H. J. Hall

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SESSION 5: EXPERIMENTAL THERMAL CONDUCTIVITY

Experimental Determinations of the Thermal and Electrical Conductivities of Molten Metals

By R. W. POWELL, D.Sc., Ph.D., F.Inst.P., and R. P. TYE

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Experimental Determinations of the Thermal and Electrical Conductivities of Molten Metals

By R. W. Powell, D.Sc., Ph.D., F.Inst.P.,* and R. P. Tye*

New determinations have been made of the thermal and electrical conductivities of lead, bismuth and the lead–bismuth eutectic from their melting points to about 500 to 600 deg. C. (932 to 1,112 deg. F.). These results are discussed, and appear to show, in agreement with other recent data, that the thermal conductivities of molten metals can be predicted from their electrical resistivities with a fair degree of certainty by using the theoretical value of the Lorenz function.

INTRODUCTION

An earlier paper (Powell 1949),† which surveyed the data available for the thermal conductivities of molten metals and alloys, disclosed the need for further experiments in this field. Not only was a dearth of information indicated, but the available results were frequently discordant. Work was therefore initiated with a view to improving the position. The molten metals so far studied have been mercury, lead, bismuth and the lead-bismuth eutectic. Although attention was first directed to mercury, for which existing values at room temperature ranged from about 0·07 to 0·11 joule cm. per sq. cm. sec. deg. C., the work on this liquid metal has not yet been completed at the lower end of the temperature range, and the present account will deal mainly with the other three liquids.

Measurements of the electrical resistivity have been included for the purpose of ascertaining the extent to which the Wiedemann–Franz–Lorenz relationship is obeyed by these liquid metals.

METALS INVESTIGATED

The samples of lead and bismuth studied in this investigation were obtained in the form of rods of 7 mm. and 5 mm. diameter. The purity of the lead (Laboratory No. 5873) as supplied was stated to be greater than 99·995 per cent, and the bismuth (Laboratory No. 7613), was stated to be of a high degree of purity.

For each test the metals were melted into the apparatus, and for the measurements on the alloy of the eutectic composition the metals were in the proportions by weight of 44·5 per cent lead, and 55·5 per cent bismuth.

EXPERIMENTAL METHODS

The apparatus employed for the thermal conductivity determinations is shown in Fig. 5.1. This is a modification of the longitudinal heat-flow apparatus normally used for comparative measurements of the thermal conductivity of metals in the solid phase. The molten metal is contained in a thin-walled tubular extension of the lower-standard bar and the heat flow to and from this section is derived from temperature gradients established in metal bars of known thermal conductivity (Powell and Hickman 1946; British Iron and Steel Research Association, 1953). For the measurements on lead these bars were of 0·8 per cent carbon steel, but stainless steel was used for bismuth and for the eutectic. The units which were in two sections were machined from 1-inch-diameter bars. The lower portion consisted of a bar of steel $\frac{31}{32}$ inch in diameter and 9·3 inches long having cavities $1\frac{1}{2}$ and $3\frac{1}{2}$ inches deep in the lower and upper ends. The larger cavity had a wall thickness of the order of 0·015 inch and served to hold the molten metal. The upper bar had a diameter of 1 inch and was 5·8 inches long. The lower end was machined to fit closely over the top of the lower section and to have an overlap of about $\frac{1}{4}$ inch. This upper portion had a cavity $1\frac{1}{2}$ inches deep and of $\frac{7}{8}$ inch diameter in which a heating coil could be inserted. It also had an axial hole $\frac{1}{4}$ inch in diameter which allowed access for excess molten metal and also provided means for the insertion of thermocouples directly into the molten metal. When experimenting with mercury such measurements had confirmed the gradient of temperature along the axis to agree closely with the gradient at the wall as measured by thermocouples spot-welded to the outer surface of the steel wall. In the present work only the spot-welded couples were used and these were of platinum and platinum + 10 per cent rhodium of 0·2 mm. diameter.

