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*THE DENSITIES OF LIQUID TIN,
LEAD, AND TIN-LEAD ALLOYS*

H. R. THRESH, A. F. CRAWLEY, AND D. W. G. WHITE

PHYSICAL METALLURGY DIVISION

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The Densities of Liquid Tin, Lead, and Tin-Lead Alloys

H. R. Thresh, A. F. Crawley, and D. W. G. White

The densities of liquid tin, lead, and Sn-Pb alloys have been measured over a range of temperature above the liquidus. In all cases, data can be adequately represented by an equation of the type $\rho = a + bT$. For pure tin, the values of a and b are, respectively, 7.139 and 7.125×10^{-4} , and for pure lead, 11.060 and 12.220×10^{-4} . At constant temperature, molar volumes in the Sn-Pb system vary linearly with composition.

DURING the course of a long-term program at the Department of Energy, Mines and Resources, Ottawa, Canada, the densities of liquid tin, lead, and Pb-Sn alloys were studied. The work reported herein draws on two sets of results independently achieved by Thresh, on the one hand, and by Crawley and White, on the other.

EXPERIMENT

The method and apparatus were originated by Thresh and have been described in detail in Mines Branch reports.^{1,2}

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In operation, the 14 cu cm graphite pycnometer is put in the furnace as shown in Fig. 1 after a machined charge has been placed inside the pycnometer and the lid screwed down. The dimensions of the charge are such that, upon melting, a small excess of liquid metal is discharged through the capillary hole to displace the weighted float above. When the pycnometer has been equilibrated at the experimental temperature, the

Table I. Constants in Equation $\rho = a + bT$

Tin, wt pct	a	$b \times 10^{-4}$
0	11.060	12.220
10	10.490	11.582
20	9.956	10.481
30	9.497	10.109
32.5	9.383	9.762
40	9.079	9.708
48.75	8.697	8.688
50	8.671	8.761
60	8.321	8.690
62.5	8.229	8.652
70	7.995	8.443
83	7.603	7.760
85	7.543	7.775
100	7.139	7.125

float chamber is swept to one side by twisting shaft *F* and in so doing establishes a known volume of liquid metal. Upon freezing, this metal is weighed.

In making and measuring the volume of the pycnometer, precision machine shop techniques are used. Dilatometric specimens are made with each pycnometer in order to determine the anisotropic coefficients of thermal expansion of the graphite used. With all sources of experimental error accounted for, it is estimated that density can be measured with this apparatus to about ± 0.05 pct.

RESULTS

In one set of data, the densities of 99.999 pct Sn, of 99.997 pct Pb, and of a series of Sn-Pb alloys made from the same metals were measured over a temperature range of about 100°C above the melting point or liquidus temperature. In the second set of data, densities were measured from the melting point or liquidus temperature to a temperature of about 520°C. In all instances, however, the change of density with change of temperature could be represented accurately by a straight line. This applied even in the case of alloys with compositions in the vicinity of the eutectic point, for which results over a temperature range of 300°C degrees or more were produced.

Particular examples of the data are the densities

of pure tin and lead presented in Figs. 2 and 3.

Because the data plot linearly, they may be represented by equations of the type:

$$\rho = a + bT$$

where

ρ is the density in grams cm^{-3} ,

a and b are constants, and

t is the temperature in °C.

Values of the constants a and b for pure tin and pure lead as well as for a number of Sn-Pb alloys are listed in Table I. The values were obtained from a computer regression analysis of the experimental data.

In Fig. 4 the densities of Sn-Pb alloys are plotted at their liquidus temperatures,³ and in Fig. 5 other of the data have been recalculated to yield two isothermal plots of molar volume against composition.

Equations to these plots, one at 350°C, the other at 550°C, are given in conjunction with Table II.

