

The Change in Thermal Conductivity of Metals on Fusion

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XXIII.—*The Change in Thermal Conductivity of Metals on Fusion.* By ALFRED W. PORTER, D.Sc., F.R.S., and F. SIMEON, B.Sc., Research Scholar University College, London.

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It is well known that when fusion of a pure metal takes place there is, in most cases, a sudden drop in its electrical conductivity. For example, the electrical conductivity of liquid mercury is only about one-quarter of that of solid mercury at the same temperature. Exceptions are bismuth and gallium, for which the conductivity in the liquid state is double that in the solid. The object of the present investigation was to find whether there is a corresponding change in the value of the thermal conductivity. According to the simple form of the electronic theory usually given, the ratio of the two types of conductivity should be $\frac{4}{3} \left(\frac{\alpha}{e} \right)^2 T$, where α and e are universal constants; and although we know that this law is obeyed only roughly, yet the correspondence is sufficiently near to show that the two phenomena are intimately connected.

The outcome of the investigation is to show that the change in the thermal conductivity on fusion is of the same order as that of the electrical.

Outline of Method.

The method of measurement consisted in the determination of the gradient of temperature in a column of the metal contained in a glass tube, and heated at one end to such an extent that half the column is molten, while the cooler half is solid. The metals employed were sodium and mercury. In both cases the column was placed vertically. In order to diminish convective loss of heat from the surface it was heated at the top in the case of sodium whose melting point is above atmospheric temperature, while in the case of mercury the lower half was frozen by insertion of the end of the containing tube in solid carbon dioxide. The apparatus used in the case of sodium is shown in Fig. 1. The heating vessel contained lead which could be melted by means of a flame and kept at a constant temperature. Into the base of the vessel was screwed a piece of brass rod about $1\frac{1}{2}$ in. long and $\frac{3}{8}$ in. diameter. This brass rod served to convey the heat to the sodium with which it came into contact. The glass tube which contained the

sodium was furnished with 12 tubular depressions which were made by locally melting the glass with a fine flame, and then pressing it in with a knitting needle. These tubular depressions were destined to receive the thermoelectric junctions by means of which the temperatures at the various points of the column of metal could be determined. Each junction consisted

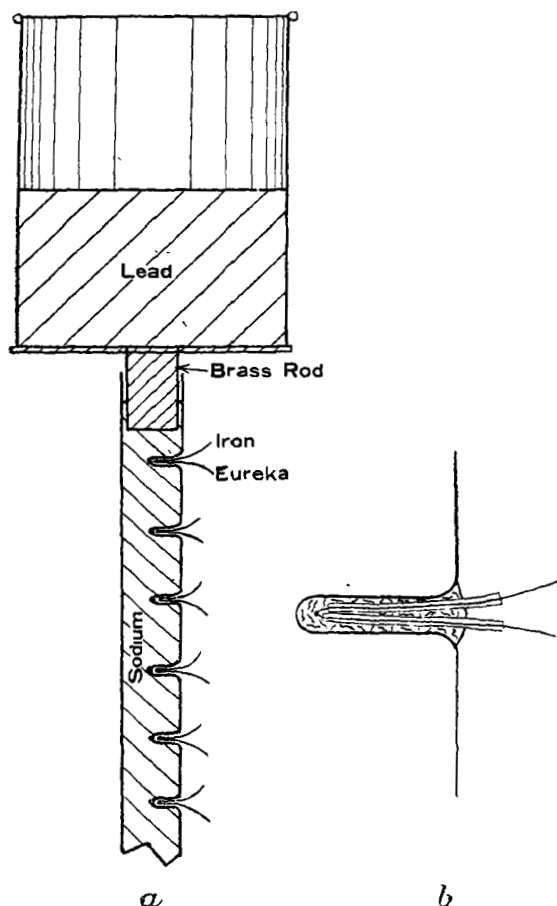


FIG. 1.

of fine iron and eureka wires (gauge 30-36). For the purposes of insulation fine glass tubes about $1\frac{1}{2}$ in. long were slipped over the wires to separate them one from the other, and were then fused to the wires. Each junction so formed was inserted in a tubular depression, and the cavity was filled up with a packing

of tinfoil so that the presence of the junctions should make as little disturbance as possible in the thermal stream lines in the sodium (Fig. 1, *b*). The arrangement is shown in Fig. 1, *a* and *b*.

