Reaction between Barium and Nitrogen in Liquid Sodium: Solubility Studies

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Nitrogen in increasing amounts has been added to separate solutions of barium in sodium of constant composition (*ca.* 4.40 mol % Ba) at 300 °C. After rendering each mixture homogeneous using an electromagnetic pump, filtration, and nitrogen analysis, all the N_2 added has been found in solution up to a solution composition approximating to Ba_4N (*i.e.* 1.1 mol % N) beyond which the quantity of dissolved N_2 decreases progressively due to precipitation of the nitride Ba_2N. The solubilization is interpreted in terms of strong preferential solvation of the nitride ion by barium cations.

MANY simple sodium salts are appreciably soluble in liquid sodium. Well known examples are provided by the halides where miscibility extends over all proportions at high enough temperatures.[1] However, liquid sodium is inert towards nitrogen, which is virtually insoluble.[2] The addition of a metallic solute to Na enhances the solubility of N_2 only if the solute metal itself normally reacts with the gas. Thus lithium [3] is effective whereas potassium, rubidium, and caesium are not. Of the Group 2 metals, barium is particularly effective at rendering N_2 soluble and our solubility studies are described in the present paper. The reaction of Ba with N_2 in the liquid-metal environment has also been studied by resistimetric and kinetic techniques and these will be described in separate papers. The results have indirect relevance to the use of liquid sodium as coolant in nuclear reactors where Ba, a metastable fission product,[4] might create a vehicle for enhanced N_2 solubility in sodium thereby influencing the corrosion characteristics. We are also interested in the extent to which the enhanced solubility may be due to solvation effects as in molecular solvents.

EXPERIMENTAL

Apparatus.—The apparatus (Figure 1) was constructed largely from stainless steel (A1S1 321) and consisted of a reservoir (A) (55 mm diameter, 55 mm long) containing the bulk of the liquid metal. A long (250 mm) steel neck (12.5 mm diameter) was attached to the reservoir to accommodate the sampling device, (B). The neck was joined to a glass tap and thence to a vacuum frame through a metal-to-glass (Kovar) seal. The sampling tube (280 mm long, 10 mm diameter) was made of Pyrex glass and was constricted every 30 mm to facilitate subsequent fracture into small samples. Glass was used since attack by the liquid metal is slow below 300 °C and this part of the apparatus was exposed to the metal only for a short period. A sintered-glass filter pad (C) (porosity 20×10^{-4} mm) was sealed into the base of the sampling tube and a soft-iron plug, (D), was used to close the top. The sampling tube was raised and lowered by magnetic means. The liquid metal was stirred by an electromagnetic pump attached to the base of the reservoir. This consisted of a metal duct, (E), positioned between the poles of a strong (0.5 T) permanent magnet. The duct was electrically insulated from the poles by mica sheets. Silver electrical leads were silver soldered to the edges of the duct. On passing a direct current (up to 40 A) through the liquid metal at right angles to the magnetic

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[1] M. A. Bredig, 'Molten Salt Chemistry,' ed. M. Blander, Interscience, New York, 1964, p. 367.

[2] E. Veleckis, K. E. Anderson, F. A. Cafasso, and H. M. Feder, *Proc. Internat. Conf. Sodium Technol. and Fast Reactor Design*, Argonne National Lab., November 1968, Part I, ANL–7520, p. 295.

[3] C. C. Addison and B. M. Davies, *J. Chem. Soc.* (*A*), 1969, 1827.

[4] H. E. Evans and W. R. Watson, 'Liquid Alkali Metals,' *Proc. Internat. Conf. Brit. Nucl. Energy Soc.*, April 1973, p. 153.

field the liquid was drawn from the base of the reservoir and returned to the reservoir at a point above the liquid level as shown. This method ensures homogeneity of the liquid and promotes rapid and complete reaction of nitrogen.

