229. *Liquid Metals. Part IX.*[1] *The Densities of Solutions of Barium in Liquid Sodium.*

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The densities (ρ) of solutions of barium in liquid sodium have been measured by the buoyancy method at six concentrations between 6 and 75 atom % of barium and at temperatures (t °c) within the range 100—650°. When expressed in the form $\rho = C - at$, the value of C changes smoothly with composition, but the temperature coefficient a passes through a maximum when the sodium : barium atom ratio is 2 : 1. The system is not therefore entirely ideal, though atomic volumes calculated for the solutions are very close to the ideal values at all temperatures.

The densities of solutions of barium in liquid sodium were measured as a preliminary step in the study of the surface properties of these solutions.[2] The density values also have intrinsic interest, in that the volumes of mixing derived therefrom give evidence concerning the atomic interactions in the solutions, and the measurements form part of our general survey of the properties of solutions of the Group II metals in liquid sodium. Of the Group II metals, barium is particularly useful in this respect as it has a high solubility in liquid sodium at relatively low temperatures.[2] The density of liquid sodium is known with precision,[3] and that of liquid barium has recently been reported from these laboratories.[4]

Experimental

Materials.—Sodium [5] and argon [4] were purified as already described. It has now become possible to determine the oxygen content of sodium (purified in this manner) by a method

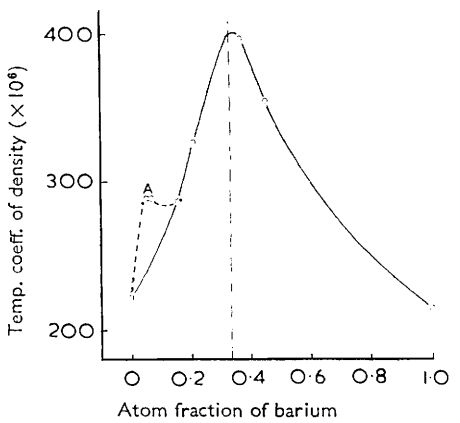

Fig. 1. Temperature coefficients of density for solutions of barium in liquid sodium.

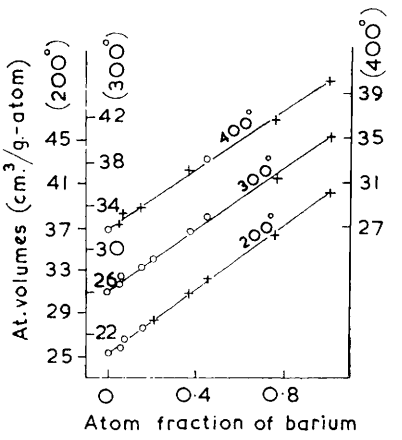

Fig. 2. Atomic volumes of solutions of barium in liquid sodium.

which involves vacuum-distillation of the sodium from a sample and titration of the remaining sodium oxide; the oxygen content is <8 p.p.m. Barium was 99·99% pure and was cleaned by the method described in Part VI.[2]

Method. Densities were measured by the buoyancy method, with a steel plummet. The

[1] Part VIII, Addison, Coldrey, and Pulham, preceding paper.
[2] Part VI, Addison, Coldrey, and Halstead, *J.*, 1962, 3868.
[3] Thomson and Garelis, "Physical and Thermodynamic Properties of Sodium," Ethyl Corpn. Res. and Eng. Dept., Detroit, 2nd edn. 1955, p. 6.
[4] Part VII, Addison and Pulham, *J.*, 1962, 3873.
[5] Part I, Addison, Kerridge, and Lewis, *J.*, 1954, 2861.

liquid metal solutions were contained in a stainless-steel vessel. The experimental precautions taken, and corrections applied, were essentially the same as those described in Part VII [4] for the determination of the density of liquid barium. The highest barium concentration studied was 75·7 atom % (94·9 wt. %) of barium. For this solution the furnace described in Part VII was also used, and stainless steel was employed for the suspension wire. Because of the high vapour pressure of sodium at the temperature required to keep this solution liquid, measurements were made at only one temperature and a value for the temperature coefficient was interpolated from Fig. 1. With the other solutions, the temperature did not exceed 400°, and the steel beaker containing the liquid metal was enclosed in the glass apparatus described in Part V.[6] The preparation, sampling, and analysis of the solutions were also carried out as described in Part V. Some density measurements were carried out by J. M. Coldrey in these laboratories with a glass dilatometer. They confirmed the values given in this paper but were restricted to dilute solutions of barium. Atomic volumes for the lowest concentration of barium (5·34 atom %) plotted in Fig. 2 were obtained by this method.