Table II. Molar Volumes of Lead-Tin Alloys as a Function of Composition at 350° and 550°C

Tin, wt pct	Tin, mol pct	350°C Molar Volume	550°C Molar Volume
0	00.000	19.489	19.947
10	16.245	19.122	19.570
20	30.382	18.805	19.224
30	42.796	18.520	
32.5	45.667	18.449	18.854
40	53.784	18.264	
48.75	62.413	18.108	18.492
50	63.579	18.046	
60	72.364	17.857	
62.5	74.826	17.788	18.184
70	80.289	17.681	
83	89.499	17.459	17.836
85	90.819	17.443	
100	100.000	17.228	17.593

Equations relating molar volume, V_m , and composition, N_{Sn} , in mol pct tin:

$$350^\circ\text{C}: V_m = 19.488 - 0.02259N_{\text{Sn}}$$

$$550^\circ\text{C}: V_m = 19.945 - 0.02353N_{\text{Sn}}$$

DISCUSSION

Tin. In Fig. 2, the density of tin is plotted as a function of temperature. Here, results of the present work are compared with data published since 1960.⁴⁻⁷ Except for the results of Kirshenbaum and Cahill⁵ it is evident that agreement is good at temperatures just above the melting point, and although the data diverge they remain within ± 0.2 pct at 500°C.

Extended comparisons with previous work are to be found in papers by Kirshenbaum and Cahill⁵ and especially by Lucas.⁷

Lead. In Fig. 3, for pure lead, a comparison is made between the density vs temperature data determined in

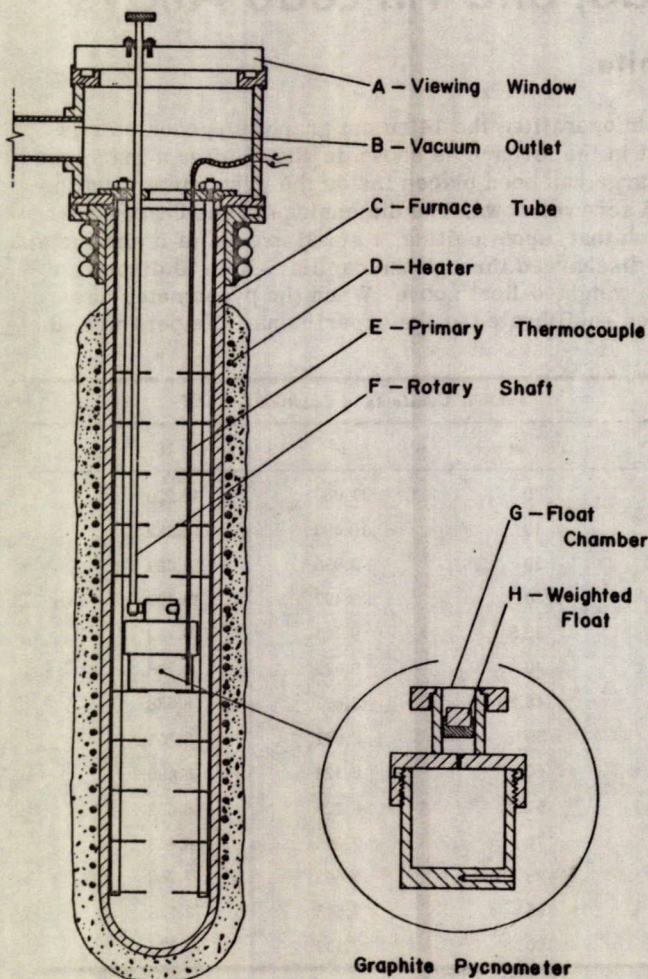


Fig. 1—Densitometer and graphite pycnometer.

