

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

THE DENSITY OF SOLUTIONS OF SODIUM, POTASSIUM AND SODIUM BROMIDE IN LIQUID AMMONIA

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Kraus and Lucasse¹ observed, in their studies of concentrated solutions of sodium and of potassium in liquid ammonia, a rather abrupt change in the conductivity in passing from saturated solutions to those more dilute in the alkali metal. They were able to determine with considerable accuracy the composition of the saturated solution at the point of discontinuity. Since the volume of the cell employed could be measured approximately, they estimated the density of a saturated solution of sodium in liquid ammonia to be 0.54 and that of a saturated solution of potassium as 0.632.

Of particular interest in these observations is the fact that in both cases the density of the saturated solution is markedly lower than the densities of the constituents comprising the solution. In other words the process of solution of the alkali metal in liquid ammonia is accompanied by a substantial increase in volume. Later, the density of solutions of sodium in ammonia was measured directly with a Westphal balance over a considerable range of concentration, from 32.6 gram molecules of ammonia per gram atom of sodium to the saturation point.² The density of the saturated solution was found to be in good agreement with the estimated value of Kraus and Lucasse,^{1b} and to increase with dilution to approach that of pure liquid ammonia.

The unusually large volume increase was interpreted as being due to the electron freed from the constraints of the metal, since studies of other physical properties of these solutions were sufficiently conclusive to show the sodium present as normal sodium ions.³

In view of the interesting properties of these solutions, it was deemed advisable to measure the density of solutions of potassium in liquid ammonia at different concentrations. In addition, the density of saturated and also highly diluted solutions of sodium is determined as a verification of the method employed. In order to demonstrate the unique behavior of the metal solutions in contrast to that of solutions of salts in liquid ammonia, similar measurements are made with sodium bromide solutions.

Apparatus and Procedure

The apparatus employed throughout the investigation was identical with that formerly used for the sodium solutions.² Several other types of apparatus were de-

¹ Kraus and Lucasse, (a) THIS JOURNAL, **43**, 2538 (1921); (b) *ibid.*, **44**, 1941 (1922).

² Kraus, Carney and Johnson, *ibid.*, **49**, 2206 (1927).

³ See Kraus, *ibid.*, **43**, 749 (1921), and previous articles.

signed and tested in the preliminary experiments, but they were discarded as inferior to the above in simplicity and in ease of manipulation.

Metallic potassium was introduced into the bottom of the density tube by the method described by Kraus and Lucasse.^{1a} At the end of a series of measurements the ammonia was allowed to evaporate and the last trace was removed by the vacuum pumps. The metal was dissolved in an alcohol-ether mixture, the solution was partially evaporated to remove the organic solvents, and then titrated with approximately 1 *N* hydrochloric acid. A small excess of the acid was added to the solution, the solvent was evaporated in a platinum dish and finally the metal was determined as chloride in order to check the titration results. A similar procedure was used for the determination of sodium. In the case of sodium bromide, a weighed amount of the salt was placed in the density tube before the addition of ammonia.

The alkali metals used in the experiments were found to be free from iron; the potassium contained a small amount of sodium. The sodium bromide was crystallized twice from water solution and was thoroughly dried at 110°.

Former measurements⁴ of the vapor pressure of solutions of potassium in liquid ammonia furnished data for the composition of the saturated solution as well as for corrections for the amount of ammonia in the vapor phase to be applied in the calculation of the concentration of the solution whose density was to be measured. In the case of the sodium and sodium bromide solutions, the concentration was sufficiently low in each instance to allow for a vapor phase correction on the basis of the vapor pressure of pure ammonia at the temperature in question.⁵

The temperature of the solutions was measured with a calibrated alcohol thermometer to read to $\pm 0.05^\circ$ between 0 and -50° . Due to changes in the barometric pressure during a period of several hours required for a determination, it was not found possible to control the temperature of the liquid ammonia bath with a variation of less than $\pm 0.2^\circ$.

