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Densities of Solutions of Potassium in Liquid Ammonia and Deutero-Ammonia*

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The densities of solutions of K in liquid NH_3 have been measured at $-33.7°$, $0.0°$, and $20.0°C$ over a concentration range from 0 to 1.2 mole liter^{-1}. The correlation of these results with paramagnetic resonance measurements is discussed in terms of a cavity trapping model.

IN contrast to the behavior of solutions of inorganic salts in liquid NH_3[1] the densities of solutions of Na in NH_3[2,3] decrease with increasing concentration of solute. With increasing temperature there is a decrease in the ratio of (a) rate of decrease of density with concentration to (b) density of the pure solvent.

In connection with investigations of the paramagnetism of solution of K in liquid NH_3 and ND_3 we have determined the densities of such solutions at $-33.7°$, $0.0°$, and $20.0°C$ over a concentration range from 0 to about 1.20 mole liter.$^{-1}$ In view of the importance of such information in discussions of the anomalous behavior of these solutions on the basis of various models,[4-12] and because of the lack of data in the literature on solutions of K in NH_3 and of any alkali metal in ND_3, we present the results of our density measurements in this paper.

EXPERIMENTAL

NH_3 used for the measurements was prepared by transferring Armour and Company NH_3 to a steel tank containing Na metal. The H_2 evolved was released from time to time until the reaction was complete. The NH_3 was stored in this tank and just before the density measurements was distilled from the tank to a glass vacuum line and redistilled from Na there before transferring to the pycnometer.

ND_3 was prepared by the reaction of Mg_3N_2 with D_2O. Samples of NH_3 and ND_3 gas were weighed in a Dumas bulb. The ratio of the density of the ND_3 sample to that of NH_3 at the same temperature and pressure was found to be 1.184 whereas the ratio for the pure ideal gases is 1.177.

The pycnometer is shown in Fig. 1. The pycnometer bulb volume (approximately 14 cm³) to various points above and below the fiducial mark C was measured by weighing the pycnometer filled to various heights with pure water at 0.1° and 5.0°C. The stand-
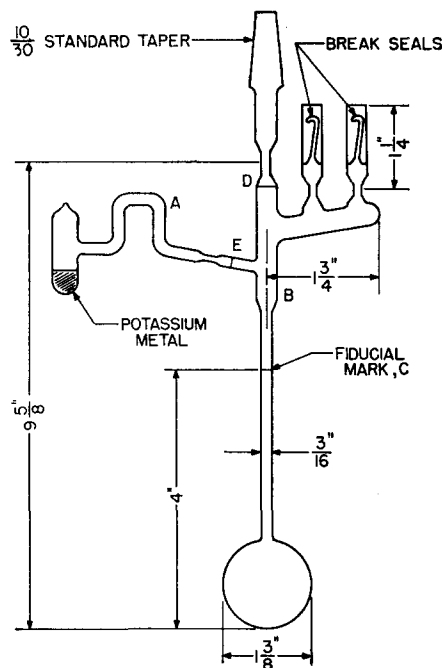

FIG. 1. Pycnometer.

ard taper joint was used for the first evacuation and for filling with NH_3 or ND_3 liquid. Before adding the liquid the K metal was distilled over to point B through arm A. Arm A was then sealed off at the constriction near E. The condensing liquid was used to wash the K down into the bulb. The temperature was then adjusted by placing the pycnometer in a water bath whose temperature was controlled to ±0.05°C at 20.0°C as measured by a Bureau of Standards calibrated thermometer. The height of the meniscus relative to the fiducial mark C was measured with a cathetometer. The pycnometer was weighed. More NH_3 or ND_3 was added

