THERMAL CONDUCTIVITIES OF SOME METALS IN THE SOLID AND LIQUID STATES

BY W. BYRON BROWN

ABSTRACT

Thermal conductivities of some metals and eutectic alloys above and below their melting points, 50° to about 400° C.—*A guard ring method of measurement* was used. A cylindrical rod of the metal, 1.5 cm in diameter and 12 cm long was surrounded by a slate tube and outside that a hollow brass cylinder. Both rod and cylinder were independently heated electrically at the top and cooled by flowing water at the bottom so as to maintain the same temperature gradient in both, as shown by thermocouples. The input of energy into the rod was corrected slightly for heat leakage and divided by the temperature gradient times the area to get the conductivity. *The conductivities of tin and cadmium* decrease at the melting point by over 1/3 and ½ respectively. *For thallium,* there is a drop of 1/10 at about 120° C. The temperature coefficients are about the same before and after melting, being -5×10^{-5} (Sn), $+21\times10^{-5}$ (Cd), $+8\times10^{-5}$ (Th). *For the eutectics: Sn .92, Zn .08; Sn .62, Pb .38; Pb .87, Sb .13; Pb .46, Bi .54;* the temperature coefficients for the liquids are all positive constants and have values at 300° C—from .0011 (Pb−Bi) to .0030 (Pb−Sb)—close to those found for gases at that temperature, indicating that the mechanism is similar in the two cases. Below the melting point the curves vary, one increasing with temperature (Sn−Zn), two decreasing, and one reaching a maximum (Pb−Sb). The sudden decrease on melting varies from 2/3 for (Sn−Zn) and (Pb−Sn) to 1/10 for (Bi−Pb).

Polymorphic change in thallium at 120° C is indicated by the conductivity results.

NORTHRUP and Pratt[1] and A. W. Porter and F. Simeon[2] have studied the change in the thermal conductivity of tin, bismuth, sodium and mercury on fusion. Konno[3] has measured the change in the conductivity of tin, lead, bismuth, zinc, aluminum and antimony from room temperature to about 700°C. Hornbeck[4] measured the conductivity of a sodium-potassium alloy in both the liquid and the solid state. No other work appears to have been done on the change of the thermal conductivity of metals and alloys at fusion and on the variation with temperature of the thermal conductivity of the molten metals. In view of the limited amount of data available it appeared worth while to extend these observations to other metals and alloys.

---

[1] Northrup and Pratt, Jour. Franklin Institute, **184**, 675, 1917

[2] Porter and Simeon, Proc. Phys. Soc. **27**, 307, 1915

[3] Konno, Science Reports, Tohoku Imperial Univ. (1) **8**, 177, 1919

[4] Hornbeck, Phys. Rev. (2) **2**, 217, 1913.

METHOD OF MEASUREMENT

The specimen to be measured (Fig. 1) was in the form of a cylindrical rod *R*, 1.5 cm in diameter and 12 cm long, encased in a slate tube *S*. Heat was supplied at the top by a heating coil of nichrome wire wound on a copper core *C*, power being furnished by a storage battery. The voltage across it was kept constant to 1/5000 by means of a potentiometer arrangement which balanced a definite fraction of the voltage against an Edison storage cell in series with a galvanometer. It was found that molten metals dissolved the copper quite rapidly, forming an alloy with a quite different conductivity. To prevent this action a steel shell *P* about 2 mm thick was screwed tightly over the lower part of the copper core. This was then screwed into the top of the specimen. The heating coil was covered with a thick layer of cement (a mixture of 1 part sodium silicate to 1 part powdered feldspar) to prevent oxidation. The rod *R* was cooled at the bottom by cold water circulating through a small jacket *J*. The flow was kept constant by an overflow tank which main-

