Electrical Conductivity of Tin, Lead, and Bismuth Near Their Boiling Points with Estimates to Their Critical Temperatures

J. A. CAHILL, GARY M. KRIEG, and A. V. GROSSE
Research Institute of Temple University, Philadelphia, Pa. 19144

The electrical resistivity of liquid tin, lead, and bismuth was measured up to 2230°, 1920°, and 1750° K., respectively, with an accuracy of ±2.5 to 3%. A plot of the reduced conductivity, $\kappa_{red} = \kappa_T/\kappa_{mp}$, against reduced temperature, $T_{red^*} = (T - T_{mp})/(T_{crit} - T_{mp})$, showed that they were related by a simple equilateral hyperbola which may be expressed as $(\kappa_{red} + b)\ (T_{red^*} + b) = a$. A similar relationship previously was discovered for liquid mercury, whose electrical conductivity was measured from its melting point to its critical point. The above equation may be written in a linear form, where a and b are the slope and the κ_{red} intercept, respectively.

RECENTLY it was found (*9*) that a simple equilateral hyperbola of the form $(\kappa_{red} + b)\ (T_{red^*} + b) = a$ relates the reduced conductivity κ_{red}, defined as $\kappa_{red} = \kappa_T/\kappa_{mp}$, to the reduced temperature T_{red^*}, defined as $T_{red^*} = (T - T_{mp})/(T_{crit} - T_{mp})$, where κ_{mp} is the electrical conductivity, T_{mp} is the melting point, and T_{crit} is the critical temperature.

The relationship has been discussed in detail (*10*) and is based on the electrical resistivity of liquid mercury as measured by Birch (*2*) and confirmed recently by Cusack (*19*) and Franck (*4*) all the way up to the critical point. The same hyperbolic relationship was also found (*10*) for Rb and Cs, whose conductivities were determined up to the critical point and for the experimental data on potassium (*8*), which cover three fifths of its liquid range.

In view of their interest in the above relationships and the measurement of the properties of liquid metals at high temperature, the authors desired to collect resistivity data at high temperature on some additional liquid metals. Tin, lead, and bismuth were chosen because preliminary experiments showed that these three metals did not dissolve 8-mm. tungsten metal rods in measurable amounts at their normal boiling points. Therefore, tungsten could be used as electrode material. Previous work on the density of these metals near their normal boiling points (*3, 16, 18*) as well as the work of Ruff *et al.* (*13*) shows that they dissolve only negligible amounts of graphite and do not react chemically with Al_2O_3 or ZrO_2. An easily investigated wide-liquidus range of 2200°, 1400°, and 1300° exists below the normal boiling points (NBP) of 2753°, 2024°, and 1830° K. for Sn (*17*) and Bi, respectively.

Finally, although previous work (*20*) had covered from 50 to 70% of the above liquidus ranges, resistivity measurements made over 80 to 95% of these ranges would clearly define the hyperbolic relationship between κ_{red} and T_{red^*} for these three metals and permit a more meaningful estimation of the conductivity to the critical point.

EXPERIMENTAL

Apparatus and Procedure. The apparatus shown in Figure 1 consisted of two tungsten electrodes 1 cm. in diameter by 40 cm. long, slide-fitted at their ends with Al_2O_3 or ZrO_2 insulator tubes 12 cm. long, which were fastened to the electrodes with tungsten pins. The tungsten electrodes were turned down to 3 mm. in diameter for a length of 2 cm. to allow liquid metal to fill the annular space formed between the 3-mm. diameter electrodes and the inside diameter of the insulator tubes. The upper end of the electrodes passed through BN insulators held in the furnace cover plate and were soldered to the current and potential leads of a Rubicon Kelvin bridge. A carbon tube resistance furnace (*11*) was the source of heat and produced a uniform hot zone 14 cm. long by 8 cm. in inside diameter. Graphite crucibles 16 cm. by 6 cm. in inside diameter were used to contain the liquid metals under a H_2 pressure of 1 mm. Hg. Liquid metal depths were kept constant at 10 cm. by an overflow hole drilled in the side wall of the

