

THE DENSITIES OF AMMONIA SOLUTIONS OF LITHIUM AND CALCIUM METAL

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Liquid ammonia solutions of sodium and potassium metal possess densities which are considerably less than the pure solvent at the same temperature. These properties first quantitatively studied by Kraus, Carney and Johnson¹ in the case of sodium and later investigated by Johnson and Meyer² in the case of potassium have enabled these investigators to calculate the expansion per mol of metal when the metal is dissolved in liquid ammonia at -33°C . In each case this volume expansion, ΔV ($\Delta V = \text{vol. of solution containing 1 g. atom of metal} - \text{vol. of solvent in pure state} - \text{vol. of 1 g. atom of metal in pure state}$) was found to exhibit a maximum of 43 c.c. and 30 c.c. for sodium and potassium respectively, at about 11 mols NH_3/metal when considered as a function of concentration.

On the basis of the Kraus³ ionic theory i.e. the alkali metals undergo ionization in liquid ammonia to form solvated positive ions and solvated electrons; it would be expected that alkali metal ammonia solutions would have in common similar effects arising from an ammoniated electron. That this is probably true for the expansions of the sodium and potassium solutions is easily demonstrated by taking into account the differences in atomic and ionic sizes of these two metals. Such a consideration leads to approximately the same ΔV values for sodium and potassium solutions.

As a further test of the applicability of the ionic theory to alkali metal solutions density measurements were made by the author on solutions of lithium metal and a saturated solution of calcium metal. The apparatus and procedure employed here, with a few modifications described below, similar to that described by Kraus.¹ A chaino-

matic Westphal balance and a pyrex bob of 2 c.c. were employed. The amount of ammonia used in each determination was measured from a small metal steel tank of about 50 g. capacity. Stirring of the solutions was attained by the use of a magnetic stirring device.

For the lithium solutions at -35°C . the following values of the density were obtained: 3.76 mols NH_3/Li (sat.) 0.4920; 4.285, 0.5065; 4.516, 0.5103; 6.432, 0.5435.

For the calcium solutions at -35°C . and at a concentration of 7 mols NH_3/Ca (sat.) the density was found to be 0.651.

By use of these data the ΔV function for lithium was found to vary, linearly, over the concentration range studied from 37.5 c.c. in the saturated solution to 41.4 c.c. in the more dilute region.

To compare the sodium and potassium solutions with the lithium solution, ΔV values at a common concentration of 6 mols NH_3/metal were selected and corrected to compare with lithium by taking into account the differences in atomic and ionic sizes of sodium and potassium. From the uncorrected values (Na, $\Delta V = 41.7$ c.c.; K, $\Delta V = 28.0$ c.c., Li $\Delta V = 40.8$ c.c.) the following corrected values were obtained: Na, $\Delta V = 47.4$; K, $\Delta V = 45$; Li $\Delta V = (40.8$ c.c.). In view of the fact that ΔV is quite sensitive to experimental errors it seems likely that the three alkali metal solutions studied so far possess a common factor, probably the solvated electron, leading to similar anomalous expansions.

The experimental density datum for the saturated calcium solution yields a ΔV of 44 c.c. which may be compared with the sodium solution value 42.5 c.c. since the atomic and ionic radii of these two elements are quite similar. In the saturated calcium solution it seems likely, then, that but one electron per atom is ionized. This appears reasonable in view of the high ionization potential of the second electron.

¹C. A. Kraus, E. S. Carney and W. C. Johnson, Jour. Am. Chem. Soc. 49, 2206 (1927).

²Johnson and Meyer, Jour. Am. Chem. Soc. 54, 3621 (1932).

³C. A. Kraus, Jour. Am. Chem. Soc. 30, 1323 (1908).