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RECENT DEVELOPMENTS IN THE CHEMISTRY OF SOLUTIONS OF SALTS IN LIQUID ALKALI METALS

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Abstract - Essential features of phase equilibria between alkali metal-salt-nonmetal are summarized and narrowed to detailed consideration of dilute solutions of salts in metals. The use of resistivity techniques is illustrated to determine nonmetal solubilities and hence derive partial molar quantities and anion solvation enthalpies. Dissolved nonmetals increase the resistivity of a specific metal by a characteristic amount and this property is exploited in the study of solute-solute interactions. Examples are given of solute association, dissociation and equilibrium in metallic solution and the reactions are correlated with the corresponding solid state reaction enthalpies.

METAL-NONMETAL PHASE EQUILIBRIA

In recent years solutions of both salts in metals and metals in salts have come under scrutiny. Most investigators have considered the metal and its normal salt to be the components of the solution and have ignored compositions richer in nonmetal than the salt due largely to the considerable disparity in the physical properties of the two elements e.g. Li and H_2, Na and Cl_2. Where melting points are not dissimilar, however, the systems are put in perspective by complete phase diagrams as shown in Fig. 1 for K-I_2(Ref.1).

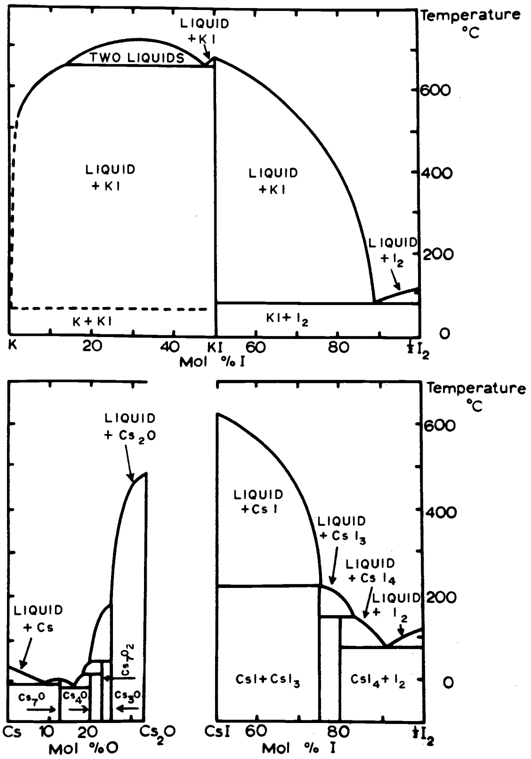

Fig.1. Metal-nonmetal phase diagrams.

The high melting salt, KI, dominates the system and, in this respect, bears considerable resemblance to systems of sodium with tellurium (and possible selenium and sulphur) and with the less electropositive metals, tin, gallium and mercury (Ref.2) so that metal-nonmetal systems can become an extension of alloy behaviour. Characteristics of the metal-salt region are (i) a eutectic adjacent the metal axis, established until recently only for Cs-Cs_2O (Ref.3) and Rb-Rb_2O (Ref.4), but now also for Li-LiH and Li-Li_3N (Ref.5). No freezing point depression nor eutectic data exist for sodium with any of its salts. (ii) a steep hypereutectic liquidus (Li-LiH (Ref.6), -Li_3N (Ref.6), -Li_2O (Ref.7), Na-Na_2C_2 (Ref.8) -NaH (Ref.9), -NaBr, NaI (Ref.10), -Na_2O (Ref.11), K-K_2O (Ref.12). (iii) two immiscible liquids (Li-LiH (Ref.7), K-K_2O (Ref.13), Li-LiX, Na-NaX, K-KX, Rb-RbX where X = F,Cl,Br and I (Ref.14). For certain metals and halides miscibility increases in the order $F < Cl < Br < I$ as ascertained by the fall in consolute temperature. Of the metals, caesium and rubidium promise greatest miscibility with their salts, a nearly flat liquidus supercedes the immiscibility hump in the halide systems (see Cs-CsX, X = F,Cl or I (Ref.14)). These metals also dissolve the largest amounts of oxygen and the phase diagrams (Ref.3,4,15) exhibit several compounds (Ref.15,16,17,18) at compositions between metal and normal monoxide (Fig.1, lower diagram). Of these, Rb_3O has electrical and magnetic properties more akin to those of a metal than salt (Ref.19). It is with the heavier metals also that complexity increases in the nonmetal-rich region with the formation of polyiodides, e.g. CsI_3, stabilized by the larger cations (Fig.1, lower diagram). Variety of compound formation also increases in chalcogen-lithium systems from sulphur to selenium to tellurium (Li_2Te, $LiTe_3$) (Ref.20,21,22). (iv) the freezing point of the salt is appreciably depressed by dissolved metal to a monotectic (Li-LiH (Ref.7) and metal-halides (Ref.14)).

