NOMENCLATURE

B, C, D = coefficients in the virial equation of state
N = ratio of volumes of pressure vessels = $(V_1 + V_2)/V_1$
n = number of moles
P = pressure
R = gas constant; pressure ratio, defined in Equation 9
T = absolute temperature
V = volume
X = defined in Equation 9
x = mole fraction
Y = defined in Equation 9
z = compressibility factor

Subscripts and Exponents

A = component A
i = designating number of any expansion, $i = 1, 2 \ldots n$
M = mixture
n = denoting last expansion
o = initial condition
1, 2 = components, pressure vessels

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Densities of Sodium-Ammonia Solutions

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Densities of sodium-ammonia solutions have been determined from −60° to 60° C., for compositions of 0.08 to 12 mole % sodium. Volumes were measured dilatometrically and corrected for loss of solvent by vaporization. Compositions were determined from electrical conductivities or by gas analysis, then densities at −33.8° C. were obtained from published density-composition data. From these densities and ratios of volumes to those at −33.8° C., densities were established at all other temperatures. Densities decrease with increasing metal concentration; the effect is smaller at higher temperatures. Over the range studied, the excess volumes of the solutions decrease continuously with increasing temperature, from 45 cc. per mole Na at −60° C. to zero just above 60° C.

SPECIFIC conductivities of sodium-ammonia solutions were measured in this laboratory from −60° to 190° C. (*8*); densities were required for conversion of these data into equivalent conductivities. There were excellent data in the literature for densities at the boiling point of ammonia (−33.8° C.) from 1.2 to 5.2*M* (*6*) and 0.6 to 1.2*M* (*2*). At other temperatures, the most complete set was that of Kikuti (*3*), who measured the densities of 1.5 to 5.2*M* solutions from −30° to 30° C. Since these data were not extensive enough for the present study, densities were determined over a wider range of temperatures and concentrations. The strength of glass was a limiting factor; cells frequently ruptured near 60° C., because of the high vapor pressures of the solutions—of the order of 25 atm.

EXPERIMENTAL

Sample Preparation and Stability. Stable sodium-ammonia solutions were prepared in a borosilicate glass, bakeable vacuum system. Sodium (U.S. Industrial Chemical 99.95%+, nitrogen packed) was triply-distilled, encapsulated, and sealed onto the system. The sample cells were calibrated, cleaned, sealed onto the vacuum system, and vacuum baked. Ammonia (Matheson 99.99%) was passed through an activated charcoal trap, stored overnight at −78° C. over sodium, then vacuum fractionated. The sodium was distilled onto a recess above the cell, the purified ammomia was condensed onto the sodium, and the solution was allowed to overflow into the cell. Then, the filled cells were chilled with liquid nitrogen, evacuated, sealed-off, and stored at dry-ice temperature. Samples prepared in this manner are stable to at least 165° C. (*8*).

About 85% of the cells ruptured between 40° and 60° C. because of the high vapor pressures of ammonia at these temperatures. Volumes and conductivities of those cells that survived at 60° C. were remeasured on cooling. The low temperature data obtained prior to heating were reproduced on cooling; this established that there had been no measurable decomposition in these cells.

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Sample Composition. The compositions of the samples were established either by measurements of the specific conductivities or by chemical analyses. Conductivity measurements were made by an inductive, electrodeless technique (*10*). The data of Kraus (*4*) at −33.8° C. were used to establish the compositions from the conductivities. The compositions of the samples that survived were determined by gas analysis. To do this, a sample and a stainless steel ball were placed in a stainless steel cylinder which was evacuated and then cooled with liquid nitrogen. The evacuated cylinder was removed, shaken to break the glass cell, and reconnected to the vacuum system. During thawing of the cylinder, the volatiles were collected and measured—hydrogen as a gas and ammonia as a liquid. Methanol was then added to the cylinder, and the additional hydrogen produced by reaction with sodium was collected and measured.

Volume Measurements. The sample containers (Figure 1) were made of borosilicate glass tubing of approximately 5-mm. I.D. Decal fiducial marks, 5 inches apart, were baked onto the stem. The volumes to the fiducial marks were calibrated volumetrically with mercury with an accuracy of ±0.01 cc. or ca. ±0.2%. The mean cross-sectional areas of the cylindrical sections were obtained from the differences in volumes at the fiducial marks and the distances between them. The average volume of a cell was 10 cc., and the average solution volume was 6 cc. at −33° C.