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* *The National Physical Laboratory, Teddington, Middlesex.*

† *An alphabetical list of references is given in Appendix 5.1.*

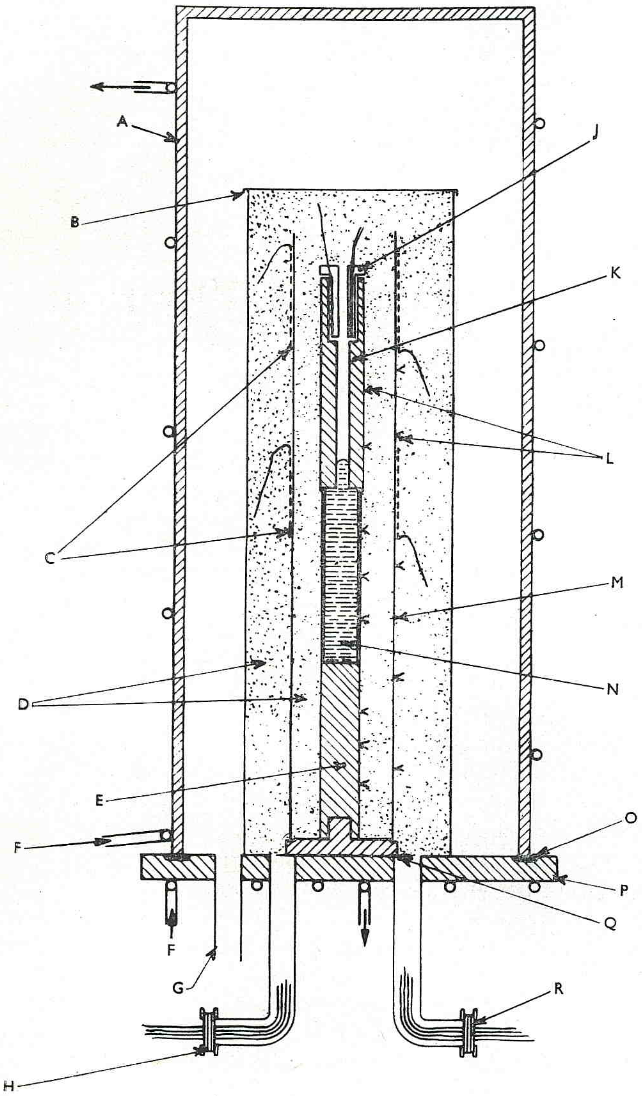

Fig. 5.1. Apparatus for Thermal Conductivity Determinations of Molten Metals

A Water-cooled steel vacuum cover.
B Lid.
C Guard heaters wound on mica.
D Insulating powder in interspace.
E Standard material.
F Water.
G To pumping system.
H Rubber seal for heater leads.
J Specimen heater wound on refractory.
K Standard material.
L Thermocouples in specimen and guard.
M Guard tube.
N Liquid metal in thin-walled cavity.
O Wax seal.
P Water-cooled base.
Q Mica.
R Rubber sheet seal for thermocouples.

Three other thermocouples were fixed to both the upper and the lower bars at spacings of about 1 inch, as shown in the figure.

The composite bar was mounted vertically within a concentric guard-tube furnace, supported on a metal baseplate, but insulated from it by a sheet of mica. The interspace between the specimen and guard was packed with heat-insulating powder and this in turn was surrounded by a further metal tube to retain more powder as insulation around and above the furnace.

Copper leads were attached to the top and bottom of the composite bars so that a current could be passed through the system when measurements of the electrical resistance of the sample were required. Current leads and thermocouple wires were brought out through compressed-rubber seals mounted in tubes welded to the base of the apparatus, and the whole assembly was enclosed by a metal cover supported and waxed to this base, so that the experiment could be carried out under vacuum conditions.

For a determination of thermal conductivity the heaters were adjusted to establish a gradient of temperature from top to bottom and to ensure that the temperature distribution was closely matched by that of the guard tube.

The effective values for the heat flow to and from the centre section were obtained from observation of the temperature gradients established in the upper and lower sections respectively. The heat flow in the centre section comprising the sample of molten liquid in parallel with the walls of the container was assumed to be the mean of these two energy quantities after correcting for any estimated lateral heat interchange occurring between the mid-points of the relevant sections. After correction, the two quantities seldom differed by more than 2 per cent. The quantity of heat required for the calculation of the thermal conductivity of the molten metal was then found by subtracting the quantity flowing in the walls of the containing tube from this mean energy. This last correction was of the order of twelve, ten and eight per cent for the molten lead, bismuth and the lead-bismuth eutectic respectively.