Results

The density values for saturated and dilute solutions of sodium in liquid ammonia are given in Table I. The concentration of the solution is expressed in terms of the number of gram molecules of ammonia per gram atom of sodium. The volume change per gram atom of sodium, ΔV , is calculated from the equation

$$\Delta V = \frac{N \times 17.032 + 22.997}{D_s} - \left(\frac{N \times 17.032}{D_{NH_3}} + \frac{22.997}{D_{Na}} \right)$$

where *N* represents the concentration as expressed above, *D_s* the density of the solution, *D_{Na}* the density of metallic sodium at -33.8° , and *D_{NH₃}* the density of pure ammonia at the same temperature. At this temperature the density of liquid ammonia is 0.6821,⁶ while that of sodium is 0.9805 according to the data of Dewar⁷ at low temperatures and of Richards and Brink⁸ at ordinary temperatures.

⁴ Johnson and Meyer, *J. Phys. Chem.*, **33**, 1922 (1929).

⁵ For the vapor pressure of liquid ammonia at different temperatures, see Cragoe, Meyers and Taylor, *Bureau of Standards, Scientific Papers*, No. 369, p. 33, 1920.

⁶ Cragoe and Harper, *Bur. Standards, Sci. Papers*, **420**, 313 (1921).

⁷ Dewar, *Chem. News*, **85**, 277 (1902).

⁸ Richards and Brink, *THIS JOURNAL*, **29**, 117 (1907).

TABLE I
DENSITY OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA
 $t = -33.8^\circ$. 0.5307 g. of sodium

NH ₃ , g.	NH ₃ /Na	Density	ΔV , cc.
Saturated soln.	5.48	0.5781	41.01
14.873	37.84	.6603	43.03
18.882	48.04	.6653	41.95
21.684	55.17	.6681	40.45
25.210	64.14	.6704	39.51

A large excess of sodium was employed in the determination of the density of the saturated solution, the result of which is shown in the above table. For the composition of this solution, the value of 5.48 gram molecules of ammonia per gram atom of sodium was taken from former data on the vapor pressure of sodium solutions.²

The density of solutions of potassium in liquid ammonia was measured from the saturation point to a concentration as low as 34.08 gram molecules of ammonia per gram atom of potassium. The volume change is calculated as described above. At the temperature of the measurements, -33.2° , the density of liquid ammonia is 0.6816,⁶ while that of metallic potassium is taken as 0.86.⁹ The data for the potassium solutions are given in Table II.

TABLE II
DENSITY OF SOLUTIONS OF POTASSIUM IN LIQUID AMMONIA AT -33.2°

NH ₃ , g.	NH ₃ /K	Density	ΔV , cc.
Series I: 1.5718 g. of potassium			
Satd. soln.	4.95	0.6282	27.28
11.105	16.22	.6583	28.30
15.870	23.18	.6659	26.91
18.322	26.76	.6685	26.15
20.978	30.64	.6701	26.08
23.333	34.08	.6721	24.73
Series II: 2.6025 g. of potassium			
Satd. soln.	4.95	0.6282	27.28
7.9695	7.03	.6351	29.00
10.940	9.65	.6433	29.67
12.697	11.20	.6483	29.20
14.963	13.20	.6522	29.36
20.122	17.75	.6598	28.44

In order to point out the abnormal behavior of metals dissolved in liquid ammonia, a series of density measurements was made with sodium bromide solutions. A rather abrupt change was found to take place in the density in

⁹ This value is selected from the data of Richards and Brink,⁸ at 20° , since measurements are not available at low temperatures. The density of metallic potassium is probably 1-2% greater at -33.5° than at 20° ; however, the value taken at the latter temperature has only a small effect on the volume change as calculated from the above equation.

passing from the saturated solutions to those containing a smaller amount of dissolved salt. An extrapolation of the density curves, representative of the saturated and dilute solutions, respectively, gave a value of 45.00 gram molecules of ammonia per gram molecule of sodium bromide for the composition of the saturated solution. In other words, at -33.2° , 13.43 g. of sodium bromide is dissolved by 100 g. of liquid ammonia. Such an extrapolation is subject to error; however, in this case, the error must not be greater than 3-4%. The results of these density measurements are shown in Table III. The volume change accompanying the process of solution is not given in the table but may be readily calculated in a manner previously described.