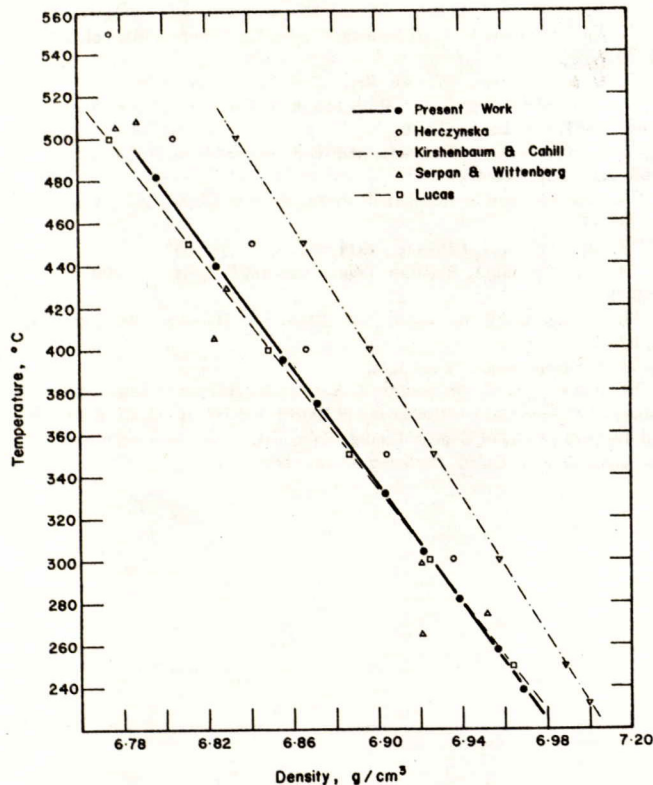


Fig. 2—Density of tin vs temperature.

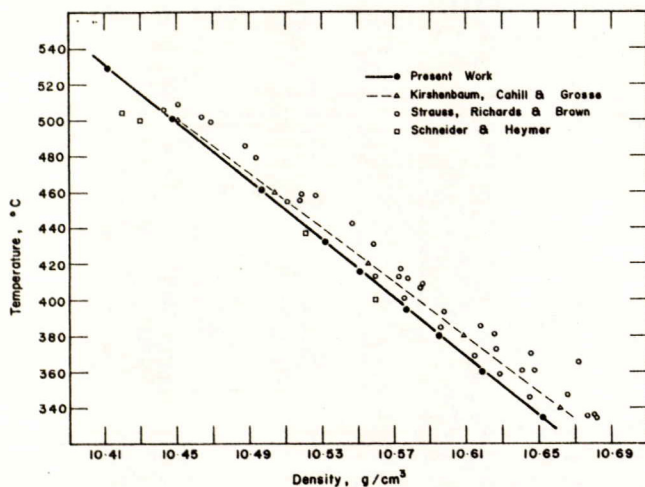


Fig. 3—Density of lead vs temperature.

the present work and the results of others⁸⁻¹⁰ published in the past 10 years. Here, there is agreement between all data within ± 0.2 pct at temperatures in the vicinity of 500°C , changing to a spread of $+0.3$ pct at temperatures just above the melting point.

In the paper by Kirshenbaum, Cahill, and Grosse,⁸ much of the previous work on the density of lead is listed.

Tin-Lead Alloys. As Fig. 4 shows, a plot of density at the liquidus temperature for a series of Sn-Pb alloys yields a smooth curve. The shape of the curve responds primarily to the dependence of density on composition but embodies also a density-temperature component arising from the form of the Sn-Pb liquidus.

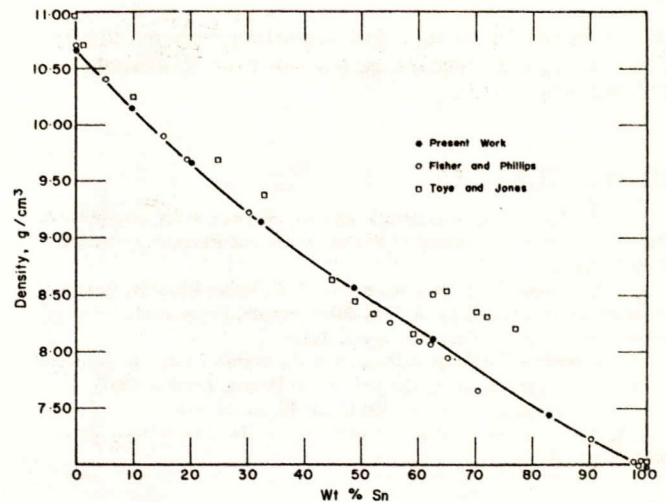


Fig. 4—The densities of Sn-Pb alloys at their liquidus temperatures.