SOLUBILITIES

The use of liquid alkali metals as coolants (Na and K) in fast nuclear reactors, and as possible coolant and tritium source (Li) in proposed fusion reactors has focussed attention on the dilute solutions of nonmetals. Trace amounts of dissolved nonmetals, notably oxygen in sodium and nitrogen in lithium introduced by atmospheric contamination, greatly enhance corrosion towards transition metal based constructional materials. Thus solution data may exist solely for sodium and only for dilute solutions (ppm nonmetal). An important aspect of phase equilibria in this technology is illustrated by metal purification. Filtration (or cold trapping) of sodium near the melting point (97.8°C) reduces oxygen concentration to ca 1 ppm since the near vertical liquidus is adjacent the sodium axis (Fig.2), but the method becomes less effective for potassium. With rubidium, the liquid can hold up to 20 mol% oxygen at the much lower temperature of 39°C and consequently purification by distillation or gettering is necessary.

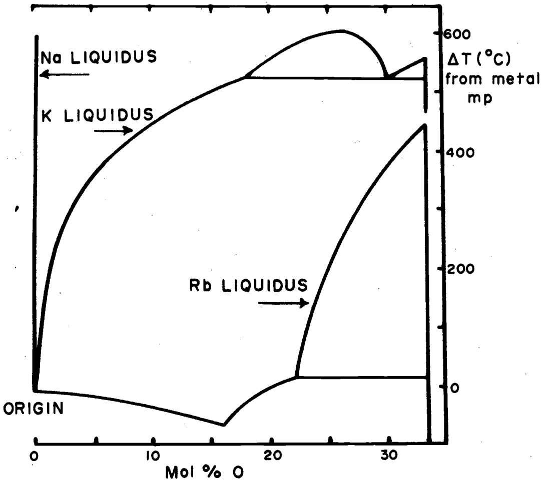

Fig. 2. A comparison of oxygen solubility in liquid alkali metals.

Although measurements in this region are difficult to make, advantages lie in the application of dilute solution theory to solvation, resistivity, thermochemical and thermodynamic functions and for these reasons and the technological importance, the present article is devoted mainly to the metal-rich solutions.

The solubility of nonmetal in the liquid metal is given by the hypereutectic liquidus of the metal-salt phase diagram. In our work we have determined solubilities by exploiting changes in electrical resistivity, which are particularly apt for steep liquidi, in the form of resistivity-composition isotherms and resistivity-temperature curves at constant composition. The overall change in resistivity for salt solutions is illustrated for potassium bromide in potassium (Ref.14) (Fig.3) and our dilute solution work indicates that this behaviour is typical. The low resistivity of the metal increases only slightly but linearly with increasing salt concentration up to several mol% but then increases more steeply towards the high value of the molten salt. Electronic to ionic conduction transitions occur at the very high salt concentrations (Ref.23). Problems associated with the very low resistivities of the alkali metals were overcome by using small (0.75mm^2) cross sectional area capillaries. The greatest breakthrough stemmed from the incorporation of high temperature dc electromagnetic pumps to provide continuous sampling. Their infallibility is attributed to lack of moving parts and the low resistivity of the liquid compared to that of glass or steel pump constructional materials. The basic apparatus (Fig.4) comprises a stainless steel reservoir, A, to hold the liquid, L, (50g) which is