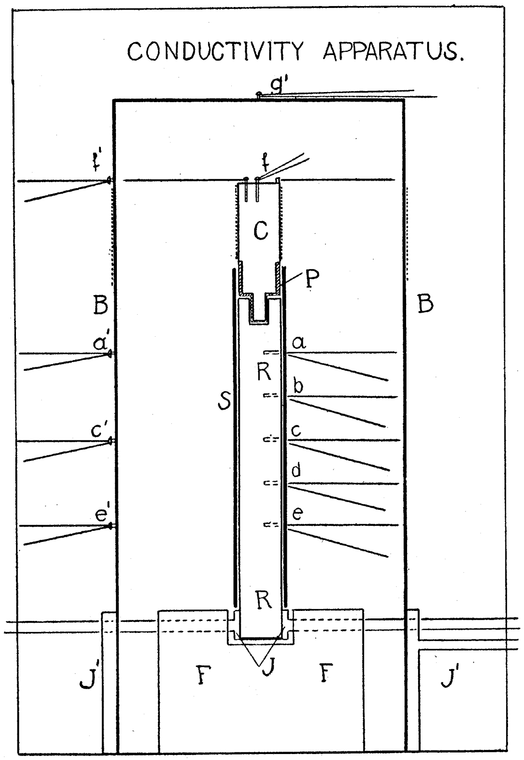

Fig. 1

tained a constant head. Outside the slate tube *S* was a brass tube *B*, 10 cm in diameter, heated at the top by a coil of wire and cooled at the bottom by a water jacket *J'* similar to *J*. By controlling the current supplied to the shield heater, the same temperature gradient could be established in the specimen and in the jacket. A second brass tube, 17.2 cm in diameter, surrounded the shield described above, and the annular spaces between the two shields and the slate tube were filled with very finely powdered, calcined magnesia.

The temperature gradient in the rod was measured by means of five thermo-couples, *a*, *b*, *c*, *d*, *e*, 1.5 cm apart. To ensure accurate spacing of the junctions, they were hard-soldered into tapered steel bushings about 1.5 mm in diameter at the large end and 5 mm long and then calibrated by means of a travelling microscope. The holes in the rod were reamed out until these bushings fitted into them flush with the surface. The wires were sealed into the slate by the cement described above. The cold junctions were in an insulated oil bath at room temperature, the temperature being estimated to 0°.01 C on a mercury thermometer.

Thermo-junctions were placed on the brass tube B at the points *a'*, *c'*, *e'*, *f'*, and *g'*, directly opposite the corresponding junctions in the rod. The junctions were held in contact with the tube by means of suitable screws, and the lead wires were insulated by lavite bushings.

The thermal electromotive forces were measured by means of a slide-wire potentiometer with necessary extension coils. It was calibrated by means of a Leeds and Northrup high precision Wheatstone bridge, which was used to compare each hundreth part of the slide wire with the total and each resistance coil with the slide wire and with the total potentiometer resistance. The table of corrections thus found was used in all subsequent work. The largest correction was 0°.14 C, most of them being of the order of 0°.04 C.

The thermo-couples were calibrated at the following points[5] (the other junction being in the oil bath as usual).

	Temp.	Pressure coefficient (deg./cm Hg).
1. Ice (m. p.)	0°.00	
2. Water (b. p.)	100°.00	0.368
3. Aniline (b. p.)	183°.9	0.51
4. Diphenylamine (b. p.)	302°	0.66*
5. Sulphur (b. p.)	444°.7	0.91

* Estimated from values for similar substances.

It was found possible to represent these points quite accurately by means of two parabolic equations, one covering the range 0°-184° and the other

---

[5] These values were taken from "Recueil de Constantes Physiques" Societe Francaise de Physique, 1913.

the range 184°-450°. A table was constructed by means of these equations and used to find the approximate temperature. Each couple was calibrated separately and its deviations from the above table tabulated, thus enabling the true temperature to be found.

THEORY OF THE MEASUREMENTS

The conductivity was calculated from the usual equation,

$$H = KAt(d\theta/dx) \tag{1}$$

If W = watts flowing and J = mechanical equivalent of heat, then the equation for the thermal conductivity K may be written,

$$K = W/JA(d\theta/dx) \tag{2}$$

If it is desired to apply (2) to a particular point such as b or c, then it is necessary to know the heat which is actually flowing down the rod at that point. This is found by subtracting from the power input, the heat leakage to or from the coil and rod above the point under consideration. For convenience the heat leakage, Δw, is divided into three parts.

