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Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713646857>

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To cite this Article Hiemstra, S. , Prins, D. , Gabrielse, G. and Van Zytveld, J. B.(1977) 'Densities of liquid metals: calcium, strontium, barium', *Physics and Chemistry of Liquids*, 6: 4, 271 – 279

To link to this Article: DOI: 10.1080/00319107708084145

URL: <http://dx.doi.org/10.1080/00319107708084145>

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Densities of Liquid Metals: Calcium, Strontium, Barium

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We report a method of measuring the densities of liquids at intermediate temperatures which employs Archimedes' Principle in a two-sinker arrangement. This method is then used to measure the densities of pure liquid calcium, strontium, and barium. We find $\rho(\text{Ca}) = 1.4931 - 1.37 \times 10^{-4} T(^{\circ}\text{C})$ from 850 - 950°C, $\rho(\text{Sr}) = 2.5547 - 2.83 \times 10^{-4} T(^{\circ}\text{C})$ from 780 - 880°C, and $\rho(\text{Ba}) = 3.5561 - 2.99 \times 10^{-4} T(^{\circ}\text{C})$ from 730 - 830°C, where the units are gm/cm³. We use relations relating critical constants for these liquids to estimate $d\rho/dT$, and compare these values of $d\rho/dT$ with those for other liquid metals; we also compare our results with recent x-ray diffraction data for these liquid metals.

INTRODUCTION

Over the past twenty years, interest in the properties of liquids has increased steadily, both from an experimental and a theoretical viewpoint. This interest has extended to a wide range of liquid properties: structural, thermodynamic, and electrical. Basic to many of these studies is a knowledge of the density of the liquid under investigation. For example, studies of the structure of a liquid by means of neutron and X-ray diffraction experiments provide information on the Radial Distribution Function if the density of the liquid is known. In many conducting liquids, knowledge of the density permits the calculation of the electronic Fermi Energy of the liquid, and thus provides an important link between theory and experiment for many important electronic properties. In addition, measurements of density can provide information about changes of phase, both at and above the melting temperature. (Kanda *et al.*¹ have recently used density measurements to study immisibility boundaries in liquid alloy systems.)

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Because of this broad interest in good liquid density data, we have attempted to develop a method of measuring densities of liquids which is both accurate and versatile. And because of the authors' present interests in the liquid alkaline earth metals, liquids for which density data is both sparse and contradictory, we have chosen initially to apply our method to these metals. In the present paper we describe our method of measurement, and report our results on the densities of pure liquid calcium, strontium, and barium near their respective melting temperatures.

EXPERIMENTAL PROCEDURE

A Method

The method of measurement chosen was one employing Archimedes' Principle. In this method, as it is commonly applied, a solid sinker of inert material is suspended in the liquid of interest. The effective mass of the sinker is measured in this liquid and in air; the density, ρ_L , of the liquid is then given roughly by:

$$\rho_L = \frac{\Delta M - s}{V + v_s} \quad (1)$$

Here ΔM is the difference between the effective masses in air and liquid, V is the volume of the sinker, v_s is the volume of the suspension wire that is immersed, and s is a correction introduced because of the effect of the surface tension of the liquid on the suspension wire. The term, s , typically about 0.5% of ΔM , can be estimated in several ways, but still introduces the greatest uncertainty into the results.

To eliminate the problem of the surface tension contribution, we have chosen to use a two-sinker technique. In this method, two sinkers of identical material but differing in volume by about 50%, are suspended one at a time in the liquid sample. If the suspension wires are identical in material and diameter, one may subtract the apparent mass differences for these sinkers from one another to eliminate the term, s . Further, one can measure the difference in volume of the sinkers by performing the same procedure in a standard liquid of known density (in this case, deionized water at 20°C). Including the thermal expansion of the sinker material in the relation, one finds that:

$$\rho_L(T) = \left\{ \frac{(M_1^A - M_2^A) - (M_1^L(T) - M_2^L(T))}{(M_1^A - M_2^A) - (M_1^W(T_0) - M_2^W(T_0))} \right\} \left\{ \frac{\rho_W(T_0) - \rho_A}{1 + f(T - T_0)} \right\} + \rho_A \quad (2)$$

Here M_i^X denotes the apparent mass of the i th sinker plus suspension wire in medium X ($A \equiv$ air; $L \equiv$ liquid sample; $W \equiv$ water). ρ_W and ρ_A are the

densities of water and air respectively; $1 + f(T - T_0)$ is the volume of the sinker normalized to 1 at $T = T_0$. (In this work, $T_0 = 20^\circ\text{C}$.)