In determining the electrical resistivity, limbs of two thermocouples attached to the walls of the container were used as potential leads, and the potential difference between them was compared with the potential drop across an external standard resistance of comparable value. The direction of the measuring current was reversed so as to enable thermal e.m.f.'s to be eliminated. A correction has again to be applied for the section of the containing tube in parallel with the molten metal.

For lead and the eutectic, experiments conducted in the above manner enabled thermal and electrical conductivity determinations to be made on the same sample in the course of the same experiment. In the case of bismuth a break which occurred in one of the copper leads prevented this being done. The electrical resistivity determinations on bismuth were made subsequently on another sample from the same supply, the method used being similar to one previously employed for molten iron (Powell 1953). This involved the use of a cell that had been calibrated in terms of mercury at normal temperatures.

RESULTS AND DISCUSSION

The thermal conductivity values obtained for the three molten metals are plotted in Fig. 5.2. The temperature range covered extended from a little above the melting point to between 500 and 600 deg. C. For each metal the measurements near the melting point were repeated after the values at a higher temperature. These repeat points agreed closely and were accepted as an indication that there had been no serious interaction of the test metal with the containing tube. In each case an increase in thermal conductivity with increase in temperature will be noted.

Fig. 5.2 also contains the results obtained by earlier workers for these molten metals. In the case of lead it will be seen that the values of Bidwell (1940) are some 40 to 50 per cent in excess of those of the present investigation, those of Konno (1919) are in close agreement near the melting temperature, but diverge at higher temperatures, whilst the most recent determination by Rosenthal (1953) gives a curve of the same form as the present work but about 10 per cent greater.

Bidwell's values would appear to be considerably in error, a fact which gives additional support to an earlier suggestion made by one of the present authors (Powell 1948) that the intercept relation proposed by Bidwell (1928, 1940) 'is not so well supported by experimental evidence as the reader is led to believe'.

For bismuth, the single value derived from the work of Northrup and Pratt (1917) is in good accord with the present results, but Konno's values are now much higher, the difference decreasing from about 50 to 10 per cent over the range 300 to 550 deg. C. (572 to 1,022 deg. F.).

For the eutectic, the early determination by Brown (1923) over the limited range of 166 to 285 deg. C. (331 to 545 deg. F.) is seen to be in good agreement with the present work. Brown's temperature coefficient is however rather smaller and the values to higher temperatures given by Newman (1947) in the Genie Report appear to be an extrapolation of this data. The rather higher line also shown in the figure is referred to in a paper by Johnson and others (1953) as from 'G.E. Laboratory personal communication'.

The results obtained from the electrical resistivity measurements made on the three molten metals are plotted in Fig. 5.3*a*. The lower portion, Fig. 5.3*b*, gives