The first part Δw_1 is the heat lost from the top and sides of the heating coil C and the case S above the point b by transfer through the magnesia and conduction along the lead wires. It is calculated by the equation,

$$\Delta w_1 = M\Delta\theta' \tag{3}$$

where $\Delta\theta'$ is the approximate temperature difference between the rod and enclosure, and M is a constant found by experiment. Δw_1 usually amounts to from 4 to 7 per cent of W.

The second part Δw_2 is the heat lost from the sides between b and the point where K is being determined. It is given by

$$\Delta w_2 = N\Delta\theta_m\Delta x \tag{4}$$

where N = constant found by experiment,
$\Delta\theta_m$ = mean temperature difference between rod and enclosure,
Δx = distance from b to the point considered.

This correction is negligible in the solid state and less than 1.5 per cent in the liquid state.

The third part Δw_3 is the heat conducted by the slate case S. It is given by

$$\Delta w_3 = CJk'A'(d\theta/dx) \tag{5}$$

where C = constant found by experiment;
k' = conductivity of the slate;
A' = area of slate.

This correction is usually about 6 per cent of w.

These corrections sometimes have different signs so that their sum Δw varies from 2 to 8 per cent of w. The error in Δw does not exceed 10 per cent, so that the effect on W is about 1 per cent or less.

In equation (2), therefore, W is given by

$$W = IV - \Delta W \tag{6}$$

where I = current in amperes and V = voltage drop over heating coil.

Both A and Δx change with the temperature on account of the expansion of the metal and case. Putting $A = A_0(1+\lambda t)$, Eq. (2) becomes

$$K = W/JA_0(1+\lambda t)\ (d\theta/dx) \tag{7}$$

Two slightly different modes of treatment were used in finding $d\theta/dx$, one when the metal was solid throughout and the other when it was partially liquid. In the latter case, the temperature difference between two adjacent junctions was divided by the distance between them and the quotient used as the value of $d\theta/dx$ midway between these junctions. In the former case, the temperature differences between adjacent junctions were much smaller and consequently the change in K between them much less. Hence the difference between every other junction was divided by the corresponding distance. This gave three values for $d\theta/dx$ at temperatures rather near together. The average of the three was used to find $d\theta/dx$ at the middle junction c.

Observations and Results

An estimate was made of the power needed to produce equilibrium for a desired region of temperature. This was then supplied and the apparatus allowed to heat until steady temperatures were attained. The couples at a and a' were connected in opposition through a fairly sensitive galvanometer and the power supplied to the enclosure B adjusted until the galvanometer showed no deflection or a very small one. From two to four hours were required according to the nature of the material under test. Readings of current, voltage and e.m.f. of the thermocouples were taken both direct and reversed, and with the exception of the couples on B, needed only for the calculation of correction terms, were repeated in inverse order. All readings were then reduced to the mean time of the observations, though the drift was never large.

The results are given in Tables I and II and also plotted in Figs. 2 and 3.

Discussion of Results

The values given in the table for cadmium were obtained by heating the specimen continuously from one temperature to the next higher. Lower values of K, increasing slowly with time, were obtained when the specimen was heated rapidly to a high temperature. For example, measurements on a specimen of cadmium heated to 262°C after cooling overnight gave the value of 0.197. After 3 hours at approximately this temperature the conductivity had increased to 0.204 at 230°C. Cohen[6] has reported three allotropic modifications of cadmium, the transition points being 65° and 95°C. If the form stable at the higher temperature

TABLE I.

Conductivity of pure metals

tin (m. p. 232° C)		cadmium (m. p. 320° C)		thallium (m. p. 302° C)	
Temp.	Cond.	Temp.	Cond.	Temp.	Cond.
50	.1428	45	.200	45	.0934
102	.1404	99	.209	72	.0938
147	.1390	125	.213	88	.0957
160	.1368	165	.221	90	.0958
209	.1297	221	.237	113	.0976
m. p.	.....				
264	*.0815	240	.239	125	.0919
		m. p.	....	149	.0927
291	.0752	355	.106	217	*.111
347	.0767	358	.105	m. p.	.....
		380	.105	353	*.059
		435	.119		

* Doubtful

TABLE II.