In the development of this equation, we have ignored several terms which contribute about $\pm 0.01\%$, for a typical choice of parameters. The experimental uncertainty associated with the term $[1 + f(T)]$ is about 0.1% ; we therefore expect to be able to measure liquid densities to about this accuracy (0.1%).

B Apparatus

The high-temperature portion of the apparatus is illustrated schematically in Figure 1. The main furnace (A) was used to bring the sample to within about 50°C of the desired temperature. The control-furnace winding (B) provided the additional heat necessary, and, by a feedback-control circuit with a thermocouple sensing element (G), stabilized the temperature to about 0.1°C . Argon gas flowed into the apparatus through inlet (I) at a rate of about 2 liters/minute so that an outward flow was maintained at the hole that introduced the suspension wire (E). Since the introduction of this cold argon gas was observed to cause vertical thermal gradients of about $10^\circ\text{C}/\text{inch}$ in the liquid sample, three baffles (H) and a gradient control winding (C) were added. (The convection currents associated with these gradients were observed to introduce substantial systematic and random errors (bobbing of the sinker) into the measurements, so that the gradients

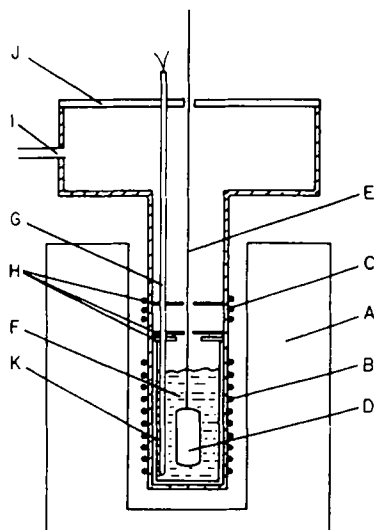


FIGURE 1 High temperature portion of liquid density apparatus. (For description see text.)

had to be removed with considerable care.) The thermocouple (G) could be moved vertically to measure vertical temperature gradients; gradients of 1°C over the 3 inches of sample were the maximum permitted. This thermocouple, of chromel-alumel, was clad in 347 stainless steel to prevent corrosion and sample contamination. The sample container (K) was of 321 stainless steel. The sinker (D) was of 321 stainless steel for liquid samples (F) of density less than about 5 gm/cm^3 , and of tungsten (99.99%) for denser liquids. Sinker volumes were in the range of $1\text{--}7\text{ cm}^3$, depending upon the sinker material. The 0.004" diameter tungsten suspension wire (E) passed around the sinker in a shallow, rounded trough designed to avoid trapping gas bubbles. (A type 304 stainless steel suspension wire of 0.005" diameter was used for the liquid barium work.) The 321 and 347 stainless steels in contact with the liquid samples showed no evidence of attack, even after repeated use. (By contrast, 304 and 302 stainless steels show flaking after a few hours.) A plexiglass cover (J) permitted viewing of the liquid surface during the experiment.

A Mettler H10 balance, adapted for below-the-pan weighing, measured the effective masses of the sinkers to 0.1 mg. These weighings could typically be reproduced to 0.2 mg. To remove deposits of sample material which might condense on the suspension wire, electrical current could be passed through the wire, heating it to about 700°C .

C Sample material and handling

The sample material was scraped clean of oxide, cut, and placed in the sample container, all under an argon atmosphere in an evacuable glove box. At no time did the sample materials come into contact with air. They were also shipped and stored under inert atmosphere and were never in contact with oil.

The samples were supplied by Atomergic Chemetals Corp., and had the following nominal purities: Ba – 99.5–99.7%; Sr – 99.5%; Ca – 99.5%. The major impurities in these metals were other alkaline earth metals.