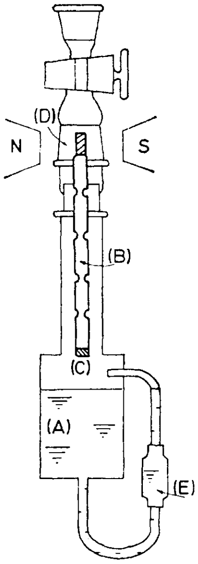

FIGURE 1 Apparatus for mixing, filtration, and sampling solutions of nitrogen in sodium–barium mixtures

Procedure.—The vessel was cleaned internally with a mixture of hydrochloric acid (54%), nitric acid (5%), and water (50%), rinsed with water and acetone, and dried by heating *in vacuo*. In each experiment a weighed quantity of liquid sodium, drawn from a stock and purified as before,[5] was pipetted into the vessel under argon. Barium, prepared as before,[6] was also weighed in. The sampling tube was inserted and the tap closed. The entire apparatus including the electromagnetic pump was then mounted in an air oven and attached to a vacuum frame through a vent in the oven roof. The sample tube was suspended well above the metal and the pressure of argon in the vessel was reduced to 25 kN m^{-2} to allow for expansion. The temperature was raised to 300 °C and metal circulated through the pump to dissolve the Ba. The remainder of the argon was pumped off and immediately replaced with a known volume of nitrogen (Air Products, 99.999%) which had been further purified by passage through molecular sieves to remove moisture, manganese(II) oxide to remove oxygen and carbon dioxide, and liquid sodium–potassium alloy for final scrubbing. The absorption of N_2 was followed by pressure changes and when complete the sampling tube was lowered to submerge the filter. On pressurizing with argon the liquid was forced through the filter and into the sampling tube. This was then raised clear of the liquid and cooled in an air stream to freeze the filtrate rapidly, and to minimize sedimentation. The vessel was opened in a glove-box and the sampling tube divided into segments for analysis. The procedure was then repeated with fresh alloy to which a larger amount of N_2 was added.

The solidified filtrate was analyzed for nitrogen by the Kjeldahl method. The contents of each ampoule were dissolved out with pure acetic acid as this reacted less vigorously than water. The excess of metal evolved hydrogen and the barium nitride, which was originally in solution, was converted to barium and ammonium acetates. When vigorous hydrolysis was allowed the nitride ignited and was converted partially into molecular nitrogen rather than ammonia. Mild solvolysis, however, produced no N_2 as confirmed by mass spectrometry.

RESULTS AND DISCUSSION

Nine solutions with compositions near 4.40 mol % Ba in sodium were studied. After reaction with N_2, at least two nitrogen analyses were made on the filtrate from each of these solutions. These are recorded in Table 1 (column 4) which also indicates the degree of reproducibility achieved. One metal solution [experiment (10)] which had not been exposed to N_2 was analyzed as a blank. Sample weights ranged from 0.35 to 1.73 g. The weights of the alloys used in reactions varied between 48.4 and 74.5 g.

TABLE 1

Nitrogen analyses of the filtered mixtures

Expt. no.	Concentration of barium mol %	Total nitrogen absorbed wt. %	Nitrogen in solution wt. %	Overall ratio Ba : N
(1)	4.10	0.111	0.099, 0.119	18.68
(2)	4.30	0.260	0.202, 0.272	8.26
(3)	4.40	0.425	0.380, 0.360, 0.420	5.14
(4)	4.30	0.514	0.490, 0.460	4.17
(5)	4.40	0.585	0.437, 0.481	3.75
(6)	4.40	0.633	0.393, 0.389	3.44
(7)	4.20	0.708	0.254, 0.242, 0.231, 0.222	2.92
(8)	4.40	0.851	0.221, 0.224	2.54
(9)	4.10	1.04	0.006, 0.013	1.95
(10)	4.20	0.00	0.016, 0.015	

Changes in Solubility during Reaction.—The change in behaviour is illustrated in Figure 2, where the amount of N_2 found in solution is plotted against the total amount of nitrogen added. The solubility of nitrogen increased until the reaction was about half completed then fell to zero. In experiments (1)—(4) all N_2 absorbed was found in solution, presumably as the nitride ion N^{3-}; this is represented by the linear part AB (Figure 2). In terms of simple solubility, if point B represented saturation of the liquid with nitrogen, then further addition of N_2 should not influence the amount in solution (line BD in Figure 2). Instead, precipitation of a barium nitride began at point B. This diminished the Ba content of the solution; with further addition of nitrogen beyond B, precipitation continued and the amount of dissolved N_2

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[5] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.*, 1961, 1482.