Conductivity of eutectic alloys

tin : .92 zinc : .08 (m. p. 200° C)		tin : .62 lead : .38 (m. p. 180° C)		lead : .87 antimony : .13 (m. p. 248° C)		lead : .46 bismuth : .54 (m. p. 130° C)	
Temp.	Cond.	Temp.	Cond.	Temp.	Cond.	Temp.	Cond.
35	.1425	40	.1178	34	.0630	42	.0236
64	.1469	70	.1177	43	.0637	60	.0229
91	.1474	102	.1125	51	.0644	92	.0230
115	.1497	122	.1120	76	.0661	m. p.	.....
120	.1440	124	.1119	97	.0670	166	.0226
148	.1505	125	.1150	118	.0678	185	.0229
m. p.	.....	139	.1115	120	.0665	200	.0233
215	.057	m. p.	.....	155	.0664	236	.0244
343	.0731	236	.0553	168	.0666	285	.0258
433	.0878	239	.0533	190	.0650		
		310	.0610	m. p.	.....		
		336	.0615	316	.0386		
		420	.0710	325	.0396		
				372	.0455		
				382	.0456		
$dK/Kd\theta = .0020$*		$dK/Kd\theta = .0014$*		$dK/Kd\theta = .0030$*		$dK/Kd\theta = .0011$*	

* Temperature coefficient $dK/Kd\theta$ at 300° C.

---

[6] Cohen, Kon Acad. van Wet. te Amsterdam **16**, 489 and **17**, 1050

has a higher conductivity than the other forms, the positive temperature coefficient can be explained by the transition even though the conductivity of one form decreases slightly with rising temperature.