A cathetometer (Gaertner M940-342, divided in 0.001 mm.) was used to measure the position of the meniscus of the solution relative to the upper fiducial mark.

The reproducibility of check readings on cells filled with mercury was better than 0.002 cm. or ca. ±0.01%. For a cross-sectional area of 0.3 sq. cm., this reproducibility corresponds to a volume of 6×10^{-4} cc., which is an order of magnitude smaller than the scatter in the measured volumes of the solutions.

Except for the most dilute solutions, the solutions are opaque. The solutions wet the glass, so that the crowns of the menisci are not visible from the normal viewing angle because of the opacity. The volumes below the bases of the menisci were estimated by assuming that the menisci are spherical.

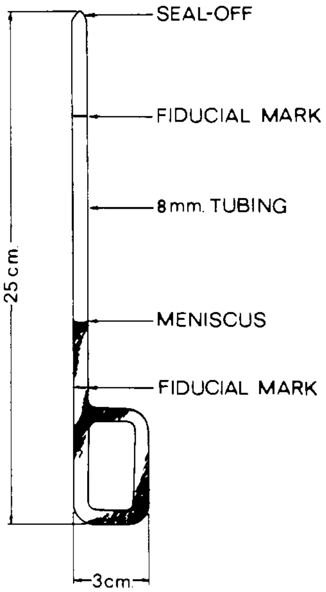

Figure 1. Sample containers
The toroid is used for inductive conductivity measurements

To illuminate the region of the meniscus, a tubular fluorescent bulb was mounted outside the rear of the oven, with the bulb perpendicular to the vertical sample tube. A simple diffuser was placed in front of the fluorescent bulb. The bulb was mounted on a movable arm and could be raised or lowered for reading the meniscus at various positions.

The solution volumes were measured from −60° to 60° C. The lower limit was set by use of expansion of tank CO_2 for cooling and the upper limit by mechanical rupture of the glass cells. Although higher temperatures were reached using capillary cells, use of such cells was not practical because bubbles, which occasionally formed, were too difficult to remove.

DENSITIES

The density at any temperature is calculated from the density at −33.8° C. and the reciprocal of the corresponding ratio of volumes at constant mass, i.e., $\rho = \rho^* V_m^* / V_m$. V_m is determined from the measured volume and the small increase in volume which would be produced if all of the vapor were condensed; thus, $V_m = V_x + V_c$.

The amount of ammonia vapor is determined from the known vapor pressures of ammonia, the perfect gas law and K, the ratio of the solution vapor pressure to that of liquid ammonia. K is assumed to be constant from −60° to 60° C.; this is an extrapolation of the vapor pressure data of Kraus (*5*) and of Marshall and Hunt (*7*) in which K is approximately constant from −45° to 15° C.

The magnitude of the correction term, V_c, is negligible at the lower temperatures and only becomes appreciable at the higher temperatures. In the worst case, that at 60° C., where V_c/V_x is largest, V_c/V_x is less than 0.01. In the absence of solution vapor pressure data in the higher temperature range, it is not possible to make an accurate estimate of the error for this case. However, even if the estimate of the amount of ammonia in the vapor phase at 60° is in error by 25%, this will only increase the error in the densities from 0.5 to 0.56%. Below 60°, the magnitude of V_c/V_x rapidly becomes smaller with decreasing temperature and the estimates become more valid so that below about 40° C. the error in ρ introduced by the approximations used to estimate V_c is negligible.

Values of saturated vapor densities of pure ammonia are obtained from the tables of Davies (*1*). The density of the solution at −33.8° C. is obtained from the composition using the density-composition data of Kraus, Carney, and Johnson (*6*), and Johnson and Meyer (*2*). The reduced density data are plotted in Figure 2.