TABLE III
DENSITY OF SOLUTIONS OF SODIUM BROMIDE IN LIQUID AMMONIA AT -33.2°

Series I: 1.0445 g. of sodium bromide		
NH ₃ , g.	NH ₃ /NaBr	Density
Satd. soln.	45.00	0.7417
11.410	66.00	.7273
14.921	86.33	.7204
17.670	102.21	.7153
Series II: 0.5143 g. of sodium bromide		
12.085	141.98	0.7073
19.646	230.85	.6983
26.920	316.29	.6941
29.803	350.15	.6933

Discussion

The density of solutions of sodium in liquid ammonia is shown in Fig. 1, curve I, with the mole fraction of the metal plotted as abscissa and the density as ordinate. The circles represent former data² while the disks are taken from the values given in Table I above. The value for a saturated solution is practically identical with the earlier work of Kraus, Carney and Johnson, in that the latter report a value of 0.5782 while that of our work is found to be 0.5781 at the same temperature. The values found at low concentrations lie well upon the line extrapolated from the earlier data to zero concentration, in other words, to the value of the density of pure liquid ammonia at -33.8° . Although our values at low concentrations are not as consistent among themselves as those at the higher concentrations, they are sufficient to demonstrate the applicability of the method. These less consistent results may be attributed in part to the greater tendency of the alkali metals to react with ammonia in dilute solutions.

In Fig. 2, curve I, the density of potassium solutions is plotted against the concentration of the dissolved metal in a manner frequently employed for this type of work. It is observed that the density increases continuously with decreasing concentration of metal to approach the density

of pure ammonia. The form of the curve is the same as that found for sodium solutions. The density of a saturated solution of potassium in

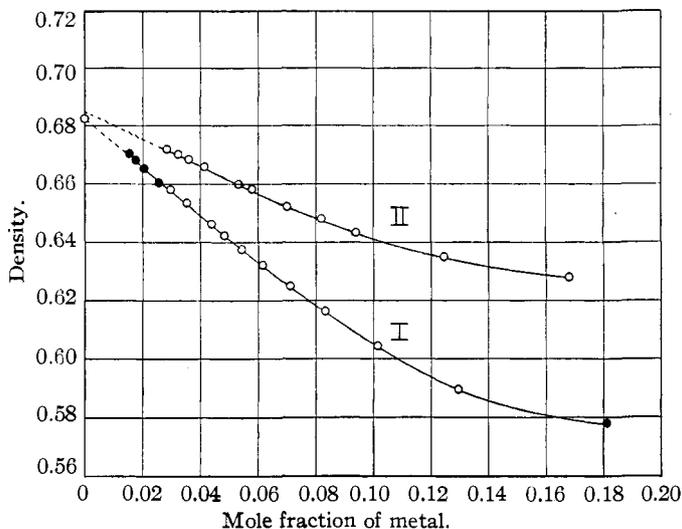


Fig. 1.—Density of solution of sodium and of potassium.

ammonia is found to be 0.6282, which is in good agreement with the estimated value (0.632) of Kraus and Lucasse.¹

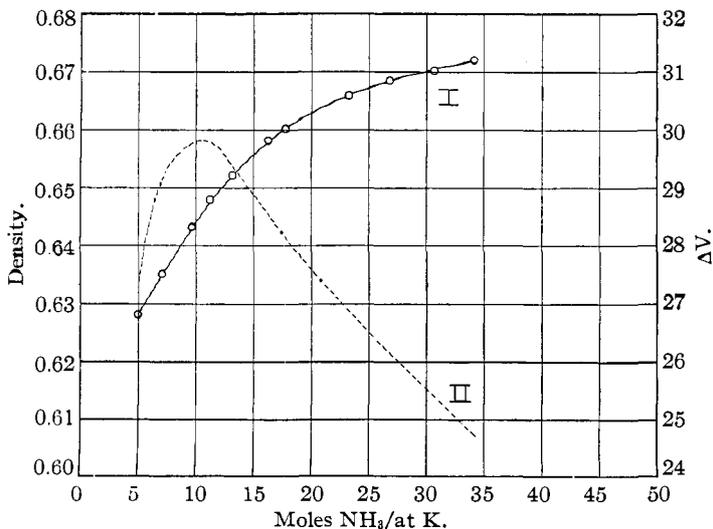


Fig. 2.—Density and volume change for potassium solution at -33.2° .