The wires were all of the same length, and were connected by copper wires (all of the same length as one another) to a moving-coil galvanometer of low resistance in series with a resistance-box for altering the sensitiveness. By making the

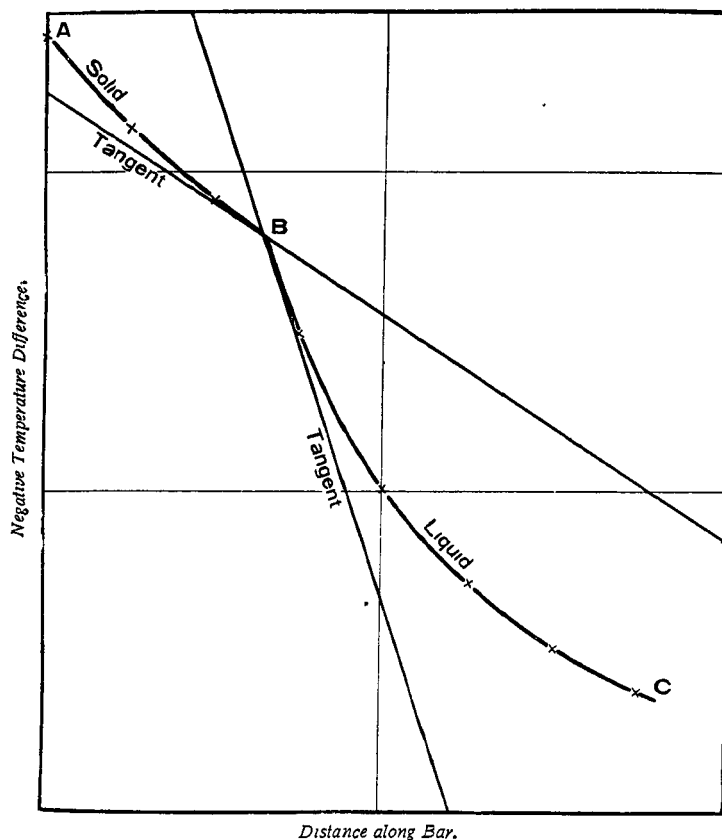


FIG. 2.—TEMPERATURE CURVES AND TANGENTS FOR MERCURY.

wires of equal length the temperature value of a scale division was made the same for all the couples. Since there was a resistance of 700 ohms in series with the galvanometer, any fine adjustment of these lengths was unnecessary.

The preparation of the sodium specimens was somewhat complicated by its solidity at ordinary temperatures, and its

oxidation on exposure to air. The following method was therefore adopted in preparing a bar. A glass tube, about 160 cms. long and 2 cms. diameter, was taken, and inset tubes made in its side as described above. About 10 cms. from the first of these tubes and 30 cms. from the nearer end, a constriction was made so that the end piece formed a funnel. A piston formed from another glass tube worked in from the other end. With the piston pushed well in, the tube was filled to a point above the constriction with pure dry paraffin oil. Pieces of sodium, carefully freed from oxide, were inserted, and the tube carefully heated to melt the sodium. The piston was then slowly drawn down, and more sodium added until all the inset tubes were covered by the sodium. The tube was then allowed to cool and the top cut off just below the constriction. The sodium rod so formed, in its casing of glass, was then ready to be placed in position below the lead bath, as shown in Fig. 1. The thermoelectric junctions were then packed into their inset tubes. In the case of mercury there was, of course, no special difficulty in the filling of the tube.

Description of Observations Made.

After putting a sodium rod in position, and connecting up the thermo-couples, the lead bath was heated to and maintained at a temperature (about $350^{\circ}\text{C}.$), such that when a steady state was set up about five of the thermo-couples were in liquid sodium. The galvanometer deflections due to each couple were then read in succession. This could be done very quickly, since the change from one to the next was made by a mercury cup interchanger. The cups were arranged in the arc of a circle, and each could be connected in turn with the centre by means of a radial arm. The readings thus obtained were then reduced by a calibration curve which had previously been determined by comparison of direct deflections with potentiometer readings.

These reduced readings were then plotted against the positions of the rod to which they correspond. To find from this curve the ratio of the conductivities of the liquid and solid, it is only necessary to find the two tangents which can be drawn at the point corresponding to the junction between the liquid and solid portions of the rod; because this ratio is inversely proportional to the ratio of the slopes of the two tangents.