RESULTS AND DISCUSSION

As an initial check on our method we have measured the density of liquid mercury at room temperature and of liquid tin from 275°C to 325°C . We find the density of pure mercury at 21°C to be 12.5346 gm/cm^3 , about 0.07% below the accepted value. Our measured density for liquid tin agrees precisely with the data of Kirshenbaum *et al.*² and falls about 0.2% above

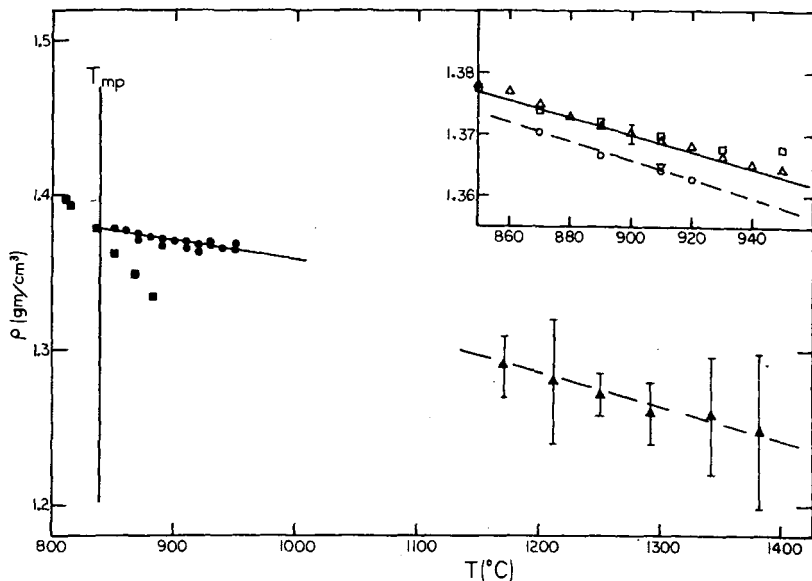


FIGURE 2 Density of liquid calcium. ●—present results, ■—Culpin,⁴ ▲—Bohdansky *et al.*⁵ Inset: present results—different figures indicate different runs. Melting temperature = 838°C.

the data of Berthou *et al.*³ (Berthou in his work applied a constant surface tension correction). We conclude that our method has the accuracy which we desire.

The densities measured for liquid calcium, strontium, and barium are displayed in Figures 2, 3 and 4, respectively. Data from other authors are also displayed where these data are available. In each case, the inset of the figure shows our present results on an expanded scale; different open figures indicate different runs; and the error bar in this inset shows the standard deviation from the best-fit straight line.

We find the densities of liquid calcium, strontium, and barium to be best approximated by the equations (fit by least-squares):

$$\rho(\text{Ca}) = 1.4931 - 1.37 \times 10^{-4} T(^{\circ}\text{C}) \pm 0.0019 \text{ gm/cm}^3 \\ (850^{\circ}\text{C}-950^{\circ}\text{C})$$

$$\rho(\text{Sr}) = 2.5547 - 2.83 \times 10^{-4} T(^{\circ}\text{C}) \pm 0.0018 \text{ gm/cm}^3 \\ (780^{\circ}\text{C}-880^{\circ}\text{C})$$

$$\rho(\text{Ba}) = 3.5561 - 2.99 \times 10^{-4} T(^{\circ}\text{C}) \pm 0.0028 \text{ gm/cm}^3 \\ (730^{\circ}\text{C}-830^{\circ}\text{C})$$

Our data on liquid Ca are seen to fall into two groups, each consistent with a straight line (see inset, Figure 2). These two groups correspond to