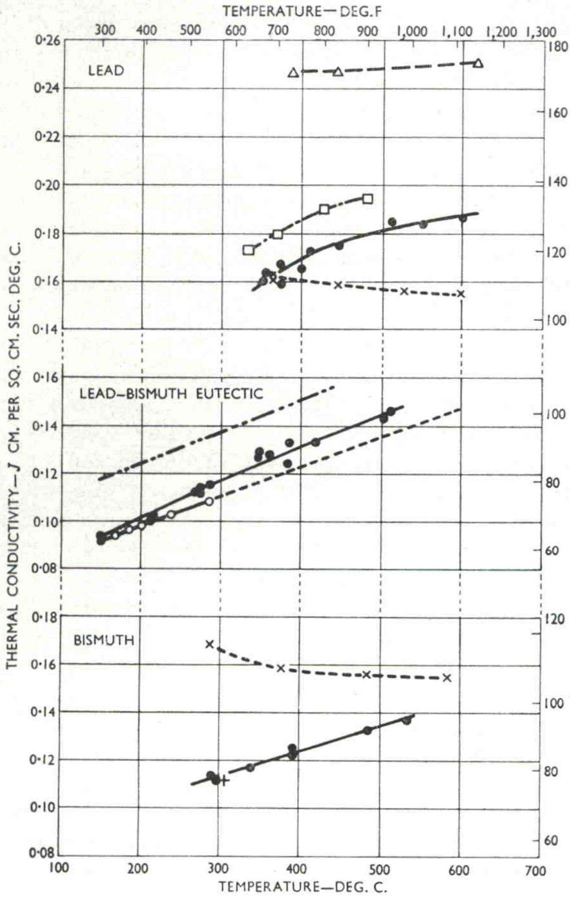

Fig. 5.2. Thermal Conductivities of Molten Lead, Bismuth and Lead–Bismuth Eutectic

△ Bidwell. □ Rosenthal. ● Present work. × Konno. + Northrup and Pratt. —·-·— G.E.C. to H. A. Johnson. ---- Newman. ○ Brown.

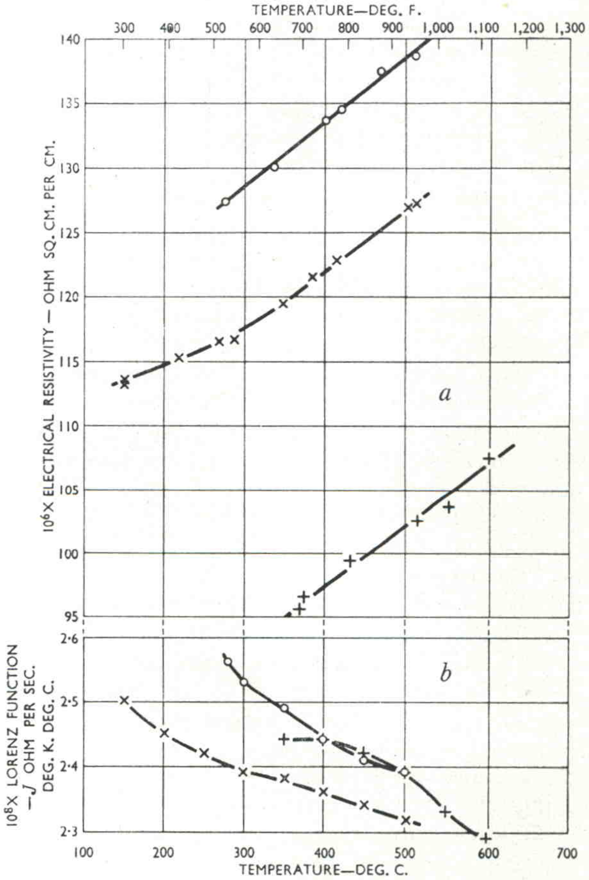

Fig. 5.3. Molten Lead, Bismuth and Lead–Bismuth Eutectic

+ Lead. × Lead-bismuth eutectic. ○ Bismuth.
a Electrical resistivity. *b* Lorenz function.

Table 5.1. Smoothed Values for Thermal Conductivity (J cm. per sq. cm. sec. deg.C.), Electrical Resistivity (10^{-6} ohm sq. cm. per cm.) and Lorenz Function (10^{-8} J ohm per sec. deg.C. deg.K.) of Lead, Bismuth and Lead-bismuth Eutectic (44·5 per cent Lead 55·5 per cent Bismuth)

Temperature		Lead			Lead–Bismuth Eutectic			Bismuth		
deg.C.	deg.F.	Thermal conductivity	Electrical resistivity	Lorenz function	Thermal conductivity	Electrical resistivity	Lorenz function	Thermal conductivity	Electrical resistivity	Lorenz function
150	302	—	—	—	0·093	113·$_5$	2·50	—	—	—
200	392	—	—	—	0·101	114·$_7$	2·45	—	—	—
250	482	—	—	—	0·109	116·$_0$	2·42	—	—	—
300	572	—	—	—	0·116$_5$	117·$_7$	2·39	0·113	128·$_6$	2·53
350	662	0·160	95·$_0$	2·44	0·124	119·$_6$	2·38	0·118	131·$_1$	2·49
400	752	0·169	97·$_2$	2·44	0·130$_5$	121·$_8$	2·36	0·123	133·$_6$	2·44
450	842	0·176	99·$_5$	2·42	0·136$_5$	124·$_2$	2·34	0·128	136·$_0$	2·41
500	932	0·181	102·$_0$	2·39	0·142	126·$_6$	2·32	0·133$_5$	138·$_5$	2·39
550	1,022	0·184	104·$_4$	2·33	—	—	—	0·139	—	—
600	1,112	0·187	106·$_8$	2·29	—	—	—	—	—	—