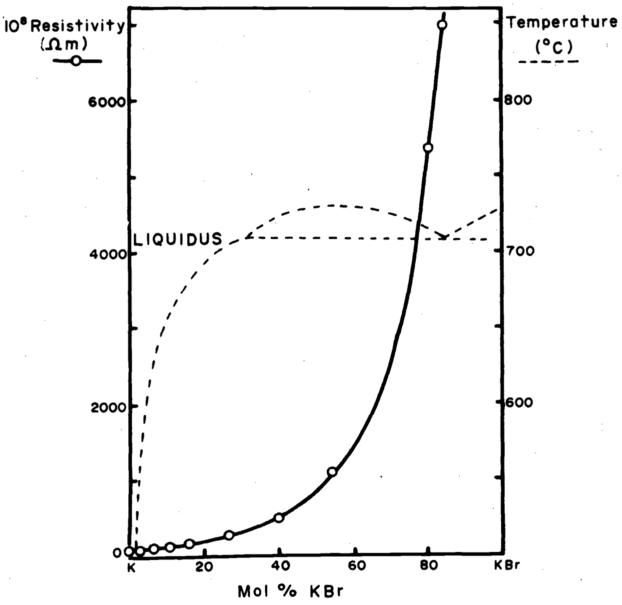

Fig. 3. The resistivity of solutions of potassium bromide in liquid potassium at 740°C.

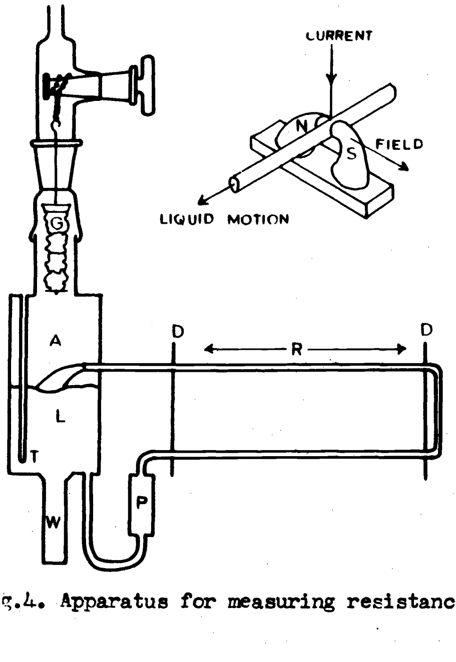

Fig.4. Apparatus for measuring resistance of metallic solutions.

continuously circulated by means of a pump, P, (see inset) round a capillary loop (300 mm long) spanned by two metal discs, D between which the resistance, R, is measured. Resistivity is calculated from the resistances of the capillary when empty, full of pure metal of known resistivity and full of solution(Ref.24). A constant (<± 0.25°C at 400°C) temperature, measured by thermocouple at T, is essential and is achieved by housing the entire assembly in an air oven with electronic temperature control. The liquid metal is rendered initially free of nonmetal by gettering at 400°C to constant resistivity with yttrium sponge, G, which is subsequently isolated in a well, W. Nonmetal, is metered into the reservoir in the form of gas, which reacts at the metal surface to form a salt which dissolves and increases the resistivity. The increase is linear with concentration (shown for Li-Li_3N, Fig. 5, upper diagram) up to saturation where, though gas continues to

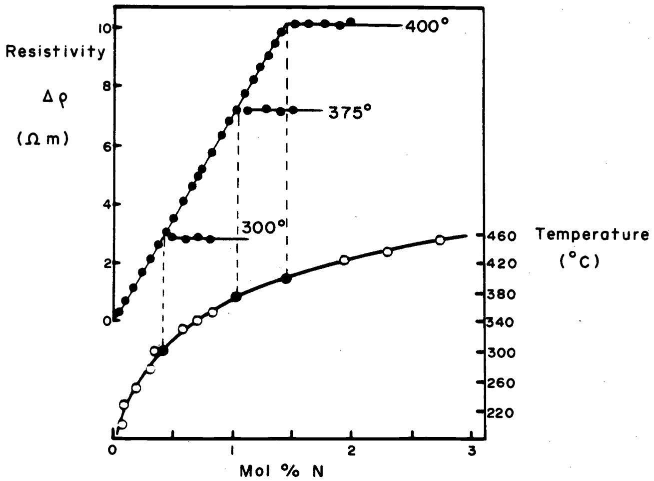

Fig.5. The correlation between resistivity and solubility for solutions of lithium nitride in liquid lithium.

react, no more salt dissolves and resistivity levels. Fortunately, precipitation of salt occurs at the gas-metal interface and not in the capillary to cause fluctuating high resistivities. The change in resistivity pinpoints the hypereutectic liquidus (shown for Li-Li_3N, Fig.5, lower diagram). By redissolving the excess nitride at a higher temperature and subsequent slow cooling, a resistivity-temperature plot shows a well defined break on precipitation to provide a second liquidus point at a higher concentration.