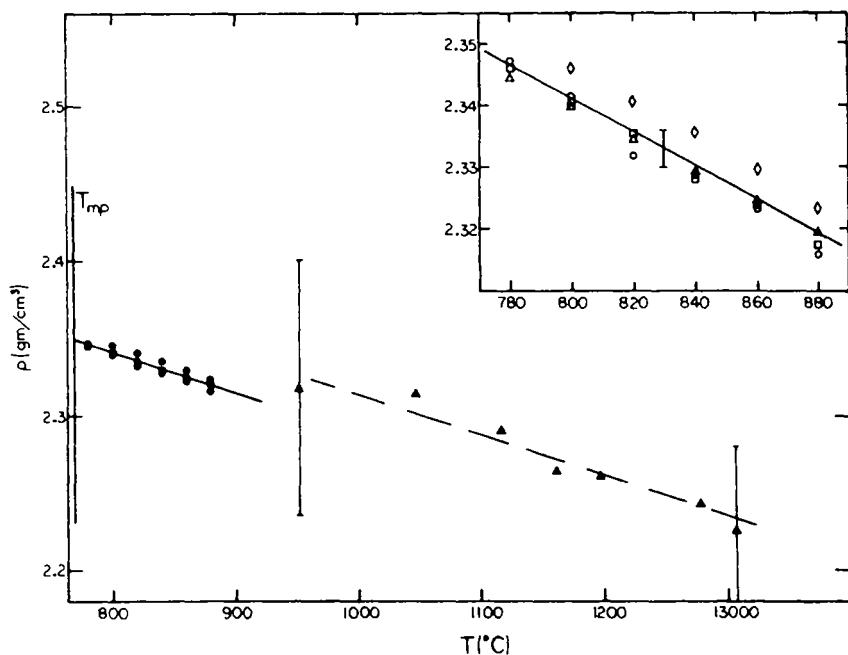


FIGURE 3 Density of liquid strontium. ●—present results, ▲—Bohdanský *et al.*⁵ Inset: present results—different figures indicate different runs. Melting temperature = 767°C.

two different batches of calcium as supplied to us. It is possible that we see here the different basic purities of these two batches. One should also note that Culpin,⁴ who measured a very large $d\rho/dT$ for liquid Ca, observed his sample to remain liquid until well below the accepted melting temperature (Figure 2). (We also see one set of data for liquid strontium lying about 0.2% above the rest of the data; it does not appear, however, that this difference can be due to a difference in the purity of the bulk strontium.)

The mean densities at the melting temperatures and the parameters $d\rho/dT$ are listed in Table 1 and are compared there with other data available. It can be seen that our values for the parameter $d\rho/dT$ agree rather well with the data of Bohdanský *et al.*⁵ for the liquids Sr and Ba, and that the $d\rho/dT$ for liquid Ca also agree to within the experimental uncertainty.

Grosse and McGonigal⁶ have attempted to calculate several parameters of liquid metals on a semiempirical basis. Among these parameters are the critical temperature and the temperature dependence of liquid density near the melting point. They apply the theorem of corresponding states to the entropy of vaporization of a liquid metal to estimate the critical temperature, T_c , of the metal (see Grosse⁷). This T_c , in conjunction with the law of

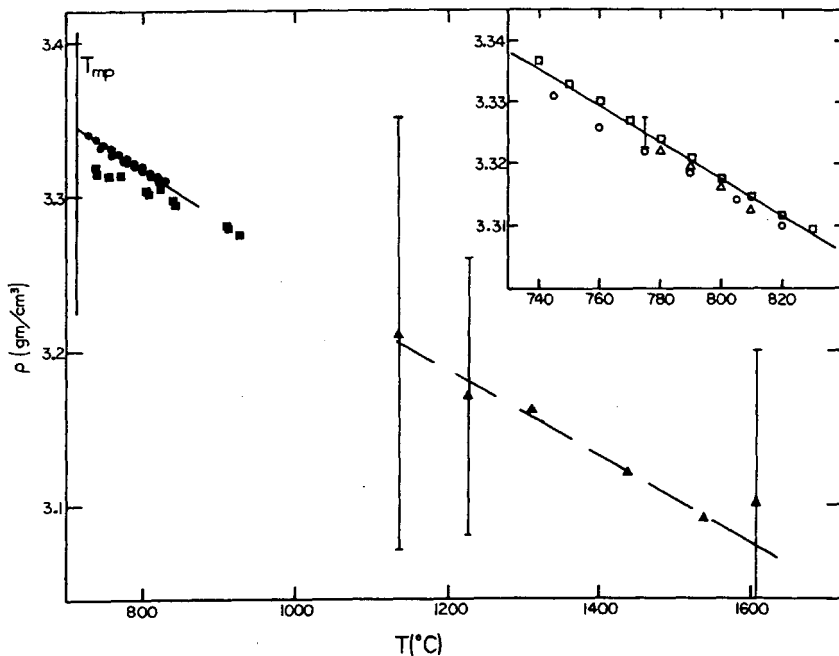


FIGURE 4 Density of liquid barium. ●—present results, ■—Addison *et al.*,¹⁰ ▲—Bohdanský *et al.*⁵ Inset: present results—different figures indicate different runs. Melting temperature = 714°C.