the values calculated at 50 deg. C. (122 deg. F.) intervals for the Lorenz function, the product of the thermal conductivity and electrical resistivity divided by the absolute temperature, deg. K. The smoothed values used in this derivation are reproduced in Table 5.1.

The striking fact which emerges from the result for the Lorenz function is not only their close agreement, but their close agreement with the theoretical value of $2{\cdot}45 \times 10^{-8}$ *J* ohm per sec. deg. K. deg. C., as derived by Sommerfeld (1928). The extreme values are seen to be $2{\cdot}56 \times 10^{-8}$ for bismuth at 280 deg. C. and $2{\cdot}29 \times 10^{-8}$ for lead at 600 deg. C. These values are respectively 4·5 per cent above and 6·5 per cent below the theoretical value.

When the data available for the thermal conductivity of molten metals were reviewed nearly ten years ago, Powell (1949), the Lorenz relationship was also considered, and the following was the final conclusion: 'The general indications are that just above the melting point the Lorenz function of most metals may have values ranging from $2{\cdot}5 \times 10^{-8}$ to $3{\cdot}35 \times 10^{-8}$, but that at some 200 deg. C. above the melting point the Lorenz function might be expected to exceed the theoretical value by not more than about 10 per cent'.

Since then Ewing, Grand and Miller (1952) have studied molten sodium and potassium, for which, using electrical resistivity values of Bornemann and Rauschenplat (1912), they obtained Lorenz functions from 2·22 to $2{\cdot}17 \times 10^{-8}$ for sodium and of $2{\cdot}07 \times 10^{-8}$ for potassium. Subsequently, Ewing, Seebold, Grand and Miller (1955) have obtained the following values:

for mercury, range 100 to 297 deg. C. (212 to 567 deg. F.), $(2{\cdot}615 \pm 0{\cdot}025)\ 10^{-8}$;

for sodium, range 200 to 500 deg. C. (392 to 932 deg. F.), $(2{\cdot}335 \pm 0{\cdot}025)\ 10^{-8}$;

for an alloy of 23 per cent sodium 77 per cent potassium, range 200 to 700 deg. C. (392 to 1,292 deg. F.), $(2{\cdot}31 \pm 0{\cdot}03)\ 10^{-8}$;

and for an alloy of 43·5 per cent sodium 56·5 per cent potassium, range 200 to 500 deg. C. (392 to 932 deg. F.), $(2{\cdot}46 \pm 0{\cdot}03)\ 10^{-8}$.

The foregoing value for potassium is only about 85 per cent of the theoretical value. This is a somewhat surprising result but is in line with other values below the theoretical, including the high temperature values of the present investigation. Apart from these potassium values it will be seen that the results obtained subsequent to the previous analysis are all within 8 per cent of the theoretical value.

It might at this stage be remarked that our own unpublished values for the thermal conductivity of mercury are lower than those of Hall (1938) and in close agreement with the results of Ewing, Seebold, Grand and Miller at 200 deg. C. The Lorenz function increases with decrease in temperature but at 50 deg. C. is not more than 15 per cent above the theoretical value.

Thus it would seem that for the prediction of the thermal conductivities of molten metals use of the theoretical Lorenz function gives values of rather greater accuracy than appeared likely from the results available ten years ago. More work clearly needs to be undertaken in this field, but the results of the present decade indicate that the uncertainty accompanying this method of derivation is unlikely to exceed 15 per cent and will for many metals be within half of this figure.

It is hoped to extend this investigation to cover other metals for which the existing information is at variance with the above conclusion, for example, tin and zinc and to make further measurements of the electrical resistivities of molten metals so as to provide the data required for the estimation of their thermal conductivities to high temperatures.