[6] C. C. Addison, G. K. Creffield, P. Hubberstey, and R. J. Pulham, *J. Chem. Soc.*, 1961, 1393.

decreased until at C all barium was precipitated as the nitride and no nitrogen dissolved in the remaining liquid sodium.

The Solid Product.—The quantities of Ba and N_2 used in experiment (9) (point C, Figure 2) correspond to a solid nitride of stoicheiometry Ba_2N and the analytical results indicate that this is the nitride which separates throughout the precipitation process. This solid must contain free electrons, and it is of interest that Ba_2N rather than the ionic solid Ba_3N_2 separates from the metallic environment.* In separate experiments residual sodium was distilled from the nitride which was further identified by *X*-ray powder diffraction. Dibarium nitride is one of the family of Group 2 metal nitrides M_2N which have the *anti*-$CdCl_2$ structure,[7,8] and is normally prepared[9] by decomposition (1) at high temperatures. Reaction of

$$2Ba_3N_2(s) \longrightarrow \tfrac{1}{2}N_2 + 3Ba_2N(s) \qquad (1)$$

Ba and N_2 in liquid sodium provides an efficient low-temperature alternative method.

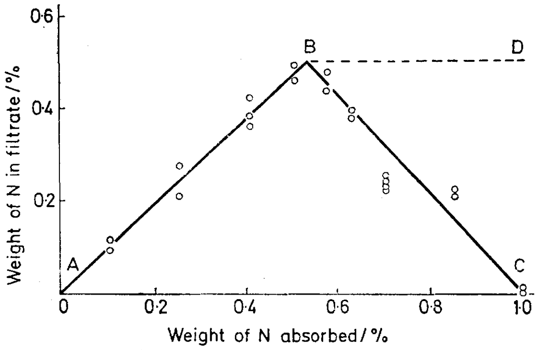

FIGURE 2 Relation between the quantity of nitrogen dissolved in filtered samples, and the total quantity of nitrogen taken up by the liquid metal

When mixtures of Ba_2N and liquid sodium [*e.g.* experiment (9)] were allowed to stand for long periods in contact with N_2 further uptake of the gas was negligible, whereas at 300 °C some reaction [represented by the reverse of equation (1)] might have been expected. This is attributed to the fact that Ba_2N is the stable nitride in a liquid-metal medium, and also to the protective effect of the liquid sodium on the nitride. On opening the vessel at the end of experiment (9) the solid nitride was seen to be completely wetted by and embedded in the solidified sodium which cannot act as a carrier for nitrogen.

Solvation of the Nitride Ion.—For a given quantity of Ba in solution, N_2 dissolves until a critical Ba : N ratio is achieved, and it is now necessary to consider why precipitation commences as soon as this critical ratio is exceeded. At point B (Figure 2) the concentrations of Ba and N are 4.40 and 1.08 mol %, so that the critical state is suitably represented by Ba_4N. When smaller quantities of nitrogen are present (*e.g.* the range AB, Figure 2) we believe that the nitride ion is held in solution as a result of the solvation energy arising from solvation of N^{3-} by four Ba^{2+} ions[10] (using the free-electron concept of the liquid-metal state). When the nitrogen added increases beyond the Ba_4N ratio, Ba^{2+} must be replaced by Na^+ in the solvation shell of some of the N^{3-} ions. The solvation energy decreases and some precipitation occurs. During the precipitation stage (BC, Figure 2) the quantity of Ba_2N which separates is such as to maintain the Ba_4N ratio in the liquid throughout the whole process. This is illustrated in Figure 3 which shows how the Ba : N ratio in solution falls towards 4 : 1 at the point where precipitation commences and remains around that value during the precipitation. From the nitrogen content of the filtered solution [for experiments (5)—(9)] it was possible to determine the quantity of nitrogen precipitated as Ba_2N, and hence the quantity of barium precipitated. The open circles in Figure 3 show the Ba : N ratio calculated in this way. In experiments (5) and (7) barium in the filtrate was also determined directly by analysis, and these results are shown in Figure 3 by filled circles. We also deduce from the above that for dilute solutions of Ba in sodium this general behaviour is independent of the concentration of barium used in the reaction (at least up to 4.4 mol % Ba) and that precipitation occurs when the ratio Ba : N = 4 : 1 is exceeded. To a large extent, therefore, sodium is no more than an inert diluent for the reaction.