TABLE I

Data on density, ρ , and temperature derivative of density, $d\rho/dT$, for liquid Ca, Sr, and Ba, at their respective melting temperatures.

Metal ($T_{m,p}$)	Author	Experimental		Calculated	
		$\rho(T_{m,p})$ (gm/cm^3)	$(d\rho/dT) \times 10^4$ ($\text{gm/cm}^3 \text{ } ^\circ\text{C}$)	$(d\rho/dT) \times 10^4$ ($\text{gm/cm}^3 \text{ } ^\circ\text{C}$)	
Ca (838°C)	present	1.378 ± 0.002	-1.37 ± 0.21		
	Bohdanský <i>et al.</i> ⁵	1.367	-2.21 ± 1.1	-2.2^a	-1.1^b
	Culpin ⁴	(extrapolated) 1.374	-8.96		
Sr (767°C)	present	2.338 ± 0.003	-2.83 ± 0.19		
	Bohdanský <i>et al.</i> ⁵	2.376 (extrapolated)	-2.62 ± 1.2	-4.1^a	-2.0^b
Ba (714°C)	present	3.343 ± 0.002	-2.99 ± 0.21		
	Bohdanský <i>et al.</i> ⁵	3.320 (extrapolated)	-2.74 ± 1.9	-5.0^a	-2.5^b
	Addison <i>et al.</i> ¹⁰	3.323	-2.14		

rectilinear diameters for liquid-vapor systems and a characteristic empirical relation between the reduced rectilinear diameter and reduced temperature ($\Delta_{red} = \Delta_{red}(T_{red})$), is used to estimate the parameter $d\rho/dT$. This procedure has proven successful, to perhaps $\pm 15\%$, for a wide variety of non-transition metals (McGonigal⁸). We follow this method to calculate $d\rho/dT$ for liquid Ca, Sr, and Ba using a generally successful $\Delta_{red}(T_{red})$; the results, indicated in Table I with a superscript "a," are seen to reproduce the experimental $d\rho/dT$ only poorly. (Calculated values for Ca and Ba have previously been reported by Grosse and McGonigal.⁶) If we, however, take a $\Delta_{red}(T_{red})$ which is characteristic of the group IIB metals, a group for which this function is clearly anomalous, we obtain a much better agreement with the experimental values (indicated in Table I by a superscript "b"). (The parameters used in this calculation, obtained from Stull *et al.*,⁹ constitute Table II.)

TABLE II

Parameters used in the calculation of $d\rho/dT$ for liquid Ca, Sr, Ba near their melting temperatures. (Data from Stull *et al.*⁹)

Metal	Normal boiling temp. ($^{\circ}\text{C}$)	Heat of vaporization (cal/g-atom)
Ca	1492	35,840
Sr	1367	33,200
Ba	1637	36,070

In a recent X-ray diffraction study, Waseda *et al.*^{11,12} report observing a similar effect in the structure factors of liquid Ca, Sr, and Ba. They comment that these measured structure factors are less dependent upon temperature than those for most liquid metals, but are rather similar in this respect to the group IIB liquid metals.

It is interesting to go a step farther as well in comparing our density data to the structure factor data of Waseda *et al.* If we assume that each of these liquid metals at the melting point behaves as a hard-sphere liquid, and if we assume an appropriate packing fraction, η , for these spheres, our density data can be used to predict the liquid structure factors for these metals (see Ashcroft and Lehner¹³). Proceeding in this way, and assuming¹³ $\eta = 0.45$, we obtain the following positions for the main peak in the structure factors of these liquids: $K_p(\text{Ca}) = 1.76$ (1.73), $K_p(\text{Sr}) = 1.81$ (1.78), $K_p(\text{Ba}) = 1.97$ (1.95), where the units are \AA^{-1} , and the experimental data of Waseda *et al.* are given in parentheses. We see that the agreement is rather good in each case; this, with the fact that the peak heights agree rather well, indicates that

the hard-sphere approximation is probably valid for these metals in this region.

Acknowledgments

We are happy to acknowledge the financial support of Research Corporation through a Cottrell College Science Grant. One of us (J. B. V. Z.) would like to thank Professor J. E. Enderby of the University of Leicester, U.K., for his kind hospitality while a portion of this work was completed.

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