For dilute solutions, solubilities obey the equation (1)

$$\ln X = -\underline{H}(\mathrm{soln})/RT + \underline{S}(\mathrm{soln})/R \qquad (1)$$

where X is mole fraction solute, $\underline{H}$(soln) and $\underline{S}$(soln) are the partial molar enthalpy and entropy, respectively, of solution, and R is the gas constant. Solubilities of nitrogen, hydrogen and deuterium in lithium (Ref.6, 25) determined from resistivities, are given by

$$\log X_N = 1.168 - 2036/T \qquad 473 \leqslant T \leqslant 708\mathrm{K} \qquad (2)$$

$$\log X_H = 1.523 - 2308/T \qquad 523 \leqslant T \leqslant 775\mathrm{K} \qquad (3)$$

$$\log X_D = 2.321 - 2873/T \qquad 549 \leqslant T \leqslant 724\mathrm{K} \qquad (4)$$

SOLVATION

Certain aspects of solvation theory developed for molecular liquids such as water can be applied to solvation of anions in liquid metals and herein lies the usefulness of solubilities and partial molar quantities. The relationship of $\underline{H}$(soln) with other terms in the solution process is shown by the cycle for nitrogen in lithium.

$$\begin{tikzcd}
3\mathrm{Li}(s) \arrow[d, "3\underline{S}"'] & +\tfrac{1}{2}N_2(g) \arrow[r, "\Delta\underline{H}^{\ominus}"] \arrow[d, "\tfrac{1}{2}\underline{D}"'] & Li_3N(s) \arrow[r, "\underline{H}(\mathrm{soln})"] & 3\mathrm{Li}^+(\mathrm{soln}) + N^{3-}(\mathrm{soln}) \\
3\mathrm{Li}(g) \arrow[d, "3\underline{I}"'] & + N(g) \arrow[d, "\underline{E}"'] & & \\
3\mathrm{Li}(g) & + N^{3-}(g) \arrow[uur, "\underline{U}_l"] \arrow[uurr, "\underline{U}_s"'] & &
\end{tikzcd} \qquad (5)$$

where $\Delta\underline{H}^{\ominus}$, $\underline{S}$, $\underline{I}$, $\underline{D}$, $\underline{U}_1$, and $\underline{U}_s$ are the formation, sublimation, ionization, dissociation, lattice and solution enthalpies, respectively, and $\underline{E}$ is the electron affinity. The solution is considered to consist of nitride anions solvated by partially charged cations in a matrix of cations and electrons, irrespective of whether nitrogen is added as element or salt, Li_3N. Using this ionic concept, the solvation enthalpy, $\underline{U}_s$, for the components of lithium nitride is analogous to the lattice enthalpy, and $\underline{H}$(soln), though generally only a small positive difference between two large negative terms ($\underline{U}_1$ and $\underline{U}_s$), is necessary to evaluate $\underline{U}_s$. The individual anion solvation enthalpy, $\underline{U}_x$, is extracted by the approximation

$$\underline{U}_x = \underline{U}_s + \underline{I} + \underline{S} - \underline{\phi} \qquad (6)$$

where ϕ is the work function of the metal (Ref.26). Values of $\underline{U}_x$, given in Table 1,

TABLE 1. Solvation enthalpies, $\underline{U}_x$, (kJmol^{-1}) for nonmetals in liquid alkali metals.

Solute	Solvent	$\underline{U}_x$	Solute	Solvent	$\underline{U}_x$
N^{3-}	lithium	-3473	O^{2-}	sodium	-1721^a
O^{2-}	lithium	-1960	O^{2-}	potassium	-1642^a
H^-	lithium	-427	H^-	sodium	-365
D^-	lithium	-413	H^-	potassium	-362

Note a: values from Ref.26, all others from Ref.9.

become more negative in lithium with increasing anion charge, and, for hydride and oxide, with diminishing solvent atom size. There may be an isotope effect for hydride and deuteride ions in lithium. Such values have been used to substantiate the validity of an ionic solvation model in which charge and coordination for anion in liquid metal are much as in the salts which precipitate (Ref.26). It has been shown that solvation enthalpies for halide ions in potassium are of the same order as in water and, moreover, that cation and anion contribute comparably to the total solvation enthalpy, $\underline{U}_s$, in both sodium and water (Ref.27).