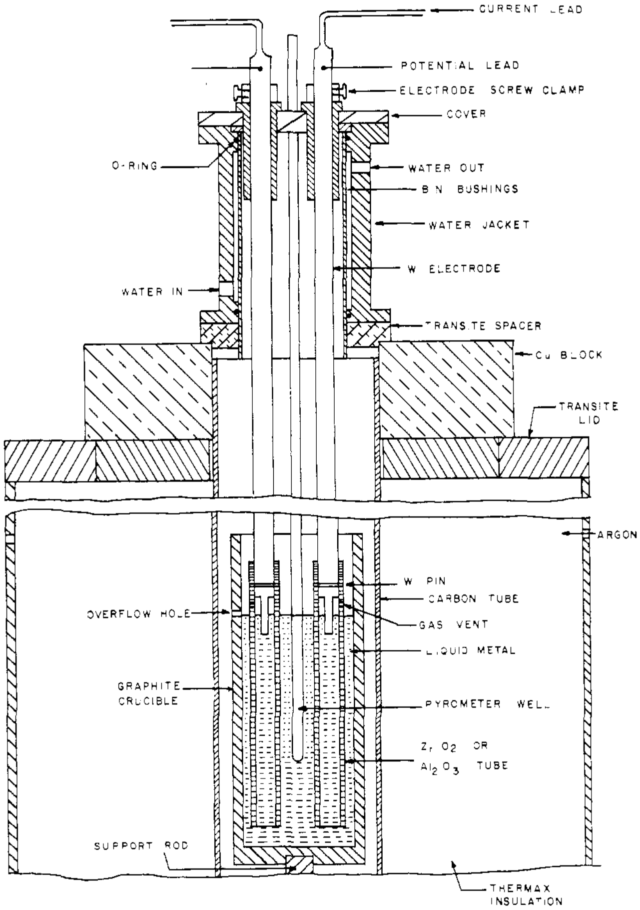


Figure 1. Conductivity apparatus

crucible, and so positioned that metal droplets falling from the crucible could be observed when an excess of metal was added. This provided a means of ensuring a constant level even at temperatures where the metals had appreciable vapor pressure. The change in resistance with electrode immersion was approximately 50 microhms per mm. Before and after actually making a resistivity measurement the lead resistance of the electrodes was determined by short-circuiting them in the liquid metal at various temperatures in exactly the position in which they would be, or were, during a run.

The electrodes were fixed in position by measuring the height of a reference mark with a cathetometer (±0.005 cm.) when a 6-volt circuit was completed between the electrode and melt and when the electrode was lowered the desired distance. The resistance of the melt was measured by placing the insulator tubes on the electrodes and immersing them in the liquid metal. The path of the electrical circuit was through one tube, across the bulk of the liquid metal at the bottom of the crucible, then through the second tube. The area and lengths of the oxide tubes were determined at room temperature and corrected to operating temperature with the expansion data of Wachtman *et al.* (*21*) for Al_2O_3 and Yavorsky (*22*) for ZrO_2. The purities of the metals used were Sn 99.93%, Pb 99.99%, and Bi 99.98%, as stated by certified analysis obtained from suppliers.

TEMPERATURE MEASUREMENTS

The temperature was measured with an optical pyrometer previously calibrated (*17*) at the Au and Pt points and at the normal boiling points of several metals at temperatures above 2000° K. Temperature readings were taken through a ¼-inch bore graphite tube closed at one end, which was immersed 10 cm. in the liquid metal, ensuring black body conditions. A number of temperature readings taken both before and after the resistivity was measured at a particular equilibrium temperature had a precision of ±10° K. The accuracy of the optical pyrometer used was ±0.5% at 2000° K.

Resistance of Current Leads. The resistance of the leads was generally 50 to 70% of the total resistance measured (5 to 8 milliohms). This was brought about partially by the large-bore insulator tubes that had to be used, ≅1 cm. A straight tube with 6-mm. bore and a tube with 4-mm. bore joined to a 1-cm. bore reservoir were tried initially, but abnormally high resistance readings of 60 to 300 ohms were obtained at and above 1700° K. for all three metals. A number of things were tried to avoid this effect, but it could be eliminated only by using 1-cm. diameter bore tubes. The resistance of the current leads could have been eliminated by extending the potential leads to the melt and immersing them next to the current leads inside the insulator tubes. This refinement, a four-probe method, as opposed to the two-probe method used would have changed the uncertainty of the measurements from ±3 to ±1%. The authors felt that at least for their initial measurements of resistivity at very high temperature the difference in precision should be sacrificed to simplify the apparatus, to increase the chance of obtaining these results in the allotted time.