Figure 1, curve II, shows the mole fraction of potassium plotted against the density. In this case, it is readily seen that the density of potassium

solutions is somewhat greater than that of sodium solutions at equivalent mole fractions. The two curves approach each other at low concentrations and should practically coincide at zero concentration. The fact that the potassium curve lies above the sodium curve at zero concentration of dissolved metal, though the temperature of the former is 0.6° higher than that of the latter, can be accounted for by the difficulties encountered in temperature control and by the greater reactivity of metallic potassium in dilute ammonia solutions. The potassium curve extrapolates to a value of 0.6844 at zero concentration while the density of pure ammonia at -33.2° is 0.6816. In other words, the values given at the lower concentrations are about 0.4% too high for the temperature in question. However, the major part of this error may be attributed to fluctuations in the temperature.

The volume change accompanying the process of solution of potassium in ammonia is found to be considerable in magnitude. The variation of this change with concentration of the solution is shown in Fig. 2, curve II. Since the volume change, ΔV , is very sensitive to small variations in the density, the above-mentioned plot was made by taking values from the smooth density curve (I). The form of the volume change curve closely resembles the analogous curve for sodium solutions. It passes through a maximum at a concentration of about 10.5 gram molecules of ammonia per gram atom of potassium while the corresponding value for the sodium solutions is 11.25. Evidently, some similar change is taking place in these concentrated solutions of sodium and of potassium which we are unable to explain with the data at our disposal. The volume change accompanying the formation of a saturated solution of potassium in ammonia is 27.28 cc. per gram atom of metal, while the maximum volume change is 29.80 cc. The corresponding volume changes for sodium solutions are 40.96 cc. and 43.37 cc., respectively. It may be possible to account for the differences in the values for sodium and potassium solutions by the relative atomic and ionic radii of the metals alone. In other words, it would appear that the function of the negative constituent, presumably the ammoniated electron, is the same in both solutions.

An examination of curve I, Fig. 3, which shows the density of solutions of sodium bromide in liquid ammonia as a function of the concentration, points out the normal behavior of salt solutions. In this case, the density of the saturated solution is 0.7417, which value is found to decrease with decreasing salt concentration to approach the density of pure ammonia. Since the density of this solution is markedly higher than the density of pure liquid ammonia, it is to be concluded that the effect of the sodium ion is to decrease the volume of the solution. Thus, the actual volume increase, due to the negative constituent present as a result of solution of metallic sodium in ammonia, must be very large to overcome the effect of the normal sodium ion. It would be interesting to compare the partial

molal volume of sodium bromide with the partial molal volume of sodium in relatively dilute ammonia solutions in order to obtain a better conception of the relative effects of the negative constituents in relation to the volume change. Such a comparison would require more data than we have at our disposal at the present time.

