Volumetric Measurements for Some Liquid Metals at High Pressures and Temperatures

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Molar volume data for liquid mercury, tin, lead, and bismuth were obtained for temperatures up to 650 °C and pressures up to 3 kbar. The dilatometric technique used to determine this information is somewhat novel, since the higher melting points of most of these metals require special crucible and furnace configurations.

Introduction

The importance of structure in developing adequate models to predict properties of solutions has long been recognized. However, the interrelationships between structural and thermodynamic variables is vague, and more work is necessary. A better understanding of volumetric properties of solutions, representing both structural and thermodynamic information, may serve to ameliorate this difficulty. This is particularly significant for metallic solutions since the chemical potentials of mobile valence electrons, and subsequent metallic properties, are very sensitive to the density of solution.

New volumetric data are presented for some liquid metals as a function of temperature and pressure. Data of this sort have not yet been obtained for the higher melting point, post-transition metals studied here.

Experimental Section

A number of techniques have been developed to measure densities of liquid metals at high pressures (see review by Ross and Greenwood (*1*)). For example, Postill et al. (*2*) used as Archimedean method that determined the melt conditions for which an immersed sinker would sink or float. At the point where the sinker's density matched the melt's density, the radioactive sinker would float and could be detected externally. The problem with this technique is that only discrete densities, for specific sinkers, could be found, limiting the range of temperatures and pressures that could be studied.

Bridgman (*3*) measured *PvT* properties by placing the liquid within a piston device and measuring pressure changes as a function of piston displacement. This method had the advantage that the liquid of interest was its own presurization medium but was limited to low temperatures, and minor leaks would quickly lead to erroneous results.

One of the most unusual techniques involves radiation counting (*4*, *5*). Here, the sample is made radioactive, and the radiation flux that reaches an external counter is measured as a function of temperature and pressure. These results can be converted to density information through the use of standard radiative equations and calibration techniques. This method is generally not as accurate as the others, though usually very self-consistent.

Perhaps one of the most accurate ways to measure densities over a wide range of conditions is through acoustic experiments, where the velocity of sound through the melt is determined (*6*, *7*). These technqiues actually measure compressibilities, but very accurate volumetric information can be found by integrating the results. These techniques, though good, have not been utilized much due to the added expense and expertise required in the experiments.

The most commonly used method, and the method chosen for this work, is dilatometry. Dilatometry involves the use of a bulb of liquid with a capillary on top to allow the liquid to expand and contract as a function of temperature and pressure. The level of the liquid within the capillary determines the volume. Due to difficulties with high temperatures and with loading the bulb, this technique has not yet been used with the post-transition metals of interest here. Therefore, the crucible, internal furnace, and even the technique used to measure the height of the melt are unique to this work. Details of the equipment are presented in the following paragraphs.

The dilatometric crucible used in this work, shown in Figure 1, was made of three pieces so that a preformed slab of metal (approximately 2 cm^3) could be inserted easily into the bottom. The top and bottom pieces were made of stainless steel and measured $^3/_4$-in. by 3-in. length (1.9 cm by 7.6 cm), while the capillary was $^1/_8 \times {}^1/_{16}$ in. (0.318 cm × 0.159 cm) alumina tubing (McDanel Refractory Co., catalog no. AXRS-0732). The pieces were held together with conductive graphite cement obtained from Aremco Products (catalog no. 551-A), and the capillary had to be filled with metal pieces and melted two or more times in order to obtain sufficient liquid levels. The crucibles were calibrated by measuring the height of liquid metal to be studied as a function of temperature at atmospheric pressure. Therefore, along with thermal expansion corrections for the crucible and atmospheric density data, a density versus liquid level profile could be obtained for each particular crucible and its loading.

The high-pressure vessel used in the experiments, shown in Figure 2, was limited to 4 kbars (60 000 psi) by the external fittings and had an internal diameter of 2.5 in. (6.35 cm) and internal length of 15 in. (38.1 cm). The vessel was made from 4340 hardened steel and had 14 electrical feedthroughs that accommodated connections for thermocouples, the furnace, and height measurement. A $^3/_4$-in diameter, two zone, internal furnace could heat the crucible to at least 800 °C at the highest pressures. The furnace was controlled by two Model 6100 temperature controllers obtained from Omega Engineering, and chromel-alumel thermocouples were used to measure temperatures. Very fine alumina powder (Aldrich Chemical Co., catalog no. 26549-7) insulation was necessary to reduce convection, and an external water jacket kept the walls of the vessel cool. A thermocouple inserted into a hole in the top piece of the crucible allowed accurate measurement of the melt temperature. The thermocouples were compared to a thermocouple calibrated by measuring the freezing points of lead,

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0021-9568/91/1736-0252$02.50/0

Figure 1. High-pressure/high-temperature dilatometric crucible.