SOLUTE SPECIES

Freezing point depressions

Since the complexity, charge and solvation of the nonmetal solute species cannot be studied directly in metal by the spectroscopic methods available for molecular solvents, resort to indirect methods is necessary. Some resemblance is expected between the nonmetal species in the metallic solution and that in the salt which precipitates. The iodide-iodine phase diagrams (e.g. Fig.1, lower diagram) reflect an increasing tendency to form solid polyiodides from rubidium to caesium, and freezing point depressions of salt and iodine are consistent with solutions which contain the species I_2, M^+ and varying proportions of I_3^- and I^-, with the proportion of I_3^- to I^- increasing from potassium to rubidium to caesium (Ref.1). Metallic solutions in equilibrium with the normal iodides, therefore, probably contain the mononuclear I^- species.

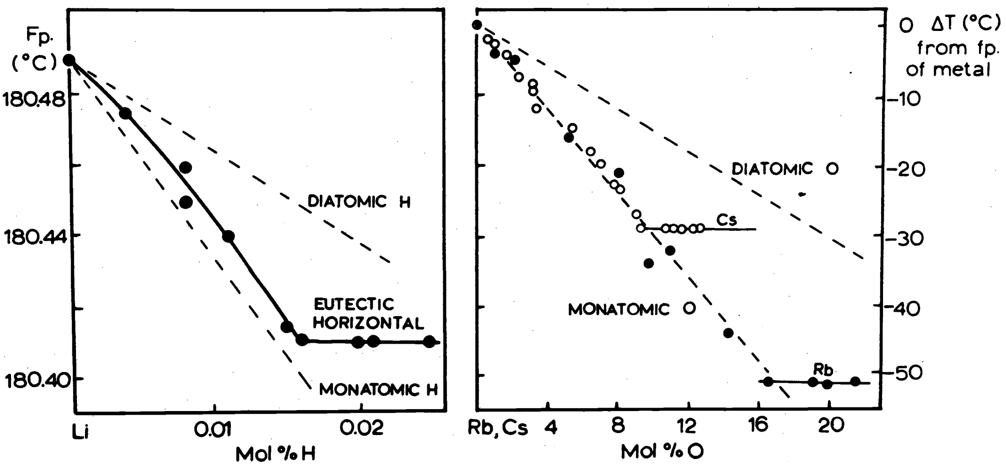

Fig. 6. Depressions of the freezing point of metals caused by hydrogen and by oxygen. Rubidium and caesium values from Ref. 4 and 15, respectively.

Until recently, metal freezing point depressions, which were large, had been observed only for oxygen in rubidium and caesium (Ref.3, 4, 15). By using very slow (15°C h^{-1}) cooling rates and circulating metal, however, depressions for lithium of less than a degree (maxima of 0.25, 0.08 and 0.075 °C for eutectic compositions 0.068, 0.016 and 0.013 mol % N, H and D, respectively) have now been determined by thermal analysis (Ref.5, 21). Figure 6 (left) shows the depression by dissolved hydride compared with calculated values (broken lines) for monatomic and diatomic species using the ideal solution equation

$$T_m - T = RT_mT(X_l - X_s)/\Delta H_f \qquad (7)$$

where T_m - T is the depression in the freezing temperature, T_m, caused by mole fraction, X_l, of solute; ΔH_f is the latent heat of fusion for lithium and R is the gas constant. The results are as expected for a monatomic species particularly since any slight solid solubility, X_s, has been neglected. The depression does not allow distinction between LiH molecules and dissociation into Li^+ and H^- ions, since the Li^+ ions introduced by the salt are deemed indistinguishable from those of the metal. Similarly oxygen is monatomic in rubidium and caesium (Fig. 6 right) and Hall effect measurements favour the expected O^{2-} ion (Ref.28). An interesting facet arises with nitrogen in lithium; the depression appears inadequate even for a monatomic solute. A realistic explanation is that the solution does contain the N^{3-} species but that the hypoeutectic liquidus is displaced by solid solubility, α, to the extent, calculated from the ideal solution equation, shown in Fig. 7. Note also that the hypereutectic liquidus rises near vertically (Fig. 7 and Fig.5 lower, are complementary) from the eutectic composition which is particularly susceptible to supercooling.