RESULTS

The present experimental data, having an accuracy of ±2.5 to 3%, and literature data (*20*) are plotted in Figure 2 together with the estimated values. The standard deviations of the present experimental data from the calculated curves are 2.19, 4.15, and 5.02 microhms cm. for Sn, Pb, and Bi, respectively. These deviations amount to an agreement of from 2.3 to 2.9, 2.6 to 3.2, and 2.48 to 2.95% between calculated values and the experimental data over the ranges covered for Sn, Pb, and Bi. Estimated resistivity data to the critical point and experimental data for the three metals are shown in Table I; the accuracy of the calculated values in the critical region is ±10%, mainly because of the error incurred in estimating $T_{crit} \cdot \kappa_{red}$ and T_{red}, were calculated from the above experimental data using ρ_{mp} (*20*) equal to 47.9, 94.6, and 129.7 microhms cm. and T_{crit} (*7*) equal to 8000° (*16*), 5200° (*18*), and 4620° K. (*3*) for Sn, Pb, and Bi, respectively. In constructing the hyperbola advantage is taken of its symmetrical shape, in that all the mirror image counterparts of the above data and literature were plotted to allow a more accurate graphical determination of Δ. The numerical value of Δ

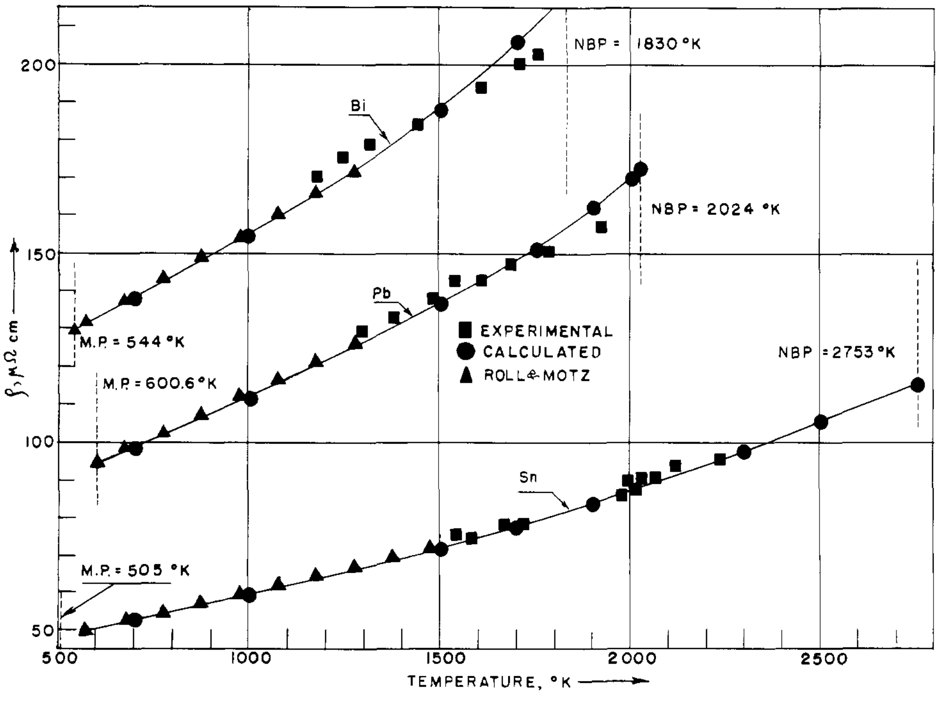


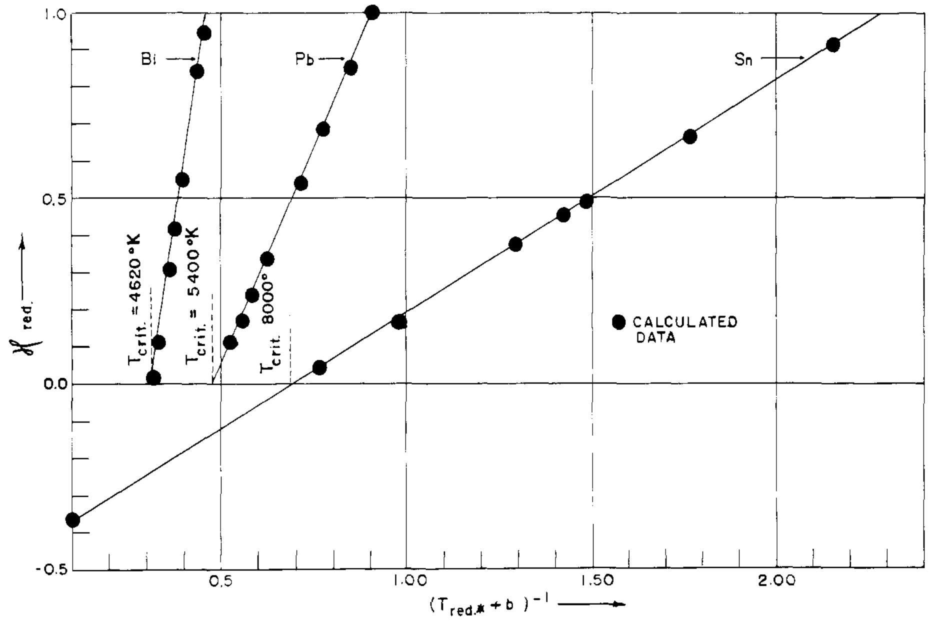
Figure 2. Experimental and calculated resistivities of tin, lead, and bismuth