In the case of mercury, arrangements had to be made to cool at the bottom instead of to heat at the top. The lower end was inserted into a carbonic acid snow and alcohol mixture. The whole tube was surrounded by a celluloid cylinder through which the thermo-electric couple wires were threaded. The object of this cylinder was to diminish the deposit of hoar frost in the lower part of the tube, which was otherwise very disturbing. The celluloid cylinder limited the rate of supply of fresh moist air to the tube, and thus achieved the desired object.

The change of slope is very much greater for mercury than for sodium. A typical curve for the former is shown in Fig. 2. The tangents at the point of change are also shown in this diagram. There is, of course, some difficulty in drawing in these tangents; hence, in different experiments considerable variation in slope was obtained. The following is a complete set of values for the ratio of the conductivity for the solid to that for the liquid at the same temperature :—

K_s/K_L for mercury.

4.44

4.62 (Curve on Fig. 2.)

3.28

3.76

3.83

3.53

3.91 = Mean K_s/K_L for mercury.

In the case of sodium it was found more satisfactory to plot $\log \theta$ against x , because the slopes, especially that on the liquid side, were then more constant.

The following slopes were obtained :—

<i>Sodium.</i>		
Solid.		Liquid.
0.0279	0.0230
0.0267	0.0188
0.0248	0.01885
0.0267	0.0209
0.0269	0.0200
<hr/>		<hr/>
Sum	0.1330	0.10155

Ratio of slopes $\frac{0.1330}{0.10155} = 1.31 = \text{mean } K_s/K_L \text{ for sodium.}$

Electrical Conductivity.

The change of electrical conductivity with fusion had been determined by other observers both for mercury and sodium. The following determination for mercury are on record :—

Cailletet and Bouty (1885)	4.08
Dewar and Fleming (1896)	4.04
C. L. Weber (1885).....	4.10

In the case of sodium, previous determination of the change in electrical conductivity are :—

Matthiesson (1857)....	1.37—1.70
Bernini (1903).....	1.35
Northrup (1911).....	1.434 (Estimated from diagram.)

It was deemed advisable to make a fresh determination for sodium. A glass tube 0.5 cm. in diameter with two platinum wires sealed in at points about 5 cms. apart, was filled with sodium in a similar way to that described above. The tube was then set up in a horizontal electric furnace in such a way that the two platinum wires were near the centre of the furnace. Current was passed through the sodium, contact being made with it by stout copper electrodes. The potential-difference tapped off by the platinum wires was balanced on a potentiometer. No absolute measurements were made. Readings of the potential drop were taken at various temperatures below and above the melting point of sodium, and for both ascending and descending temperatures. The constancy of current through the sodium was checked by taking the potential drop along a piece of thick copper wire connected in series with it. The potentiometer readings were plotted against the temperature, and the ratio of the temperature coefficients for liquid and solid obtained by determining the slopes of the curves on the two sides of the melting point.

Four independent values obtained for the ratio were—

1.453
1.402
1.430
1.467

giving a mean of 1.438. This value is very similar to Northrup's, but is rather higher than our thermal values.

It may be of interest to mention some of the other changes which occur during fusion. There is, of course, a change in the specific energy (or internal latent heat)—that of the liquid being

the greater; a change in the density that of the liquid being less in the case both of sodium and mercury, but greater in the case of bismuth; a change in the coefficient of expansion that of the liquid being the greater; the specific heat of sodium undergoes no appreciable change, but its rate of variation with temperature changes from positive to negative on fusion (Ezer Griffiths, Roy. Soc. "Proc.," A., Vol. LXXXIX., 1913-14, p. 561); the temperature coefficient of the electrical resistance of mercury changes from 0.00455 between -55°C. and -40°C. to 0.000834 between 0°C. and 5°C.

With regard to thermo-electric effects the evidence is somewhat more conflicting. W. B. Burnie ("Phil. Mag.," 1897) finds a continuity in the curve of E.M.F. against temperature in the case of a copper-mercury element with, however, a marked change in its slope, $\frac{dE}{d\tau}$, at the melting point of mercury.