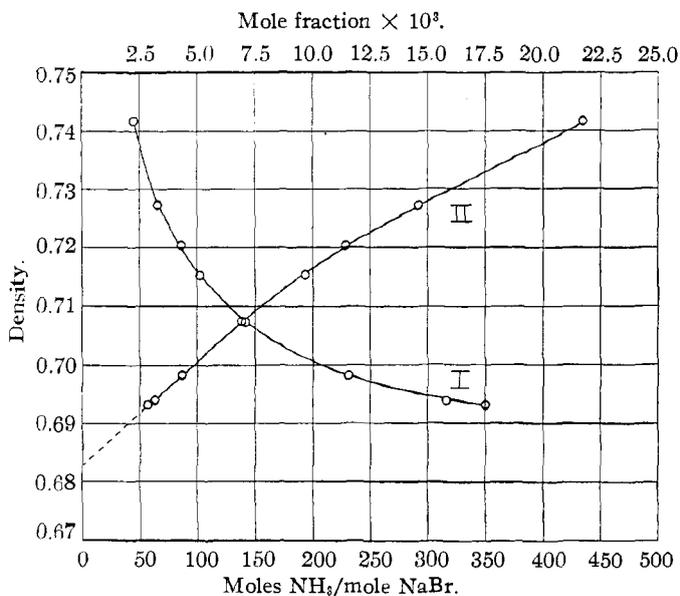


Fig. 3.—Density of solution of sodium bromide in ammonia at -33.2° .

Curve II, Fig. 3, shows the mole fraction of sodium bromide plotted against the density. In the more dilute solutions the curve follows a straight line which, upon extrapolation to zero concentration, intersects the density axis at a value of 0.6828. This value is slightly greater than the density of pure ammonia at -33.2° , namely, 0.6816, but is well within the limits of error due to fluctuations in the temperature.

Summary

The density of saturated and dilute solutions of sodium in liquid ammonia at -33.8° has been determined to check the method and former data.

Similar measurements have been made for solutions of potassium in liquid ammonia, the results of which resemble closely those found for sodium solutions. The density of a saturated solution of potassium in ammonia is 0.6282 at -33.2° ; with decreasing concentration of metal, the density increases to approach that of pure ammonia.

The increase in volume accompanying the solution of potassium in liquid ammonia has been calculated from the density values. The volume

increase for a saturated solution is 27.28 cc. per gram atom of potassium. It is found to increase at lower concentrations to a maximum value of 29.80 cc. and then to decrease in solutions containing a smaller amount of dissolved metal.

In order to point out the abnormal behavior of solutions of metals in liquid ammonia, the density of solutions of sodium bromide has been measured at -33.2° over a considerable concentration range. The density of these solutions is found to decrease with decreasing concentration of sodium bromide in a normal manner.

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[CONTRIBUTION FROM THE FERTILIZER AND FIXED NITROGEN INVESTIGATIONS
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THE THERMAL DECOMPOSITION OF AZINES

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A NOTE ON THE THERMAL DECOMPOSITION OF BENZALDAZINE UNDER 1000 ATMOSPHERES PRESSURE OF NITROGEN, HYDROGEN AND AMMONIA

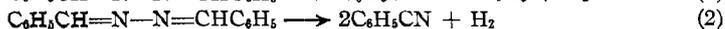
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THE THERMAL DECOMPOSITION OF AZINES

Curtius and Jay¹ observed that aldazines, notably benzaldazine, decompose upon distillation into stilbenes and nitrogen. Later Meisenheimer² pointed out that benzonitrile was also one of the thermal decomposition products of benzaldazine and postulated two simultaneous reactions.



The most comprehensive study was that of Pascal and Normand,³ who demonstrated in the case of benzaldazine that in addition to stilbene and nitrogen, some ammonia, a small amount of phenanthrene and a stable compound containing nuclear nitrogen were also produced. Azines in which the ortho position of the benzene ring was substituted yielded none of the phenanthrene derivatives. They suggested that the stable nuclear nitrogen compound (yield 15%) had the empirical formula of $\text{C}_{28}\text{H}_{29}\text{N}_3$ (melting point 261° and boiling point 460°) and probably was identical with the unknown product obtained by Curtius and Blumer⁴ in the pyrolysis of benzoinhydrazone. The purposes of the present investigation were to

¹ Curtius and Jay, *J. prakt. Chem.*, [2] 39, 45 (1889).

² Meisenheimer and Heim, *Ann.*, 355, 274 (1907).

³ Pascal and Normand, *Bull. soc. chim.*, [4] 9, 1029 (1911); [4] 9, 1059 (1911); [4] 11, 21 (1912).

⁴ Curtius and Blumer, *J. prakt. Chem.*, [2] 52, 126 (1895).