Results and Discussion

Densities.—Density values for six solutions are given in Table 1. For each concentration studied over a temperature range the plot of temperature (t, °C) against density (ρ)

Table 1.

Atom % barium	Temp.	Density (g./c.c.)	Atom % barium	Temp.	Density (g./c.c.)	Atom % barium	Temp.	Density (g./c.c.)
6·18	111°	1·1862	21·17	212	1·6543	45·20	294°	2·2781
,,	153	1·1732	,,	234	1·6492	,,	326	2·2671
,,	198	1·1607	,,	238	1·6482	,,	326	2·2670
,,	200	1·1594	,,	251	1·6430	,,	355	2·2561
,,	236	1·1505	,,	259	1·6414	,,	358	2·2560
,,	238	1·1495	,,	287	1·6320	,,	364	2·2536
,,	276	1·1380	,,	316	1·6225	,,	399	2·2419
,,	280	1·1366	,,	369	1·6020			
,,	312	1·1278				75·70	640	2·9221
,,	320	1·1255	37·18	251°	2·0950			
			,,	284	2·0821			
15·88	202	1·4898	,,	303	2·0737			
,,	204	1·4879	,,	343	2·0577			
,,	257	1·4740	,,	363	2·0492			
,,	274	1·4688						
,,	301	1·4619						
,,	303	1·4608						
,,	331	1·4521						
,,	333	1·4516						

is a straight line. The relevant constants in the equation $\rho = C - at$ are given in Table 2.

The value of C varies with composition on a smooth curve, but the temperature coefficients (a) pass through a maximum at a composition of 33 atom % of barium (Fig. 1).

Table 2.

Constants in the equation $\rho = C - at$.

Ba concn. (atom %)	0	5·34	6·18	15·88	21·17	37·18	45·20	100	
C	0·949	1·179	1·218	1·547	1·725	2·195	2·382	3·476	
10^6a	223	289	289	287	327	397	354	214	(ref. 4)

This does not imply the formation of a compound Na_2Ba in the normal sense, but the physical nature of the solutions undergoes definite change at this composition; the fact that the solution is most sensitive to temperature when the components are present in 2 : 1 ratio must imply some atomic interaction. There is probably also a minor peak at low barium concentrations which will take in points A (Fig. 1). This would be consistent with the barium–sodium phase diagram, which shows a maximum at 4 atom % of barium, and with the surface tensions of these solutions which pass through a minimum at this concentration.[2]

[6] Part V, Addison, Iberson, and Manning, *J.*, 1962, 2699.

Atomic Volumes.—Interaction between sodium and barium in the liquid state has also been examined by reference to volume changes on mixing. By interpolation or extrapolation of the data in Table 1, density values were determined at 200°, 250°, 300°, 350°, and 400° for each concentration. The atomic volume of the ideal solution is given by $V_0 = x_1V_1$ and x_2V_2, where suffixes 1 and 2 denote sodium and barium, respectively, and x is the atom fraction. On an atomic volume–atomic fraction graph, ideal solutions are represented by the straight lines (Fig. 2) joining the atomic volumes of pure sodium and pure barium. Sodium is liquid over the 200—400° range and atomic volumes are known; the atomic volumes of the mixtures refer to barium in the liquid state also, and the barium-axis values should therefore be the atomic volumes of liquid barium. Since the temperature range available for study lies below the melting point of barium, atomic volumes on the barium axis have been obtained by extrapolation of the density data for liquid barium.[4] The experimental atomic volumes (V) were determined from the relation $V = (x_1W_1 + x_2W_2)/\rho$, where ρ is the measured density and W the atomic weight of the metal concerned.

The results for three temperatures are shown in Fig. 2. At any one temperature the solutions are liquid for only part of the composition range; values shown as circles lie within the experimental range, while values shown as crosses are obtained by extrapolation. All points are seen to lie very close to the ideal line, so that the variations in atomic volume which result from the changes in temperature coefficient mentioned above represent only slight deviations from ideality. In the magnesium–zinc system,[7] a deviation from ideality of 7% was observed at a composition corresponding to $MgZn_2$. In the sodium–barium system, there are no deviations in atomic volumes sufficiently great to suggest any interatomic association of the kind normally found when intermetallic compounds occur, though the variations in temperature coefficient of density show that the system is not entirely ideal.

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[7] Pelzel and Sauerwald, *Z. Metallk.*, 1941, **33**, 229.