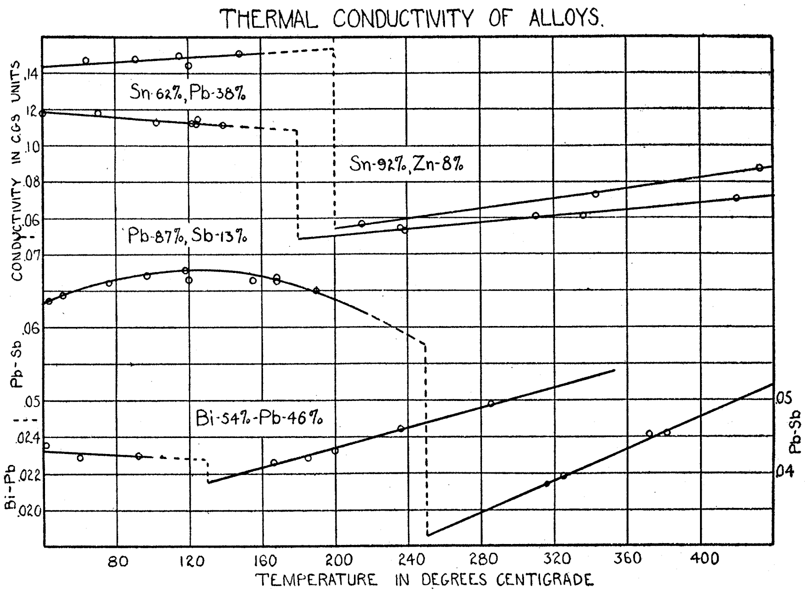

Fig. 2

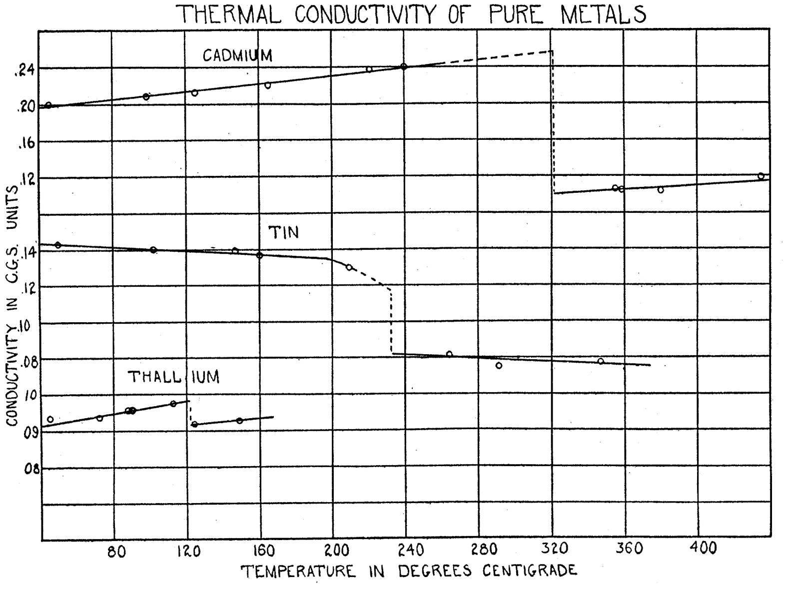

Fig. 3

A similar erratic behavior was observed in the case of thallium and consequently it, as well as the alloys, were heated continuously from one temperature to the next without shutting off the power over night. The last two observations were not plotted because the specimen burned out at the top before the set was quite finished and no more thallium was available. They are included in the table because they show, qualitatively at least, the change in the conductivity of thallium on fusion.

No previous data were available for comparison above 100°C except in the case of tin. At 100°C, however, the following were found

TABLE III

Conductivity of tin and cadmium at 100° C

Lorenz[7]:	.1432 (Sn)	.204 (Cd)
J and D[8]:	.1358 (Sn)	.216 (Cd)
Lees[9]:	.147* (Sn)	.210* (Cd)
Mean (other observers):	.1420 (Sn)	.210 (Cd)
Brown;	.1405 (Sn)	.209 (Cd)

* Extrapolated from 18° C by means of J. and D.'s temperature coefficient.

Konno,[3] using a relative method, found the ratio of the thermal conductivity of molten tin at 292°C to solid tin at 209°C to be .081/.143 = .57. The value found here is .0752/.1297 = .579.

Northrup and Pratt's[1] observations give a rough value of 0.32 for this ratio. This low value can be explained by the fact that the heat loss in their experiments with molten tin was relatively larger than that with solid tin, both on account of the higher temperature and the lower conductivity of molten tin. Since in both cases the heat loss from their apparatus was very large, the difference in the two cases might become excessive.

All the alloys tested show a rather rapid increase of thermal conductivity with increasing temperatures. This agrees with the observations of Hornbeck,[4] who found the same for the Na-K alloy he tested.

The Kinetic Theory of gases shows that K for gases is proportional to η the viscosity, and that η is proportional to T^n where T is the absolute temperature and n is a constant depending on the nature of the gas.[10] Therefore $K = CT^n$ and

$$\frac{1}{\ } \cdot \frac{dK}{dT} = \frac{n}{T} \tag{8}$$

When $T = 573°$ K, the values of n/T range from .0012 for H to .0017 for CO_2 while the coefficients of our molten alloys go from .0011 to .0030.

---

[7] Lorenz, Wied, Ann. **13**, 422, 1881

[8] Jaeger and Diessellhorst, Abh. d. Phys.—Techn. Teichsanstalt, **3**, 269, 1900

[9] Lees, Phil. Trans. **208**, 381, 1908

[10] Jeans, Dynamical Theory of Gases, 2nd. Ed. p. 302

It appears probable, therefore, that the mechanism of heat conduction in these alloys is quite similar to that which exists in the case of gases.

In conclusion, I wish to acknowledge the constant encouragement and help of Professor Alpheus W. Smith, who suggested the subject and supervised the work throughout, and express my thanks to Drs. F. B. Silsbee and M. S. Van Dusen of the Bureau of Standards, who read the manuscript.

Physical Laboratory
Ohio State University
February 7, 1923.