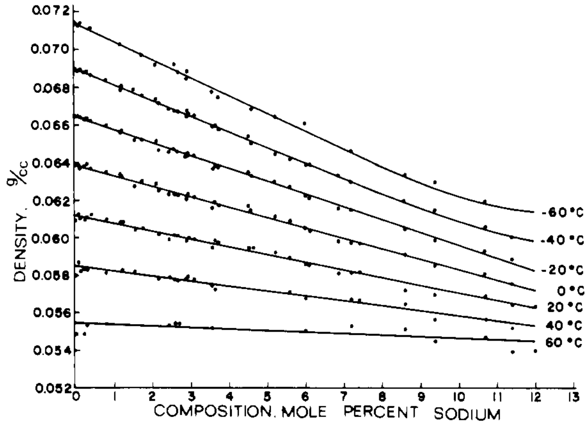

Figure 2. Density-composition isotherms

EXPERIMENTAL DATA

As a check on the procedure, the mass of one solution was measured directly by weighing the sample tube containing the solution and subtracting the weight of the glass alone, making appropriate corrections for air bouyancy. The directly measured density of this solution at −33.8° C. was 0.6624 gram per cc. For comparison, the measured conductivity was equivalent to a mole fraction of 2.43 $\times 10^{-2}$, and the density corresponding to this composition at −33.8° C. was 0.6617 gram per cc. Thus the agreement between the two methods at −33.8° C. (0.1%) is much better than the over-all statistical scatter in the density data itself (0.5%).

The scatter in the data is greatest at high temperatures, where it amounts to 0.5%. This scatter is more pronounced for sodium-ammonia solutions than for liquid ammonia, perhaps owing to a greater tendency for bubble formation in the solutions. Some runs were discarded because of a sudden decrease in density, which was attributed to bubble formation. At the end of these runs, the samples were gently shaken down, and the specific conductivities were remeasured at low temperatures and found to be unchanged. This showed the effects were not caused by decomposition. Bubble formation was troublesome in capillaries. Therefore all measurements were made with the solutions contained in standard wall tubing, whose use limited the working temperature to about 60° C.

Densities of Ammonia. Densities of liquid ammonia have been measured from −60° to +80° C. to establish the accuracy of the technique.

Below 40° C., the average densities agree with accepted values in the literature (*9*) within 0.05% (Table I). At higher temperatures the divergence increases to 0.3%. Insofar as single points are concerned, only a few differ from the literature values by as much as 0.5%.

Densities of Sodium-Ammonia Solutions. Densities have been determined from −60° to +60° C. for 0.082 to 12.0 mole % solutions. The data are summarized in Table II at 20° intervals, and plotted in Figure 2. In this figure, each vertical string of points at a single mole fraction represents measurements on a single sample.

If the data are extrapolated linearly, the densities at zero concentration are higher than those for liquid ammonia, especially above 0° C. This difference is present both with the literature densities as well as with the authors' measured

Table I. Densities of Liquid Ammonia

Sample No.	Densities, Grams per Cc. −60° C.	−40° C.	−20° C.	0° C.	20° C.	40° C.	60° C.	80° C.
241	...	...	0.6640	0.6382	0.6098	0.5791	0.5456	0.5072
180	...	...	0.6650	0.6379	0.6094	0.5796	...	...
110	...	...	0.6650	0.6389	0.6089	0.5823	...	...
242	...	...	0.6646	0.6391	0.6103	0.5813	0.5465	0.5084
110	0.7137	0.6901	0.6649	0.6383	0.6097	...	...	...
242	...	0.6895	0.6644	0.6397	0.6106	0.5778	0.5477	0.5078
Av.	0.7137	0.6898	0.6646	0.6387	0.6098	0.5800	0.5466	0.5078
Davies (*1*)	0.7138	0.6898	0.6650	0.6382	0.6103	0.5793	0.5447	0.5051

