greater than the probable errors of experiment between the values obtained by NERNST and those given by the methods described in this paper. Hence, for Al, Cu, Zn, Ag, and Pb it is possible to extend the atomic heat curves by means of the data given by NERNST for these metals at the temperatures of liquid air and hydrogen.

4. The most probable values of the atomic heat at various temperatures are tabulated in Table XV., together with the calculated difference between C_p and C_v.

5. In Part II. a brief review is given of the various theoretical formulæ and the assumptions upon which they are based.

6. It is shown that none of the formulæ are capable of representing the experimental results over the entire range of temperature.

The formula of DEBYE appears to give the nearest approximation to the experimental values over the lowest portion of the range, but systematic divergences occur at the higher temperatures. This may be due either to the assumptions made by DEBYE being valid only at very low temperatures, or that additional heat energy to that involved in the three degrees of freedom, ascribed to the atom, must be taken into account.

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7. Above liquid air temperatures the three formulæ above referred to are capable of approximately representing the results, but in some cases the discrepancies are considerable.

At these higher temperatures the difference between C_p and C_v is considerable, and for some of the metals the increase in C_v is small.

We take this opportunity of expressing our great indebtedness to Mr. D. A. Thomas for his gift of a complete liquid air plant. It was through his generosity that we were able to continue the investigation to low temperatures.

Our thanks are due to the Court of the University of Wales for a contribution towards the expenses of this investigation, also to Mr. Edgar A. Griffiths, student in Engineering at this College, for constructing the special apparatus required and for his skilful management of the plant during the course of the work.

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