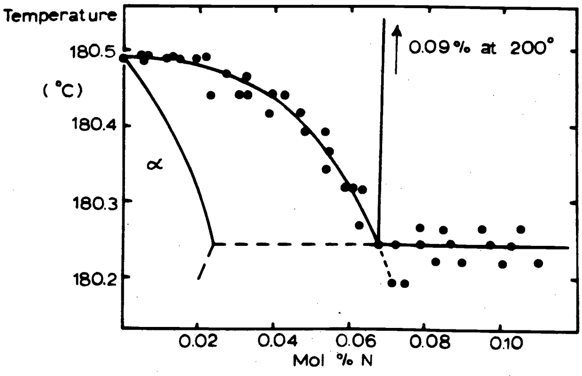

Fig. 7. Freezing point depression and solid solubility, α, in the lithium-nitrogen system.

Electrical resistivity

Dissolution of salt invariably increases the resistivity of liquid alkali metal. The increase is attributed to substitution of a metal electron by a single anion which enhances electron scattering and resistivity generally increases linearly (Fig.5, upper diagram). A comparison of resistivity increases, dρ/dx which are slightly temperature dependent, for a mole percent of nonmetal in metal is shown in Table 2. A correlation

TABLE 2. Increase in resistivity (Ωm x 10^{-8}) for a mole % solute in alkali metals at 400°C (other temperatures in parentheses).

Solute	Solvent			Solute	Solvent
	Li	Na	Cs		K
N^{3-}	7.0	8.8^a(300)	-	I^-	9.1 (700)
H^-	4.9	4.6	-	Br^-	6.9 (740)
D^-	4.9	-	-	Cl^-	5.7^c(700-740)
O^{2-}	2.1^b(300)	2.0^b	3.2(30)	F	3.9 (700)

Note a: in Na-Ba
Note b: extrapolated from lower concentrations.
Note c: interpolated from adjacent solutes.

is developing whereby effective scattering cross section for electrons increases with increasing anionic crystal radius, r, (Å), e.g. $d\rho/dx$ increases for solutes in lithium in the order $O^{2-} < H^{-} < N^{3-}$ for radii 1.45, 1.54 and 1.71, respectively, and for halides in potassium (Ref.14)

$$d\rho/dx = 1.6 \times 10^{18} r^2 + 1.2 \qquad (8)$$

Scattering may be similar, e.g. for H^- in lithium and sodium, and for Cl^- in potassium and bismuth, but not invariably so as shown by O^{2-} in sodium and caesium. For each metal solvent, therefore, resistivity reflects the relative size of the solute, albeit solvated, and though the technique is incapable of directly identifying the solute species in binary solutions, it provides a formidable tool for studying interactions and subsequent precipitation of pairs or more of solutes.

REACTIONS IN METALS

A metal-nonmetal interaction is illustrated by barium and nitrogen in liquid sodium. Nitrogen neither reacts directly nor dissolves as the ion in liquid sodium but addition of barium, strontium or lithium, which do form nitrides, dissociates the molecule and preferential solvation renders the N^{3-} ion soluble. Thus nitrogen dissolves in a solution of 4 mol % barium in sodium up to a ratio of Ba:N of 4:1. Further addition of nitrogen precipitates the conducting nitride Ba_2N which is most readily prepared by this method. Throughout precipitation the mother liquor maintains the 4:1 ratio and the solution is apparently composed of a complex Ba_4N solute, whatever the charge, in a sodium solvent (Ref.29). The reaction, as monitored by resistivity changes, is shown in Fig. 8.

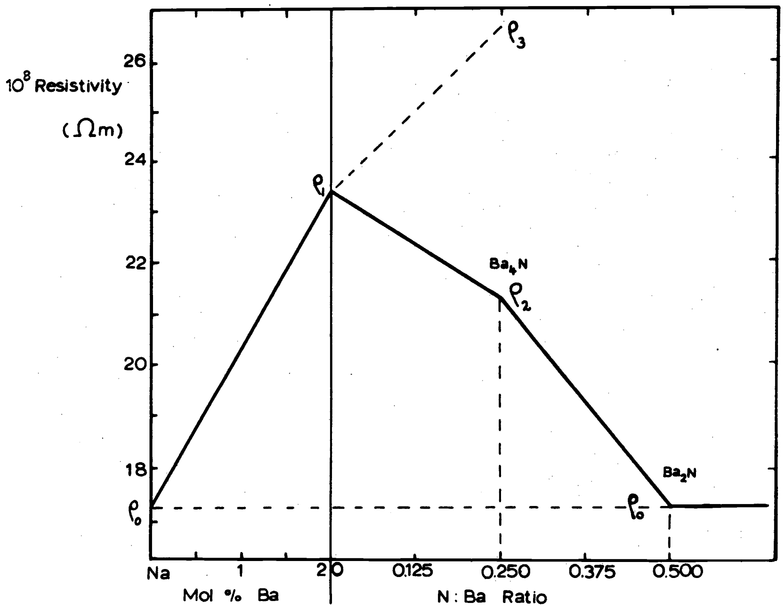

Fig.8. Resistivity changes in the reaction of nitrogen with a solution of barium in liquid sodium at 300°C.