Table I. Experimental and Calculated Resistivities of Tin, Lead, and Bismuth

Tin				Lead				Bismuth			
Experimental		Estimated		Experimental		Estimated		Experimental		Estimated	
T, °K.	ρ, $\mu\Omega$ cm.	ρ, $\mu\Omega$ cm.	κ mho cm.$^{-1}$	T, °K.	ρ, $\mu\Omega$ cm.	ρ, $\mu\Omega$ cm.	κ, mho cm.$^{-1}$	T, °K.	ρ, $\mu\Omega$ cm.	ρ, $\mu\Omega$ cm.	κ, mho cm.$^{-1}$
505[a]	47.9[d]	47.9	20,876	600.4[a]	94.6[d]	94.6	10,570	544[a]	129.7[d]	129.7	7,710
1540	75.5	73.1	13,679	1295	129.6	126	7,936	1173	170.0	154	6,097
1579	77.6	74.3	13,458	1373	133.0	130	7,692	1245	175.1	171	5,848
1662	78.0	76.6	13,054	1472	137.9	135	7,407	1312	178.4	175	5,714
1717	78.2	78.4	12,755	1484	138.2	136	7,353	1440	183.9	185	5,405
1976	85.4	86.3	11,587	1534	142.7	139	7,194	1601	193.5	197	5,076
1993	89.8	86.9	11,507	1602	142.3	143	6,993	1706	201.9	203	4,926
2013	87.7	87.6	11,415	1684	146.5	148	6,756	1751	202.2	209	4,785
2028	90.5	88.1	11,350	1779	150.5	154	6,493	1830[b]		216	4,630
2068	90.7	89.4	11,185	1913	156.5	164	6,097	2000		236	4,237
2113	93.7	90.9	11,001	2024[b]		172	5,814	2500		309	3,235
2230	95.1	94.9	10,537	2500		214	4,673	3000		418	2,390
2753[b]		115	8,695	3000		280	3,570	4000		1180	850
3000		127	7,875	4000		880	1,140	4500		6480	155
5000		280	3,570					4620[c]			0
7000		1090	917	5000[c]		2250	440				
7500		2280	440	5400			0				
8000[c]			0								

[a] Melting point. [b] Normal boiling point. [c] Critical point. [d] *(20)*.

Figure 3. κ_{red} vs. $(T_{\text{red}^*} + b)^{-1}$ for tin, lead, and bismuth



characterizes constants a and b of the equilateral hyperbola equation:

$$(\kappa_{\text{red}} + b)\,(T_{\text{red}^*} + b) = a \tag{1}$$

where

$$a = b(1 + b) \text{ and } b = \Delta^2/(1 - 2\Delta)$$

Once the constants of the hyperbola are defined, one can write its equation in terms of the reduced variables.

For Sn

$$(\kappa_{\text{red}} + 0.437)(T_{\text{red}^*} + 0.437) = 0.628,\ \Delta = 0.356 \tag{2}$$

For Pb

$$(\kappa_{\text{red}} + 1.105)(T_{\text{red}^*} + 1.105) = 2.32,\ \Delta = 0.420 \tag{3}$$

For Bi

$$(\kappa_{\text{red}} + 2.18)\,(T_{\text{red}^*} + 2.18) = 6.93,\ \Delta = 0.453 \tag{4}$$

Since it is desirable to have a linear relationship between these reduced variables over their entire liquid ranges from the melting point to the critical point, the authors transformed these hyperbolic forms to linear relations by simply dividing by $(T_{\text{red}^*} + b)$. In general, this operation gives

$$\kappa_{\text{red}} = a(T_{\text{red}^*} + b)^{-1} - b \tag{5}$$

where a and b have their usual meaning for a first-degree equation—the slope and κ_{red} intercept. Treatment of Equations 2 to 4 gave