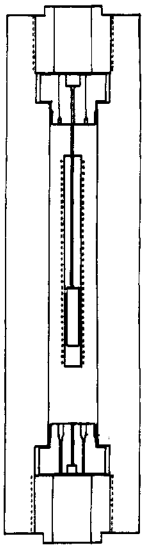

Figure 2. High-pressure vessel internal furnace and dilatometric crucible.

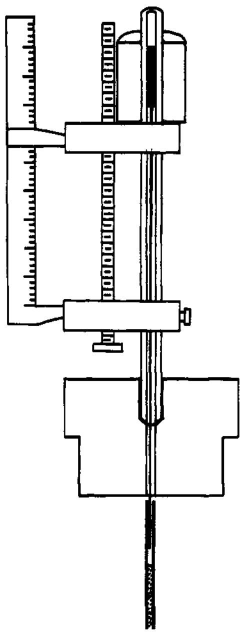

Figure 3. Liquid level measurement equipment.

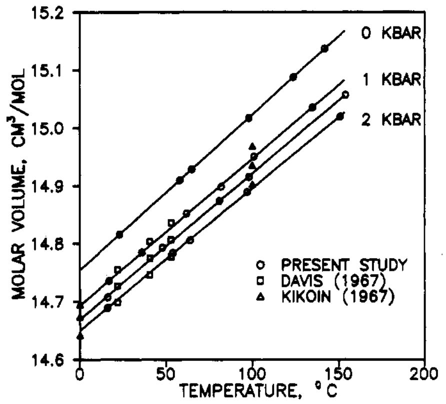

Figure 4. *PvT* results for liquid mercury: (○, □, △) experimental data; (—) empirical Tait equation fit.

zinc, and silver and found to be accurate to better than ±5 °C.

Pressures up to 1.5 kbar (14 500 psi) were produced by a commercial gas booster (Haskell, Model no. AG-152), and an intensifier, built on-site along with the pressure vessel, was used to create pressures up to 4 kbar. Argon was used as the pressurization medium since there is no liquid that is appropriate for the high temperatures involved in this work. Pressures were measured with a 100 000 psi Heise gauge (Model no. CM-9008) and a 20 000 psi digital Heise gauge (Model no. 715A), which agreed well in the region of overlap. The system could also be evacuated while the metal was melted to eliminate bubbles within the crucible.

The technique utilized to measure the height of the melt the capillary is depicted in Figure 3. A 24-in. (61-cm) stainless steel, 20-gauge syringe needle connected to a 1.5-in. (3.81-cm)-length by $^1/_8$-in. (0.318-cm)-diameter iron bar extended from the capillary, up and out of the high pressure vessel, and into austenitic, 3/8-in. (0.952-cm)-o.d. stainless steel high-pressure tubing that emerged from the top of the vessel. The iron bar and needle were then raised and lowered with an external electromagnet that surrounded the high-pressure tubing. The magnet, in turn, was raised and lowered by a screw device with high-precision calipers attached to measure changes in height. When the syringe needle made contact with the liquid metal within the capillary, an electrical circuit was completed between the crucible and needle; the level of the liquid was measured with an accuracy of ±0.005 cm. This was much more accurate than necessary since the temperature could only be held steady to 1 °C, which generally corresponded to changes in the liquid level of approximately 0.020–0.040 cm.

Results and Discussion

In order to test the validity of the method, volumetric data for mercury were first obtained, and the results are presented in Table I and Figure 4. A stainless steel crucible was used to obtain these data, and a coefficient of linear thermal expansion of $\epsilon = 23 \times 10^{-6}$ °C^{-1} and a compressibility of $\beta = 5.9 \times 10^{-4}$ kbar^{-1} (*2*) were used to correct for changes in the volume of the crucible and the length of the contact lead. A coefficient of linear expansion for stainless steel of $\epsilon = 19 \times 10^{-6}$ °C^{-1} is recommended by Bockris et al. (*8*) but was found to give results that were consistently off by about 0.05% compared to other very reliable data (*5*, *6*). Even though this is a very small, acceptable error, it can lead to undesirable errors at high temperatures. Therefore, $\epsilon = 23 \times 10^{-6}$ °C^{-1} was utilized since this brings our results into line. Experiments on mercury were also attempted with use of a molybdenum crucible, but the materials were found to interact undesirably.

Data were obtained along isobars and for both increasing and decreasing temperatures and pressures. No significant hystereses were observed.

