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Concerning the Densities and Temperature Coefficients of Liquid Barium and Calcium

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The density of liquid barium has been measured recently by Addison and Pulham[2] and the density of liquid calcium was measured previously by Culpin[3] in connection with his viscosity studies. No other data are available. The present authors have had occasion to question the accuracy of these data with regard to the slopes of the density *vs.* temperature lines.

The situation here is similar to that which existed in the case of magnesium and which was discussed by the authors previously.[4] However, in contrast, there was an abundance of experimental density data for liquid magnesium and it was the *very great discrepancies* between values reported by various workers that first attracted our attention. It was possible to *predict* values for the density at the normal boiling point, critical density, and slope of the density *vs.* temperature line or the temperature coefficient of density for magnesium and these predictions were found subsequently to agree rather closely with our experimental results and extrapolations based thereon. Our calculated results for barium and calcium, obtained by methods to be discussed below, are contrasted with the experimental values in Table I. The discrepancy is substantial.

Table I: Data for Barium and Calcium

	Barium	Calcium
Melting point, °K.	1002[a]	1123[b]
Reference density at m.p., g./cm.^{3}	3.320	1.364
$-dD/dT \times 10^4$ g./cm.^{3} °K.		
Experimental	2.14	8.87
Calculated:		
Method 1	5.04	2.18
Method 2	5.10	2.20
Method 3	5.64	2.24
Critical density, g./cm.^{3}		
Method 1	0.722	0.304
Method 2	0.712	0.299
Method 3	0.620	0.292
Estimated critical temp., °K.	4720 ± 10%	4590 ± 10%
Density at normal boiling point, g./cm.^{3}		
Method 1	2.862	1.224
Method 2	2.857	1.223
Method 3	2.806	1.220
Normal boiling point, °K.	1910[c]	1765[c]
Reduced temperature at normal boiling point	0.405	0.384
ΔH_{vap} at normal boiling point, cal./g. atom	36,070[c]	35,840[c]

[a] D. T. Peterson and J. A. Hinkebein, *J. Phys. Chem.*, **63**, 1360 (1959). [b] O. Kubaschewski and R. Hörnle, *Z. Metallk.*, **42**, 129 (1951). [c] D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," Advances in Chemistry Series, No. 18, American Chemical Society, Washington, D. C., 1956.

It has been shown[5-7] that critical temperatures of metals can be estimated to a fair degree of reliability by application of the *theorem of corresponding states* to entropy of vaporization data. Critical temperatures estimated on this basis show good agreement with those estimated by use of extrapolated liquid and vapor densities and the law of the rectilinear diameters.

The metal selected as a reference for the application of the theorem of corresponding states is mercury, the only metal whose critical constants have been experimentally determined.[8] The most reliable data for the entropy of vaporization of mercury are those of Busey and Giauque.[9] The estimated critical temperatures of barium and calcium together with some other pertinent physical properties are shown in Table I.

Treatment of the data reported by Culpin[3] yielded the equation

$$D\ (\text{g./cm.}^3) = 2.360 - 8.87 \times 10^{-4}T\ (°\text{K.}) \quad (1)$$

for the density of liquid calcium. The melting point observed by Culpin was 1075°K., which is considerably lower than 1123°K. as reported by Kubaschewski and Hörnle. No subsequent data have been reported. Without introduction of significant error, the reference density of liquid calcium will be taken as 1.364 g./cm.^{3} at 1123°K.

The data of Addison and Pulham[2] fit the equation

$$D\ (\text{g./cm.}^3) = 3.534 - 2.14 \times 10^{-4}T\ (°\text{K.}) \quad (2)$$

for the density of liquid barium. Their measurements covered the range 1013–1103°K. and a slight extrapolation yields a reference density of 3.320 g./cm.^{3} at the melting point (1002°K.).