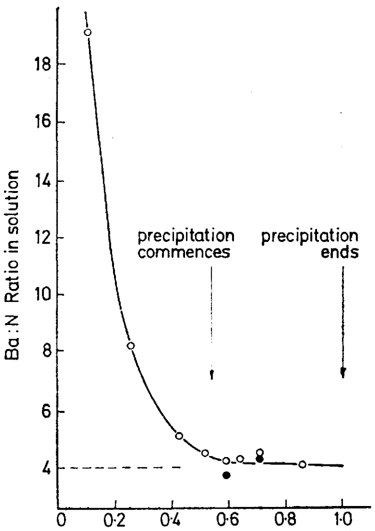

FIGURE 3 Change in the ratio Ba : N in solution: (○), from N analysis; (●), from N and Ba analysis

Energy Factors.—The liquid-alkali and heavier alkaline-earth metals represent the nearest approach to the free-electron model; simple non-metals may take up electrons from the conduction band and dissolve as anions (*e.g.*

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* The Ba–Na–N system is therefore represented by the phase diagram for the components Ba, Na, and Ba_2N.

[7] E. T. Keve and A. C. Skapski, *Inorg. Chem.*, 1968, **7**, 1757.

[8] J. Gaude, P. L.'Haridon, Y. Laurent, and J. Lang, *Bull. Soc. France Mineral. Crist.*, 1972, **95**, 56.

[9] S. M. Ariya, E. A. Prokofyeva, and I. I. Matveeva, *Zhur. obshchei Khim.*, 1955, **25**, 634.

[10] C. C. Addison, *Sci. Progr. Oxf.*, 1972, **60**, 385.

H^-, O^{2-}, and N^{3-}). Whether or not solution does occur depends on several factors, amongst which solvation enthalpy is important. There is a close correlation between solubility of a non-metal in a liquid metal and the ability of that metal to form a stable compound. This is expected since the lattice enthalpy U_L and solvation enthalpy U_S are of the same order of magnitude. In fact they differ only by $H_{soln.}$ (Figure 4) so that in formation of solutions the solvation enthalpy plays the same important role as does lattice enthalpy in formation of solid compounds. In the present context nitrogen dissolves in liquid barium; the Ba–N phase diagram shows a eutectic at 508 °C at which temperature the solution contains 14 mol % N.[11] in contrast, the solubility of nitrogen in sodium is negligible; values of 1.5×10^{-9} and 7.1×10^{-9} mol % N at 450 and 600 °C respectively have been quoted.[2] Nitrogen appears to be present in these liquids as the undissociated N_2 molecule, so that no electron transfer from the conduction band occurs.

The solution of nitrogen in sodium as N_3^- ions would depend on factors shown in the enthalpy cycle in Figure 4. The solvation enthalpy U_s embodies solvation of both cation and anion. Using calculated values for the lattice energy of solid Na_3N, $\Delta H^\ominus$ is near zero. For sodium (as well as potassium, rubidium, and caesium) U_s is inadequate to offset $(D + E + S + I)$ so that $(\Delta H^\ominus + H_{soln})$ becomes positive and no solution occurs. (The smaller lithium cation increases U_s and solution occurs readily.)