The slope changes abruptly from a large nearly constant positive to a smaller negative value. This would, of course, imply a change in the Peltier coefficient $\left(\tau \frac{dE}{d\tau}\right)$. Assuming

that the Peltier coefficient is proportional to the logarithm of the ratio of the concentrations of the electrons in copper and mercury, his values would give $n_{\text{solid}}/n_{\text{liquid}} = \text{about } 5$. This is sufficiently near to the ratio found for the electrical conductivities to tempt one to suppose that the two phenomena are telling consistent stories. On the other hand, Peddie and Shand ("Proc." Roy. Soc., Edin., 23, p. 15, 1900) find no change; nor also did P. Cermak ("Ann. der Phys.," 26, 1908, p. 521) for either the thermo-electric power or the Peltier effect.

Lastly, the photo-electric effect shows no change on fusion of the metal (sodium) according to Dember ("Ann. der Phys.," 23, 1907, p. 957). These results are discussed by E. Wagner ("Ann. der Phys.," 33, 1910, p. 1484).

The experimental part of this Paper was finished in July, 1913. In September, 1913, of the "Physical Review" appeared a Paper by J. W. Hornbeck on "Thermal and Electrical Conductivities of the Alkali Metals," in which is described a very similar method of investigation. In the case neither of sodium nor potassium was the investigation carried as high as the melting point; the thermal conductivity for both the solid and the liquid was determined for potassium-sodium alloy, the value being less in the liquid state. As the values were not obtained at the melting point itself, and as

there is only one value for the solid, it is not possible to state the exact ratio of reduction for this case.

The only other determination with which we are acquainted is one made by C. Barus ("Phil. Mag.," 33, p. 431 (1892), on thymol, a dielectric). He finds for the ratio of the thermal conductivity of solid to that of liquid the value 359/313. He had previously measured the change in specific heat. The corresponding change in thermometric conductivity is 1077/691.

ABSTRACT.

The change in question was determined for mercury and for sodium by finding the temperatures at different points of a cylinder of the metal contained in a glass tube. The ends of the cylinder were maintained at such temperatures that the metal was liquid half-way down its length, the remaining part being solid. The temperatures were taken by means of thermoelectric junctions inserted in narrow tubular depressions which had been formed in the glass tube by forcing a knitting needle down into the locally heated glass. The ratio of the thermal conductivity for solid and liquid was estimated from the slope of tangents drawn to the temperature-curve on each side of the melting point. The values of these ratios are of the same order as the ratio of the corresponding values of the electrical conductivities. The mean value for mercury is 3.91, and for sodium 1.31.

A summary list is given of other data concerned with fusion.

DISCUSSION.

Prof. O. W. RICHARDSON congratulated the authors on their satisfactory treatment of an important problem. The change of thermal conductivity with fusion had not, he believed, been attacked experimentally before. In listening to the reading of the Paper one felt impressed by the small amount of effort and the simplicity of the apparatus with which the authors had been able to solve what was generally regarded as a very difficult problem. This research, it was interesting to note, was one of the few of which the results agreed with the deductions from the elementary electronic theory.

Prof. F. G. DONNAN referred to the researches carried out at his suggestion by Dr. C. M. Stubbs on the radiation emitted by copper, silver and gold at high temperatures. These experiments showed that there was a marked change in the distribution of energy throughout the visible spectrum when passing from solid to molten metal, and pointed to some change in the electronic structure, or in the inter-electronic forces, occurring at the transition from solid to liquid. The complexity of the problem had, so far, prevented any mathematical treatment, but there appeared no doubt that results such as these, coupled with the discontinuities in thermal and electrical conductivity, would be of value in throwing light on the inner mechanism of the phenomenon of melting. Photometric measurements of the light radiated by polished plates of metals at high temperatures presented considerable difficulties owing to the tendency of the "flowed" surfaces to crystallise, but in spite of these difficulties Dr. Stubbs had clearly demonstrated the existence of an

abrupt change in the radiation-spectrum on passing from solid to liquid in the case of certain metals.

Dr. PORTER, in reply, said that while isolated measurements of thermal conductivity of some substances above and below the melting point had been made by previous workers, in no case that he was aware of had sufficient data been obtained from which to deduce the sudden change which takes place on fusion. He was cognisant of the work of Dr. Stubbs but had always thought the nature of the surface was of such importance in radiation experiments as to make it difficult, on account of crystallisation and contamination of the surface at high temperatures, to obtain conclusive results. He had forgotten at the moment the degree of consistency obtained by Dr. Stubbs, but if the results were more or less in agreement they would undoubtedly point to a change at the fusion point in the radiation emitted by the substances.