For Sn

$$\kappa_{\text{red}} = 0.628\,(T_{\text{red}^*} + 0.437)^{-1} - 0.437 \tag{6}$$

For Pb

$$\kappa_{\text{red}} = 2.32\,(T_{\text{red}^*} + 1.105)^{-1} - 1.105 \tag{7}$$

For Bi

$$\kappa_{\text{red}} = 6.93\,(T_{\text{red}^*} + 2.18)^{-1} - 2.18 \tag{8}$$

These equations are shown in Figure 3 with the calculated values plotted to the critical point and, like their hyperbolic counterparts, have physical significance all the way to the critical point. By definition, κ_{red} goes to zero because κ_T goes to zero at T_{crit}. Also by definition, $T_{\text{red}^*} = 1$; therefore $(T_{\text{red}^*} + b)^{-1}$ must in fact be $(1 + b)^{-1}$, which reduces the right-hand side of Equation 5 to zero. Intercept b on the κ_{red} axis is illustrated for tin in Figure 3.

METHODS FOR ESTIMATING CRITICAL TEMPERATURES

The accuracy of the critical temperature determines the value of the calculated conductivity data in the critical region.

Method 1. Law of Rectilinear Diameters. The simple empirical law of rectilinear diameters has been upheld, in first approximation, for metals by the experimental measurements of vapor and liquid densities to the critical point of Hg, Cs, and Rb. The experimental data on the latter two have been discussed in detail recently (*5*) and the data on Hg were the subject of a previous paper (*7*). Intersection of the ideal vapor density curve with the D_{rect} line on a density temperature plot sets an upper limit for T_{crit}—i.e., 10,000°, 6700°, and 6400° K. for Sn, Pb, and Bi, respectively. From the experimental data on Hg, Cs, and Rb it was noted that the ideal gas density is identical with the saturated vapor density to $T_{\text{red}} = 0.75$, and beyond $T_{\text{red}} = 0.85$ deviation from ideal behavior becomes pronounced. To estimate T_{crit}—i.e., where both the D_v and D_l curves intersect the rectilinear diameter—one can consult the D_l/D_v *vs.* T_{red} curve for Ar (*13*). AT $T_{\text{red}} = 0.75$ the ideal vapor density should equal the real saturated vapor density; since D_{rect} is known for any temperature, D_v can be calculated from the D_l/D_v value for argon (25 at $T_{\text{red}} = 0.75$) for various candidate T_{crit} values. When the vapor density at 0.75 T_{crit} equals the ideal vapor density for that temperature, the candidate T_{crit} value should be accurate to within $\pm 10\%$. The nature of the real gas density curve above T_{red} then corresponds to the D_l/D_v *vs.* T_{red} curve for argon (*12*).

The choice of argon is not arbitrary; it is a simple monatomic liquid, which corresponds closely to the monionic or monatomic nature of liquid metals. Furthermore, its physical properties have been determined accurately to its critical temperature. Thus it is a good model to use for liquid metals. For easy reference, values for D_l/D_v *vs.* T_{red} for Ar (*12*) are given in Table II.

Method 2. Entropy of Vaporization. The critical temperature of a metal can also be estimated from its entropy of vaporization (*20*) by use of the reduced temperature *vs.* ΔS_{vap} curve of Hg (whose critical temperature and heat of vaporization have been accurately determined experimentally) and application of the theorem of corresponding states. Recently (*6*) an analysis of the experimentally determined critical temperatures (*14, 15*) of Cs and Rb and determination of their ΔH_{vap} (*1*) to $T_{\text{red}} = 0.75$ show that their ΔS_{vap} *vs.* T_{red} curves correspond to that of Hg. It is expected that most metals except transition and semimetals will conform closely to the behavior of the Hg, Cs, and Rb curves. Results of the two methods of estimating T_{crit} for Sn, Pb, and Bi are compared in Table III.

Table II. D_l/D_v vs. T_{red} for Argon

T_{red}	0.6	0.7	0.8	0.85	0.90	0.95	1.00
D_l/D_v	172	45	17	11.2	7.2	4.4	1.00

Table III. Estimation of Critical Temperatures of Sn, Pb, and Bi

	T_{crit}, ° K.	
	Method I	Method II
Sn	8800	8000
Pb	5400	5400
Bi	5000	4620

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