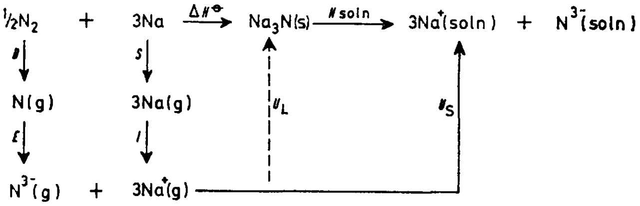

FIGURE 4 Enthalpy cycle for the solution of nitrogen in liquid sodium

TABLE 2

Lattice enthalpies [kJ (mol N)$^{-1}$] of Group 1 and 2 metal nitrides derived from the Kapustinskii equation [12]

M_3N		M_3N_2	
Li	5 104	Be	7 394
Na	4 711	Mg	6 517
K	4 201	Ca	5 823
Rb	4 030	Sr	5 572
Cs	3 808	Ba	5 221

Table 2 compares calculated values for the lattice enthalpies of the Group 1 and 2 metal nitrides.[12] Due to the greater charge and smaller size of the Group 2 metal ions, the lattice enthalpies of their nitrides are appreciably greater. We assume that the greater attraction between the N_3^- and M^{2+} ions will be reflected in the solvation enthalpies also so that in a liquid consisting of Na^+, Ba^{2+}, and free electrons the N_3^- ion will be solvated preferentially by Ba^{2+}. The experiments indicate that this preferential solvation is strong enough to set up Ba_4N units, and that the decrease in solvation enthalpy on substitution of Ba^{2+} by Na^+ is sufficient to cause precipitation.

Insufficient enthalpy values are available to construct a cycle (like Figure 4) for the solution of N_2 in Ba or in barium–sodium mixtures. However, some corroborative evidence in support of the general premise outlined above is available from the lithium–sodium system, where the general behaviour (though not the stoicheiometry) is similar. It has been estimated [13] that the free-energy change for the process $N_2(g) \longrightarrow 2N^{3-}(soln)$ in liquid lithium is -82 kJ g-ion^{-1} at 700 K, whereas in liquid sodium it would be $+518$ kJ g-ion^{-1} at the same temperature.

Calcium Solutions.—The unusual feature in the experiments described above is that for limited amounts of N_2 barium enhances the solubility, but that when excess of gas is available the solubility decreases to zero. This could explain the apparently conflicting opinions concerning the effect of calcium on the corrosive properties of nitrogen in sodium. Epstein [14] considered that calcium impurity in sodium would enhance the solubility of N_2 and promote nitriding of steel. Experiments by Cafasso,[15] however, using an excess of nitrogen, showed diminished corrosion, and these findings form the basis of a patent on corrosion prevention.[16] In all probability the Na–Ca–N system is analogous to Na–Ba–N, and whether N_2 remains in solution depends entirely on the amount of gas available.

Calcium is the main impurity introduced in the electrolytic production of sodium from NaCl–$CaCl_2$ melts. A purification method uses excess of oxygen to precipitate calcium oxide which is then filtered off. Treating the Na with excess of nitrogen, however, could also provide a method of removing calcium from sodium by precipitation as calcium nitride; no sodium is lost as oxide and the process is potentially less dangerous.

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[11] V. A. Russell, M.S. Thesis, Syracuse, 1949.

[12] G. J. Moody and J. D. R. Thomas, *J. Chem. Educ.*, 1966, **43**, 205.

[13] R. Thompson, *J. Inorg. Nuclear Chem.*, 1972, **34**, 2513 (Report A.E.R.E. R–6566, 1971).

[14] L. F. Epstein, *Proc. Internat. Conf. Sodium Technol. and Fast Reactor Design*, Argonne National Lab., November 1968, Part I, ANL–7520, p. 33.

[15] P. A. Cafasso and A. K. Fischer, Sodium Technol. Quart. Rept. Argonne National Lab., ed. G. M. Kesser, Illinois, ANL/ST–8, March 1971, p. 37.

[16] A. K. Fischer, U.S.P. 3,745,068 (Cl 176–38, BOlj, G21c)/1973.