Reasonably good data were also obtained for liquid tin in the range 0–2 kbar and 350–650 °C, and the results are presented

Table I. Experimental *PvT* Data for Liquid Mercury, Tin, Lead, and Bismuth. Atmospheric Molar Volumes may be Calculated from $v(T,0) \pm 0.1\% = aT + b$ with a and b Taken from Table II

	p, kbar	T, °C	v, cm^3/mol $\pm$ 0.2%
mercury	1.0	17	14.736
		36	14.784
		62	14.852
		82	14.899
		101	14.951
		135	15.035
	1.5	16	14.707
		48	14.793
		81	14.874
		98	14.916
		154	15.057
	2.0	16	14.689
		54	14.784
		64	14.805
		97	14.889
		151	15.020
tin	1.0	449	17.303
		502	17.389
		553	17.473
		602	17.559
		644	17.628
	2.0	500	17.339
		548	17.427
		598	17.521
		658	17.621
lead	1.0	396	19.519
		458	19.655
		495	19.752
		549	19.862
		597	19.977
		648	20.092
	2.0	455	19.589
		501	19.677
		552	19.783
		600	19.890
		648	19.988
	3.0	446	19.513
bismuth	1.0	394	20.990
		446	21.128
		495	21.268
		548	21.396
		599	21.539
	2.0	498	21.217
		596	21.454

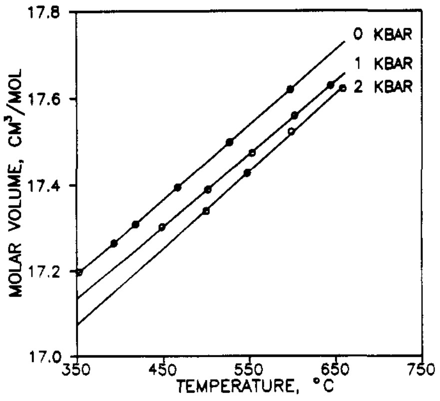

Figure 5. *PvT* results for liquid tin: (O) experimental data; (—) empirical Tait equation fit.

In Table I and Figure 5. Above 650 °C, liquid tin is somewhat corrosive to steel, limiting the temperature range slightly. The authors are aware of no other data of this sort for comparison. The tin was obtained from Aldrich (catalog no. 26568-3).

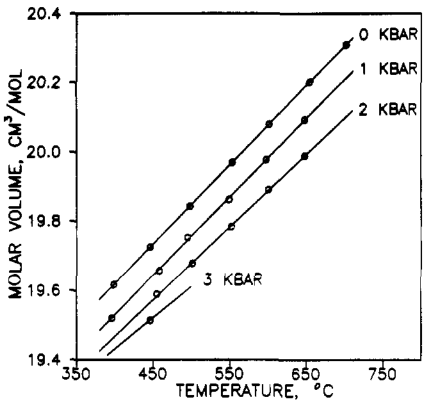

Figure 6. *PvT* results for liquid lead: (O) experimental data; (—) empirical Tait equation fit.

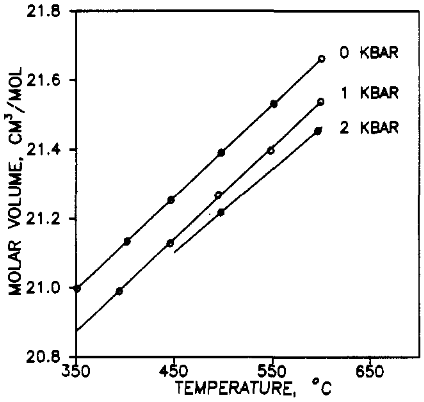

Figure 7. *PvT* results for liquid bismuth: (O) experimental data; (—) empirical Tait equation fit.

Table II. Empirical Constants for the Tait Equation

	mercury	tin	lead	bismuth
a,[a] 10^{-3} cm^3/(mol °C)	2.695	1.730	2.290	2.671
b,[a] cm^3/mol	14.754	16.586	18.703	20.060
C_0, 10^{-5} °C^{-1}	4.349	−0.0648	1.673	0.5662
C_1, 10^{-2}	2.084	0.5764	1.083	0.2989
B_0, 10^{-4} kbar/°C	7.586	0.0486	−0.9785	7.137
B_1, kbar	4.811	0.9672	3.704	0.2436

[a] Atmospheric density data for mercury came from Weast and Astle (*10*), and other liquid metal values were taken from Hansen et al. (*11*).

The results for liquid Pb and Bi are also given in Table I and Figures 6 and 7, respectively. The experiments to obtain data for these metals both ended abruptly due to equipment failure, exemplifying the complex nature of the experiments. The lead and bismuth were also obtained from Aldrich (catalog no. 26,593-4 and 26,547-0 respectively). All of the metals had a purity of at least three nines.