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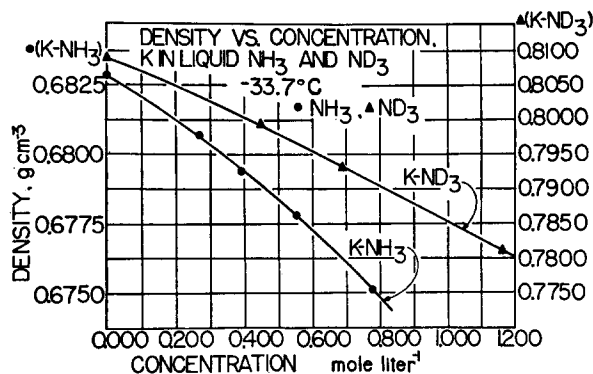[7] W. N. Lipscomb, J. Chem. Phys. 21, 52 (1953).
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FIG. 2. Density vs concentration at −33.7°C.
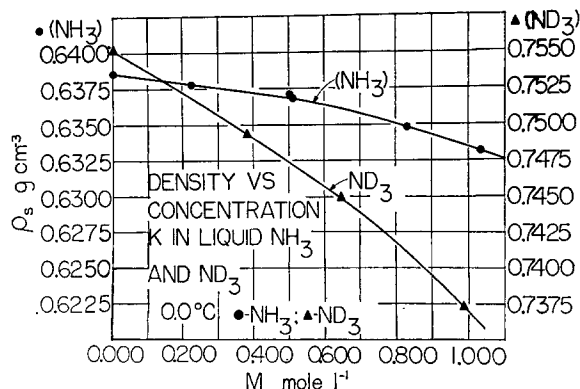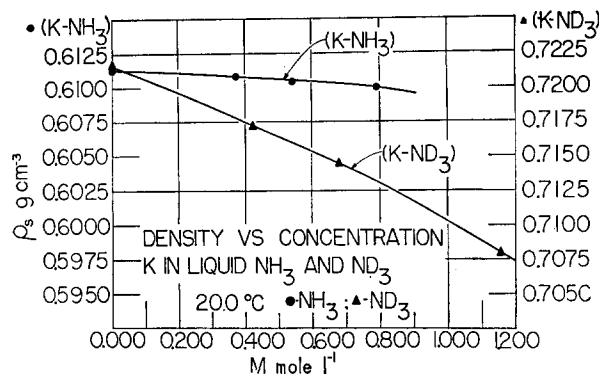
through a break seal after adding a weighed taper joint, the meniscus height measured at 0.0°C and the pycnometer and break seal assembly weighed. Still more NH₃ or ND₃ was added and the final measurement of meniscus height was made with the pycnometer immersed in boiling NH₃. The temperature of the NH₃ bath was measured with a copper-constantan thermocouple which had been calibrated at the CO_2 sublimation point, the freezing point of Hg and the boiling point of pure NH₃.

At the end of such a series of measurements the NH₃ or ND₃ was removed and the amount of K determined by conversion to hydroxide with moist air, dissolving in H_2O and titrating with HCl.

Appropriate buoyancy corrections, corrections for weight of vapor in the pycnometer and corrections for the thermal coefficient of expansion of glass were made.

Thirty measurements of the density were made and the results are given in Figs. 2–4. In Table I are given the densities read from the graphs at selected concentrations.

The expected error in the density estimated from assumed reasonable errors in the various individual measurements involved in the procedure leading to a single determination is approximately one part in 7000. Three measurements of the density of pure NH₃ at 0.0°C gave 0.6386 g cm^{-3} with an average deviation of 0.0003 from the mean. Two measurements of the

density of pure ND₃ at 0.0°C gave 0.7552 g cm^{-3} with an average deviation of 0.0001 from the mean. The error in the determination of the concentration was approximately 0.1%.

The best evidence concerning the extent of the reaction of K with NH₃ in the solutions prepared in the manner described here, came from the measurement of the intensities of paramagnetic resonance absorption.[13] Accurate measurements of absorption intensities of a large number of similarly prepared samples used in the

FIG. 4. Density vs concentration at 20.0°C.

TABLE I. Density vs. concentration.

M, mole liter⁻¹	ρ, g cm⁻³	M, mole liter⁻¹	ρ, g cm⁻³
K—NH₃, 20.0°C		K—ND₃, 20.0°C	
0.000	0.6113	0.000	0.7216
0.150	0.6112	0.150	0.7202
0.300	0.6109	0.300	0.7186
0.600	0.6104	0.600	0.7153
0.900	0.6091	0.900	0.7118
		1.200	0.7074
NH₃, 0.0°C		ND₃, 0.0°C	
M		M	
0.000	0.6386	0.000	0.7552
0.150	0.6381	0.150	0.7530
0.300	0.6375	0.300	0.7506
0.600	0.6363	0.600	0.7457
0.900	0.6343	0.900	0.7395
1.200	0.6316		
NH₃, −33.7°C		ND₃, −33.7°C	
M		M	
0.000	0.6828	0.000	0.8090
0.150	0.6816	0.150	0.8061
0.300	0.6803	0.300	0.8028
0.600	0.6772	0.600	0.7955
0.900	0.6733	0.900	0.7867
		1.200	0.7760

FIG. 3. Density vs concentration at 0.0°C.

[13] C. A. Hutchison, Jr., and D. E. O'Reilly (unpublished results).

resonance experiments showed no decrease in suscepti-bility for periods of time several times as large as those employed for the density determinations. In addition no noncondensable gas could be found when the pycnom-eter was opened at the end of a series of measurements. Consequently the chemical analyses for K could be relied on to give the concentration of unreacted metal.

The only data available heretofore in the literature are the value[14] 0.6816 g cm^{-3} for the density of pure NH$_3$ at $-33.2°$C and the value[3] 0.6721 g cm^{-3} for 1.158 molar K in NH$_3$ at $-33.2°$C.