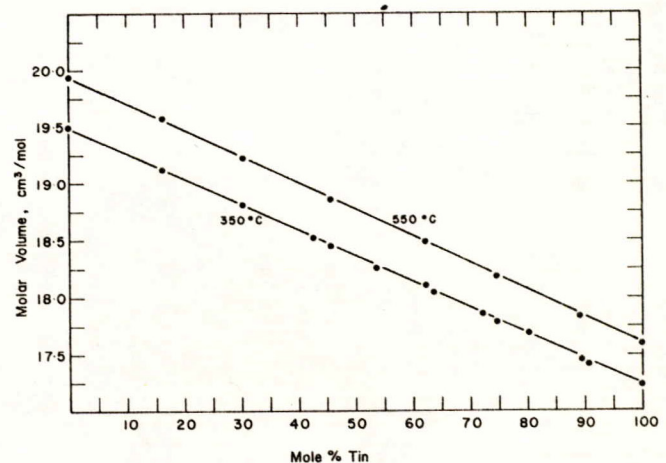


Fig. 5—The molar volumes of Sn-Pb alloys.

Similar work on Sn-Pb alloys has been done before by Arpi,¹¹ Fisher and Phillips,¹² and Toye and Jones.¹³ The first is a pioneer work, which now appears to be inaccurate. The last embodies spurious inflections with experimental origins and, while the work of Fisher and Phillips agrees closely (with ours) at the liquidus temperature, their results are not as self-consistent when recalculated at higher temperatures.¹⁴

In Fig. 5, the present data replot as straight lines on axes of molar volume vs mol pct tin. Thus, at all concentrations, the partial molar volumes of tin and lead are equal to their molar volumes.

For its implications of ideal behavior, this result should be compared with the most recent supplementary thermodynamic data from Hultgren *et al.*¹⁵ which gives, for example, a value of 327 ± 30 cal per g-atom for the integral heat of mixing of a 50 at. pct solution at 1050°K .

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REFERENCES

- ¹H. R. Thresh: Physical Metallurgy Division Internal Report PM-M-66-25, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada, 1966.
- ²H. R. Thresh, A. F. Crawley, and D. W. G. White: Physical Metallurgy Division Internal Report PM-R-67-4, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada, 1967.
- ³G. V. Raynor: Equilibrium Diagram of the System Lead-Tin, Annotated Equilibrium Diagrams No. 6, The Institute of Metals, London, 1947.
- ⁴E. Herczynska: *Naturwiss.*, 1960, vol. 47, pp. 200-01.
- ⁵A. D. Kirshenbaum and J. A. Cahill: *Trans. Am. Soc. Metals*, 1962, vol. 55, pp. 844-48.

- ⁶C. Z. Serpan and L. J. Wittenberg: *Trans. TMS-AIME*, 1961, vol. 221, pp. 1017-20.
- ⁷L. D. Lucas: *Mem. Sci. Rev. Met.*, 1964, vol. 61, pp. 1-24.
- ⁸A. D. Kirshenbaum, J. A. Cahill, and A. V. Grosse: *J. Inorg. Nucl. Chem.*, 1961, vol. 22, pp. 33-38.
- ⁹S. W. Strauss, L. E. Richards, and B. F. Brown: *Nucl. Sci. Eng.*, 1960, vol. 7, pp. 442-47.
- ¹⁰A. Schneider and G. Heymer: *Z. Anorg. Allgem. Chem.*, 1956, vol. 286, pp. 118-35.
- ¹¹R. Arpi: *Intern. Z. Metallog.*, 1914, vol. 5, pp. 142-68.
- ¹²H. J. Fisher and A. Phillips: *Trans. TMS-AIME*, 1954, vol. 200, pp. 1060-70.
- ¹³T. C. Toye and E. R. Jones: *Proc. Phys. Soc. (London)*, 1958, vol. 71, pp. 88-99.
- ¹⁴H. J. Fisher: unpublished data.
- ¹⁵R. Hultgren, R. L. Orr, and K. K. Kelley: Supplement to Selected Values of Thermodynamic Properties of Metals and Alloys, Dept. of Mineral Technol., Coll. of Eng. and Inorg. Mater. Res. Div., Lawrence Radiation Lab., Univ. of Calif., Berkeley, Calif., 1966.