Dissolution of barium in sodium increases the resistivity from ρ_0 to ρ_1. Reaction and solution of nitrogen reduces this to ρ_2 as opposed to an increase to ρ_3 expected for nitride ions in a single solvent, e.g. Li (Table 2). Although the effective number of barium scattering centres decreases, no precipitation occurs and preferential solvation of nitride occurs, therefore, to form the strongly bonded Ba_4N unit. In effect, one complex scattering centre replaces four Ba^{2+} and one N^{3-}. The linear region ρ_1 to ρ_2 signifies that each nitrogen incorporates the same number of barium atoms in its solvation shell throughout. At ρ_2 the solution consists entirely of Ba_4N units in sodium and provides a value of $d\rho/dx$ of 8.8×10^{-8} Ωm (mol % N)$^{-1}$ for this species (Table 2). Further addition of nitrogen beyond ρ_2 precipitates Ba_2N since there is then insufficient barium to solvate the nonmetal as a Ba_4N unit. Precipitation removes both solutes from solution and the resistivity eventually falls to the sodium value, ρ_0 (Ref.30).

A similar interaction occurs between two nonmetals. Resistivities can be interpreted on the basis that C_2^{2-} and N^{3-} ions associate in liquid lithium to produce successively CN^-

and CN_2^{2-} ions with increasing nitride concentration, and cyanamide is consistently found on hydrolysis. There are strong indications that when carbon atoms, as a solid solution in nickel or iron, are exposed to liquid sodium, they dissolve and associate in the liquid as C_2^{2-} ions; a nitrogen over pressure then increases the carbon content and chemical analysis confirms the presence of cyanide (Ref. 8), which dissolves up to 0.035 mol % CN at 565°C (Ref. 31). Perhaps the strongest evidence for an equilibrium between dissolved species is provided by oxygen and hydrogen in sodium (9)

$$H^- + O^{2-} \rightleftharpoons OH^- + 2e \qquad (9)$$

For hydrogen solutions alone equilibrium pressures of hydrogen obey (10)

$$[H] = k_s P_e^{\frac{1}{2}} \qquad (10)$$

where k_s is the Sieverts' coefficient and [H] the dissolved hydrogen concentration, thereby providing a measure of monatomic hydride concentration in solution. Assuming that this proportionality holds for mixtures, oxygen is then dissolved or, more conveniently the two elements are introduced simultaneously as water vapour, to obtain the relationship shown in Fig. 9. For dilute solutions all water hydrogen is converted to hydride and initially the curve follows the top line. This is enhanced at lower temperatures. With increasing concentration, however, progressively less hydride is produced and hydroxide is formed at the expense of hydride and oxide (Ref. 32). Support for an equilibrium is provided by the sodium-sodium hydroxide phase diagram (Ref. 33) in which hydroxide (which contains hydride) and oxide phases coexist with sodium solution. Equilibrium shifts towards hydroxide, however, with the heavier alkali metals; hydroxide is the only phase in equilibrium with potassium rubidium or caesium (Ref. 34, 35 and 36). Moreover, solid state reaction enthalpies (in the absence of energies), which differ from solution enthalpies only by $\underline{H}$(soln), are not inconsistent with increasing hydroxide stability for the heavier metals in contrast to complete dissociation to oxide and hydride with lithium (11)