DISCUSSION

Many types of evidence[4-12,15-17] indicate that in solutions of metallic K in liquid NH$_3$ the metal is dis-sociated into (a) K$^+$ ions which exist in a form similar to that found in solutions of K salts in NH$_3$ and (b) electrons trapped or solvated in some manner by the NH$_3$.

Paramagnetic resonance data[16] enable one to measure the number of unpaired electrons contributing to the spin susceptibility. We will refer to these as singly trapped electrons. The resonance data also permit the calculation of the number of trapped electrons with paired spins assuming that all K exists as K$^+$ and that all the electrons are trapped in some manner by the solvent. We will refer to these paired electrons as doubly trapped electrons. In the present paper the numbers of unpaired electron spins were computed from measurements[13] of the paramagnetic resonance absorp-tion intensities based on absolute measurements of the detection circuit parameters.

The very marked decrease in density with increasing concentration of solutions of K in liquid NH$_3$ and ND$_3$ may be interpreted as the sum of four effects:

(a) the volume increase due to the volume of the K$^+$ ions;

(b) the volume decrease due to the electrostrictive effects of the K$^+$ ions;

(c) the volume decrease due to the electrostrictive effects of the singly and doubly trapped electrons;

(d) the volume increases due to the singly and doubly trapped electrons.

We assume that the volume of K$^+$ is that obtained by using the crystal radius.[18] This volume is 9.9A^3. The volume decrease due to electrostriction by K$^+$ is obtained from the available experimental data[1] on

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TABLE II. Calculated densities.

M(K) (1) mole liter^{-1}	α (2)	ρ_{wt} (3) g cm^{-3}	ρ_{exptl} (4) g cm^{-3}	$\rho_{wt}-\rho_{exptl}$ (5) g mc^{-3}	$\rho_{wt}-\rho$ (6) g cm^{-3}
NH$_3$, $-33.7°$C					
0.000	1.000	0.6828	0.6828	0.0000	0.0000
0.060	0.141	0.6851	0.6823	0.0028	0.0028
0.100	0.100	0.6867	0.6820	0.0047	0.0047
0.200	0.076	0.6906	0.6812	0.0094	0.0095
0.300	0.068	0.6945	0.6803	0.0142	0.0143
0.400	0.052	0.6984	0.6794	0.0190	0.0191
0.500	0.048	0.7023	0.6783	0.0240	0.0240
ND$_3$, $-33.7°$C					
0.000	1.000	0.8090	0.8090	0.0000	0.0000
0.060	0.140	0.8113	0.8078	0.0035	0.0035
0.100	0.111	0.8129	0.8070	0.0059	0.0059
0.200	0.079	0.8168	0.8050	0.0118	0.0119
0.300	0.066	0.8207	0.8028	0.0179	0.0180
0.400	0.060	0.8246	0.8005	0.0241	0.0240
0.500	0.057	0.8285	0.7981	0.0304	0.0301
NH$_3$, 0.0°C					
0.000	1.000	0.6386	0.6386	0.0000	0.0000
0.060	0.364	0.6412	0.6384	0.0028	0.0028
0.100	0.258	0.6429	0.6382	0.0047	0.0047
0.200	0.160	0.6473	0.6378	0.0094	0.0094
0.300	0.125	0.6516	0.6375	0.0141	0.0141
0.400	0.109	0.6560	0.6372	0.0188	0.0188
0.500	0.084	0.6603	0.6368	0.0235	0.0236
ND$_3$, 0.0°C					
0.000	1.000	0.7552	0.7552	0.0000	0.0000
0.060	0.364	0.7579	0.7543	0.0035	0.0035
0.100	0.262	0.7596	0.7538	0.0058	0.0059
0.200	0.189	0.7641	0.7522	0.0118	0.0118
0.300	0.147	0.7685	0.7506	0.0179	0.0179
0.400	0.124	0.7729	0.7490	0.0239	0.0239
0.500	0.096	0.7773	0.7474	0.0299	0.0299
NH$_3$, 20.0°C					
0.000	1.000	0.6113	0.6113	0.0000	0.0000
0.060	0.433	0.6141	0.6112	0.0029	0.0028
0.100	0.338	0.6160	0.6112	0.0048	0.0047
0.200	0.223	0.6207	0.6110	0.0097	0.0096
0.300	0.170	0.6254	0.6109	0.0145	0.0145
0.400	0.144	0.6301	0.6107	0.0194	0.0194
0.500	0.131	0.6348	0.6106	0.0242	0.0243
ND$_3$, 20.0°C					
0.000	1.000	0.7216	0.7216	0.0000	0.0000
0.060	0.483	0.7245	0.7210	0.0035	0.0035
0.100	0.361	0.7265	0.7206	0.0058	0.0058
0.200	0.247	0.7313	0.7196	0.0117	0.0118
0.300	0.198	0.7362	0.7185	0.0176	0.0177
0.400	0.168	0.7410	0.7174	0.0236	0.0237
0.500	0.141	0.7459	0.7164	0.0295	0.0296

TABLE III. Parameters.