It is noted that the temperature coefficient for calcium is very steep and indeed extrapolation of the rectilinear diameter indicates that it crosses the temperature axis at 2660°K., which is well below the critical temperature. The slope in the case of barium, on the other hand, is very slight and leads to a very high

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(1) A report of this work will constitute a portion of a dissertation to be submitted by P. J. McGonigal to the Graduate Board of Temple University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) C. C. Addison and R. J. Pulham, *J. Chem. Soc.*, 3873 (1962).

(3) M. F. Culpin, *Proc. Phys. Soc.* (London), 203, 1079 (1957).

(4) P. J. McGonigal, A. D. Kirshenbaum, and A. V. Grosse, *J. Phys. Chem.*, **66**, 737 (1962).

(5) A. V. Grosse, *J. Inorg. Nucl. Chem.*, **22**, 23 (1961).

(6) A. V. Grosse, "The Liquid Range of Metals, and Some of their Physical Properties at High Temperatures," Paper No. 2159, A.R.S., Space Flight Report to the Nation, New York N. Y., October 9–15, 1961.

(7) A. V. Grosse, "The Liquid Range of Metals and Some of their Physical Properties at High Temperatures," Report of the Research Institute of Temple University, October 19, 1960.

(8) F. Birch, *Phys. Rev.*, **41**, 641 (1932).

(9) R. H. Busey and W. F. Giauque, *J. Am. Chem. Soc.*, **75**, 806 (1953).

critical density or requires the assumption of a very high critical temperature.

In view of these facts, the critical densities, temperature coefficients of the density *vs.* temperature lines (which are valid up to at least the normal boiling points), and the densities at the normal boiling points were estimated by three separate but related methods. The *first* method was the same as used by us in the work on magnesium.[4] An average reduced rectilinear diameter *vs.* reduced temperature line for six metals (Hg, Bi, Ag, Pb, Sn, and Ga) was constructed and assumed to be fairly representative of the reduced density *vs.* reduced temperature behavior of metals in general. The *second* method is the same as the first except that the average line was constructed from data for sodium, potassium, and magnesium. The *third* method involved application of a generalized relation between reduced density and temperature which is valid for liquid metals as well as other classes of liquids.[10]

Table I shows our calculated density data for barium and calcium. It is seen that the three methods yield results which agree rather closely with each other. The reliability of our calculations is, of course, dependent upon the accuracy of the experimental reference density as well as errors in estimation of critical temperatures which are discussed elsewhere.[5] Although our calculated data are given to three or four significant figures to illustrate the agreement of the three methods, it should be remembered that the error possibility may be ±10%.

The final results calculated for the density *vs.* temperature relationship may be expressed by the equation

$$D_{\mathrm{Ba}}\ (\mathrm{g./cm.^3}) = 3.847 - 5.26 \times 10^{-4}T\ (^\circ\mathrm{K.}) \qquad (3)$$

for barium, and

$$D_{\mathrm{Ca}}\ (\mathrm{g./cm.^3}) = 1.613 - 2.21 \times 10^{-4}\ T(^\circ\mathrm{K.}) \qquad (4)$$

for calcium.

The differences between the experimental and calculated temperature coefficients, -8.87×10^{-4} *vs.* -2.21×10^{-4} g./cm.^{3} °K., respectively, for calcium and -2.14×10^{-4} *vs.* -5.26×10^{-4} g./cm.^{3} °K. for barium, are substantial.

These differences between the experimental and calculated results are even more striking if the coefficients of cubical expansion, $-1/D\ \mathrm{d}D/\mathrm{d}T$, which would be expected to have similar values for barium and calcium, are compared. The coefficients of cubical expansion at the melting point obtained from an average of calculated data are very similar (1.58×10^{-4} °K.$^{-1}$ for barium and 1.62×10^{-4} °K.$^{-1}$ for calcium) while the values obtained from the experimental data differ by a factor of ten (0.645×10^{-4} °K.$^{-1}$ and 6.49×10^{-4} °K.$^{-1}$, respectively). These discrepancies serve to illustrate the difficulties inherent in measuring the physical properties of liquid metals, especially for the first time, at elevated temperatures.

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(10) P. J. McGonigal, *J. Phys. Chem.*, **66**, 1686 (1962), and further unreported work in progress.