Before concluding this paper it is considered desirable to include a revised graph, of the data at present available for the thermal conductivities of molten metals, and to refer to any influence the present results may have on previous heat transfer measurements. The revised data are plotted in Fig. 5.4 where the starred items are those which have become available since the earlier figure of this nature was published (Powell 1949), except that the results of Hall (1938), which were overlooked at that time, are now treated in this way. The references to these starred items are included in the present bibliography, but for the other items reference should be made to the earlier paper.

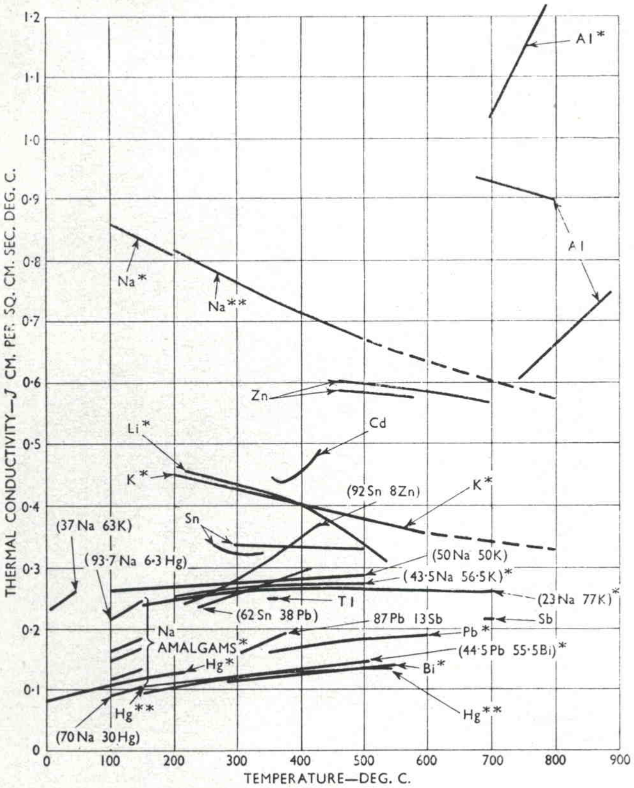

Fig. 5.4. Thermal Conductivities of Molten Metals

(Available data January, 1957).

Sodium Na*	Hall 1938.
Mercury Hg*	
Sodium amalgams*	
Aluminium, Al*	Hogan 1950.
Sodium, Na**	Ewing, Grand and Miller, 1952.
Potassium, K*	
Mercury, Hg**	Ewing, Seebold, Grand and Miller 1955.
(43·5 Na, 56·5 K)*	
(23 Na, 77 K)*	
Lithium, Li*	Webber, Goldstein, and Fellinger 1955.
Lead, Pb*	Present investigation.
Bismuth, Bi*	
(44·5 Pb, 55·5 Bi)*	

For other references *see* Powell 1949.

Of the present metals, the lead-bismuth eutectic seems to have been the fluid most frequently used for heat-transfer investigations. Johnson, Hartnett and Clabaugh (1953) studied the heat transfer for turbulent flow of this molten alloy in a mild-steel pipe. They found that the resulting Nusselt moduli, Hd/k, were 25 to 35 per cent lower than predicted by the Lyon–Martinelli momentum theory for turbulent flow. For the same fluid they quote the results of Untermeyer as agreeing with the theory and those of other American workers, Seban and Lubarsky as also being well below the predicted curve. Johnson and others made use of the thermal conductivity values suggested by Newman (1947) and, stated that they all used the same property values. The present thermal conductivity results have been seen to agree closely with Newman's curve towards the melting point and to be 6 per cent above this curve at 500 deg. C. (932 deg. F.). As Johnson and others gave 10 per cent as the accuracy of their work it will be seen that any change due to revision of the thermal conductivity values would be well within the stated accuracy. Furthermore, it would only serve to increase the observed discrepancy, which receives further discussion in a subsequent paper, Johnson, Hartnett and Clabaugh (1954).

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APPENDIX 5.I

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