T	V A^3	NH$_3$ a, A	NH$_3$ b, A	ND$_3$ a, A	ND$_3$ b, A
−33.7°C	0.0	2.85	3.83	2.84	3.91
0.0°C	−11.4	3.05	3.89	3.05	3.99
20.0°C	−21.9	3.05	4.00	3.16	4.03

solutions of KBr in NH$_3$. It is assumed that the apparent volume per ion pair in such a solution is the sum of the ionic volumes of K$^+$ and Br$^-$ (taken to be those calculated, from the crystal radii,[13] namely, 1.33 and 1.95 A) and the electrostrictive effects of K$^+$ and Br$^-$.[1] The electrostriction volume of K$^+$ is calculated from the total electrostrictive effect from both ions, assuming that the electrostriction volumes of the two ions are inversely proportional to their radii. The electrostriction volume of the singly trapped electrons is calculated from that for K$^+$ assuming that for these two species this volume is inversely proportional to the radius of the species. The radius of the singly trapped electronic species is taken to be an adjustable parameter. For the doubly trapped electrons the electrostriction per pair is taken to be twice that for the singly trapped species. This will be seen from the results given in Table III to be essentially the same as assuming that the electrostrictions of the two types of trapped species are inversely proportional to their radii and directly proportional to the square of their charges.

The sum of all these volume changes which have just been described and which are included under (a)–(c) will be referred to as V. It is to be noted that this sum, so calculated, when divided by the number of K atoms in solution is independent of concentration because the electrostrictive effect of the doubly trapped species is taken to be just twice that of the singly trapped species.

We have in this way calculated the densities ρ_{wt} of hypothetical solutions in which the traps do not occupy volume but in which the electrostrictive effects of the traps are taken into account.

In Table II are listed values of (a) ρ_{wt}, (b) the experimental density ρ_{exptl}, and (c) the difference, $\rho_{wt} - \rho_{exptl}$, of these two densities. The value of the radius of the singly trapped species was taken to be the value given in Table III for purpose of calculating the electrostrictive effect described previously.

Paramagnetic resonance data permit the calculation of the numbers of singly and doubly trapped electrons as described previously. The degree of dissociation α of doubly trapped electrons into singly trapped electrons is given by

$$\alpha = [M(\text{K}) - 2M(e_2^-)]/M(\text{K})$$

$$= M(e^-)/M(\text{K}),$$

where $M(\text{K})$ is the molarity of K in NH$_3$ or ND$_3$,

$M(e_2^-)$ is the molarity of doubly trapped electrons, $M(e^-)$ is the molarity of singly trapped electrons. It is assumed that α is related to the paramagnetic component χ_M of the molar static field susceptibility as determined from the rf susceptibility data by the relation,[16]

$$\alpha = \chi_M(kT/N_{av}\beta^2),$$

where $(N_{av}\beta^2/kT)$ is the paramagnetic static field susceptibility of one mole of free spins. The values of χ_M were obtained from paramagnetic resonance measurements[13] as described previously.

We now assume for simplicity that with each singly trapped electron is associated a spherical cavity of radius a, and with each pair of doubly trapped electrons is associated a spherical cavity of radius b. Assuming such radii to be independent of concentration, we can calculate $\rho_{wt} - \rho$, where ρ is the density of the solution given by the assumed model. The value of this quantity is also listed in Table II.

In Table III we list the values of V calculated as described previously and also the values of a and b used to get the values of $\rho_{wt} - \rho$ which are listed in Table II.

It is clear that the experimental data can be fit very well with this model. It is also to be remarked that the radii a and b are approximately independent of temperature and solvent.

In addition, it should be noted that the radii a and b are very close to the values calculated from the diamagnetic susceptibility of the trapped electrons. This diamagnetic susceptibility is obtained as the difference between the susceptibilities as determined from rf and static measurements. Assuming again that the electrons are trapped in spherical cavities, these cavities must have radii very close to the a and b values given previously in order to account for the observed diamagnetism.

At the boiling point of NH$_3$ the difference between the molar susceptibilities calculated from rf[13] and dc[4] measurements is 47×10^{-6} cm^3 mole^{-1}. This difference is due mainly to the diamagnetism of the doubly trapped electrons. As seen from Table II, only 5% of the electrons are dissociated into singly trapped species. If the electrons were trapped in a spherical square well 5.0 ev deep and 4.0 A in radius, the observed diamagnetism would be just accounted for.

It is, of course, possible for other models to give good agreement between the very large observed density changes caused by the trapped electrons and the very large diamagnetism of the trapped electrons. The model described gives a good correlation in a particularly simple manner.