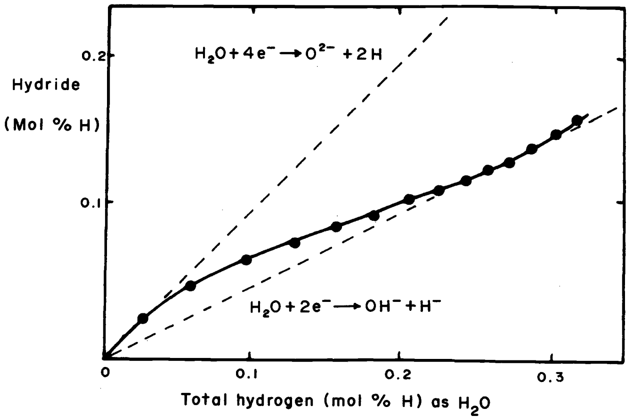

Fig. 9. Variation in hydride concentration during the reaction of liquid sodium with water vapour at 400°C.

$$2M + MOH \overset{\Delta\underline{H}^{\ominus}}{\rightleftharpoons} M_2O + MH \qquad (11)$$

M	$\Delta\underline{H}^{\ominus}$
Li	= −176.8 kJ
Na	− 46.5
K	7.4
Rb	29.3
Cs	30.6

The analogous polyatomic amide ion differs in that two dissociation routes are open depending on the metal solvent

$$NH_2^- \xrightarrow{e} 2H^- + \tfrac{1}{2}N_2 \qquad (12)$$

$$NH_2^- \xrightarrow{4e} 2H^- + N^{3-} \qquad (13)$$

The complex ion is not expected nor found in liquid lithium due mainly to the unique ability of lithium to strongly solvate the N^{3-} ion. It can be argued, again from enthalpies, that negligible driving force exists to dissociate amide as in (12) for any of the alkali metals since the enthalpy gained from forming 2MH equals that lost (Fig. 10). With lithium, however, the large negative enthalpy of formation of the well characterized nitride, Li_3N, is decisive in promoting dissociation (12). Enthalpies (broken line, Fig.10) which are estimated (Ref.37) for the other unknown nitrides are positive (except for sodium) and discourage dissociation of the heavier metal amides. Experimentally resistivities (Fig.11) show that lithium reacts with ammonia vapour to produce only nitride and hydride ions in solution; the line AB has slope 22 x 10^{-8} Ωm (mol % NH_3)$^{-1}$ in agreement with dissociation to one nitride and three hydride ions (Table 2). The increases AC and CD are for the separate dissolution of nitride and hydride, added consecutively, and AE and ED for the addition of the same quantities in the reverse order. Each solute in the mixture increases the resistivity by its characteristic amount irrespective of the order in which added and this additivity precludes association of these species to amide (Ref. 38).

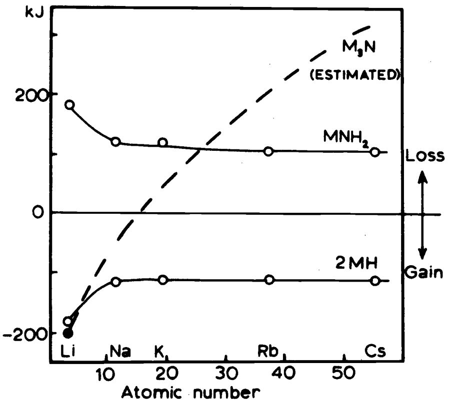

Fig.10. Enthalpies (kJ mol^{-1}) for the reaction $MNH_2 + 4M \rightarrow 2MH + M_3N$

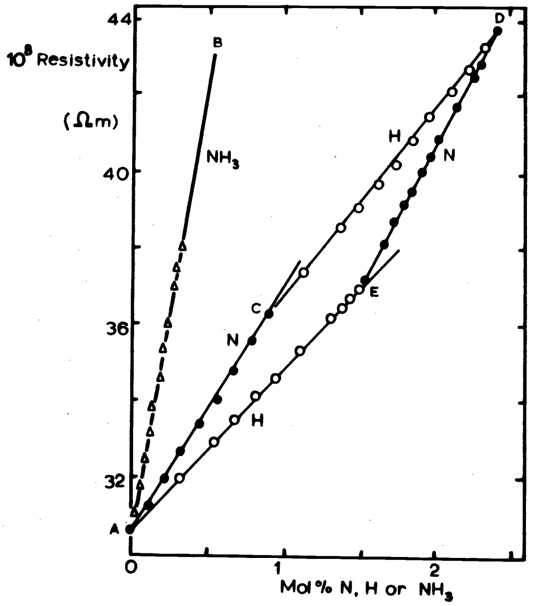

Fig. 11. Resistivity changes for the reaction of ammonia and of mixtures of nitrogen and hydrogen with liquid lithium.

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