The experimental results were fit to the empirical Tait relationship (*9*)

$$v(T,P) \pm 0.2\% = v(T,0)[1 - C \ln (B + P)/B] \qquad (1)$$

where $v(T,0) \pm 0.1\% = aT + b$ is the molar volume of the liquid metal at atmospheric pressure. The coefficients B and C are constants that will be assumed to be linearly dependent on temperature such that $B = B_0T + B_1$ and $C = C_0T + C_1$. The best constants to be used in eq 1 are tabulated in Table II.

The accuracy of the data are limited by the accuracy of the atmospheric density data used to calibrate the crucible, which is generally about ±0.1%. The other large source of error is due to uncertainties in the temperature and pressure corrections for the crucible. This error can add another 0.1% uncertainty to the results for the molar volume when a stainless steel crucible is used. Therefore, an accuracy of 0.2% is suggested for the molar volume data for the liquid metals as a function of temperature and pressure. Due to the limited amount of data, the compressibilities can be determined presently with an accuracy only on the order of 10%. Other uncertainties related to temperature or pressure measurement and liquid level measurements are considered to be insignificant compared to the errors described above. Finally, adverse interactions between the melt and the crucible can lead to anomalous liquid level measurements. However, this problem is basically eliminated by the appropriate selection of materials.

The *PvT* trends observed in the results obtained here are the same as those generally observed for organic liquids. For example, the compressibility decreases quickly with increasing pressures, making the isobar lines much more linear than the isotherms. Also, the slopes of the molar volume vs temperature lines (at constant pressure) decrease with increasing pressure, and the liquids are generally more compressible at higher temperatures.

List of Symbols

a,b	Atmospheric molar volume parameters
β	Compressibility
B,C	Constants in Tait equation
ϵ	Linear coefficient of thermal expansion
P	Pressure
T	Temperature
v	Molar volume

Registry No. Mercury, 7439-97-6; tin, 7440-31-5; lead, 7439-92-1; bismuth, 7440-69-9.

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Received for review August 6, 1990. Accepted December 20, 1990.

Solubility and Heat of Solution of Potassium Dihydrogen Citrate

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The aqueous solubility of potassium dihydrogen citrate from 15 to 55 °C has been determined. From these data the heat of solution has been calculated to be 8.10 kcal/mol. The densities of saturated solutions of potassium dihydrogen citrate from 15 to 55 °C are also reported. A previously unreported dihydrate—$KH_2C_6H_5O_7 \cdot 2H_2O$—has been discovered. Potassium dihydrogen citrate readily tends to form supersaturated solutions, which are sometimes stable for weeks.

Introduction

Bielig (*1*) measured the solubility of potassium dihydrogen citrate in concentrated sugar solution (65° Brix). These are reported as follows:

20 °C = ca. 260 g
10 °C = ca. 150 g
2 °C = ca. 85 g

The volume of these solutions was not reported, but probably was 1000 mL. Kimball (*2*) used these values to estimate the heat of solution to be 8.065 kcal/mol. I have measured the solubility of potassium dihydrogen citrate in pure water form 15 to 55 °C.

Experimental Section

Potassium dihydrogen citrate is not commercially available, so it was prepared by the stoichiometric reaction of 1 mol of tripotassium citrate (Fisher Certified ACS grade) with 2 mol of citric acid (Fisher Certified ACS grade) in distilled water. This produced a crystalline mass of long needles, which was removed by vacuum filtration. Second crops were obtained by cooling the filtrate in a refrigerator. The crystals were dried at room temperature in a strong flow of air. Sometimes crystallization did not begin for several days without the aid of a seed crystal.

Saturated solutions were prepared by heating water to about 5 °C above the target temperature and adding potassium dihydrogen citrate slowly with stirring. When salt remained after a considerable time, the flask was stoppered and placed in a thermostated water bath. Temperatures were set by using an NBS certified thermometer and were held to within 0.1 °C. The solutions were allowed to equilibrate for at least 3 days.

*1. **Solubilities**.* Concentrations were determined by titration and by gravimetry.

*a. **Titrimetric Method**.* Aliquots (10.0 mL) were taken with a calibrated pipet, weighed into 100-mL volumetric flasks, and then diluted. The solutions were titrated with 0.1 N sodium hydroxide solution to a phenolphthalein end point.

*b. **Gravimetric Method**.* Aliquots (10.0 mL) were taken from the thermostated solution with a calibrated pipet and placed in tared weighing dishes. The solutions were evaporated in a strong air flow until weights were nearly constant. Drying to constant weight was finished in a desiccator with Drierite.

*2. **Densities**.* Densities were determined by weighing 10-mL samples of the saturated solutions held at target temperature. Volumes (10.0 mL) were measured with either a "to deliver" pipet, a graduated pipet, or a calibrated volumetric flask.

0021-9568/91/1736-0255$02.50/0