

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.<sup>4</sup> 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.<sup>10</sup>

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.<sup>5</sup> 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  $\pm 10\%$ .

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

$$D_{\text{Ba}} (\text{g./cm.}^3) = 3.847 - 5.26 \times 10^{-4} T (\text{°K.}) \quad (3)$$

for barium, and

$$D_{\text{Ca}} (\text{g./cm.}^3) = 1.613 - 2.21 \times 10^{-4} T (\text{°K.}) \quad (4)$$

for calcium.

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

These differences between the experimental and calculated results are even more striking if the coefficients of cubical expansion,  $-1/D \, dD/dT$ , 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 ( $1.58 \times 10^{-4}$  °K.<sup>-1</sup> for barium and  $1.62 \times 10^{-4}$  °K.<sup>-1</sup> for calcium) while the values obtained from the experimental data differ by a factor of ten ( $0.645 \times 10^{-4}$  °K.<sup>-1</sup> and  $6.49 \times 10^{-4}$  °K.<sup>-1</sup>, 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.