Table II. Densities of Na-NH_3 Solutions

Sample No.	Mole % Sodium	Densities, Grams per Cc. −33.8° C.	−60° C.	−40° C.	−20° C.	0° C.	20° C.	40° C.	60° C.
150	0.082	0.6818	0.7126	0.6894	0.6644	0.6385	0.6124	0.5851	...
149	0.120	0.6816	0.7133	0.6891	0.6643	0.6370	0.6098	0.5819	...
265	0.229	0.6808	...	0.6881	0.6636	0.6377	0.6099	0.5825	0.5484
245	0.250	0.6806	...	0.6883	0.6638	0.6388	0.6112	0.5831	0.5525
125	0.405	0.6793	0.7083	0.6869	0.6617	0.6371	0.6122	...	...
246	0.803	0.6762	...	0.6837	0.6599	0.6348	0.6099	0.5813	0.5544
130	1.17	0.6733	0.7024	0.6790	0.6566	0.6338	0.6087	...	...
172	1.20	0.6733	...	0.6803	0.6572	0.6326	0.6084	0.5829	...
171	1.54	0.6700	...	0.6787	0.6521	0.6274	0.6040	0.5824	...
134	1.74	0.6686	0.6970	0.6753	0.6524	0.6296	0.6055	...	...
83	2.08	0.6648	0.6915	0.6705	0.6512	0.6287	...	...	...
170	2.17	0.6638	...	0.6709	0.6464	0.6231	0.6014	0.5783	...
244	2.43	0.6616	...	0.6683	0.6455	0.6237	0.5997	0.5791	0.5530
251	2.58	0.6605	0.6920	0.6675	0.6472	0.6230	0.6015	0.5782	0.5545
131	2.65	0.6600	0.6875	0.6668	0.6459	0.6230	0.6010	0.5780	0.5544
70	2.90	0.6587	0.6842	0.6644	0.6436	0.6204	0.5986	...	...
79	2.91	0.6587	0.6884	0.6653	0.6435	0.6223	0.6010	0.5796	...
164	2.93	0.6585	...	0.6649	0.6435	0.6214	0.5995	0.5775	...
158	3.12	0.6567	...	0.6624	0.6423	0.6203	0.5994	0.5815	...
126	3.58	0.6526	0.6769	0.6591	0.6376	0.6155	0.5947	0.5736	0.5519
161	3.63	0.6526	...	0.6584	0.6381	0.6185	0.5990	0.5728	...
114	3.73	0.6515	0.6745	0.6573	0.6377	0.6177	0.5970	...	...
48	4.51	0.6452	...	0.6489	0.6361	0.6173	0.5939	...	...
104	4.56	0.6449	0.6682	0.6503	0.6328	0.6136	0.5947	...	...
40	5.2	0.6392	0.6585	0.6432	0.6272	0.6091	0.5908	...	...
159	5.61	0.6365	...	0.6422	0.6247	0.6068	0.5889	0.5710	...
148	6.0	0.6341	0.6565	0.6391	0.6218	0.6037	0.5855	0.5675	0.5499
132	6.08	0.6335	...	0.6389	0.6205	0.6031	0.5848	...	...
175	6.88	0.6271	...	0.6324	0.6155	0.5986	0.5812	...	...
123	7.2	0.6244	0.6453	0.6293	0.6143	0.5976	0.5822	0.5669	0.5533
178	7.42	0.6227	...	...	...	0.5969	0.5828	0.5665	...
182	8.6	0.6140	0.6331	0.6183	0.6044	0.5907	0.5773	0.5641	0.5508
253	9.4	0.6088	0.6293	0.6134	0.5984	0.5845	0.5699	0.5566	0.5433
181	10.7	0.6015	0.6191	0.6056	0.5929	0.5804	0.5686	0.5567	0.5451
163	11.40	0.5968	...	0.6005	0.5879	0.5753	0.5635	0.5513	0.5391
250	12.0	0.5945	...	...	...	...	0.5628	...	0.5386

liquid ammonia densities (Table I). Hence, the behavior of the solutions must change at concentrations below the authors' range of measurements.

Apparent Molal Volumes. The nonideality of metal-ammonia solutions has been expressed in terms of excess volumes, V_e, or apparent molal volumes, V_a, which are defined by

$$V_e = (V_m - n_1v_{10} - n_{20}v_{20})/n_2, \tag{1}$$

and

$$V_a = (V_m - n_1v_{10})/n_2 \tag{2}$$

where V_m is the solution volume, v_{10} and v_{20} the molal volumes of liquid ammonia and sodium, and n_1 and n_2 the number of moles of ammonia and sodium in the solution.

The apparent molal volumes of the data in Table II are plotted in Figure 3. The data, taken from the curves in Figure 3, are replotted in Figure 4 to display the effect of temperature on the excess functions. At lower temperatures, the apparent molal volumes are almost independent of concentration over the concentration range studied. At higher temperatures, the apparent molal volumes drop more rapidly for the more dilute solutions. The implications of these results and their relationship to conductivities and susceptibilities will be discussed in a separate communication.

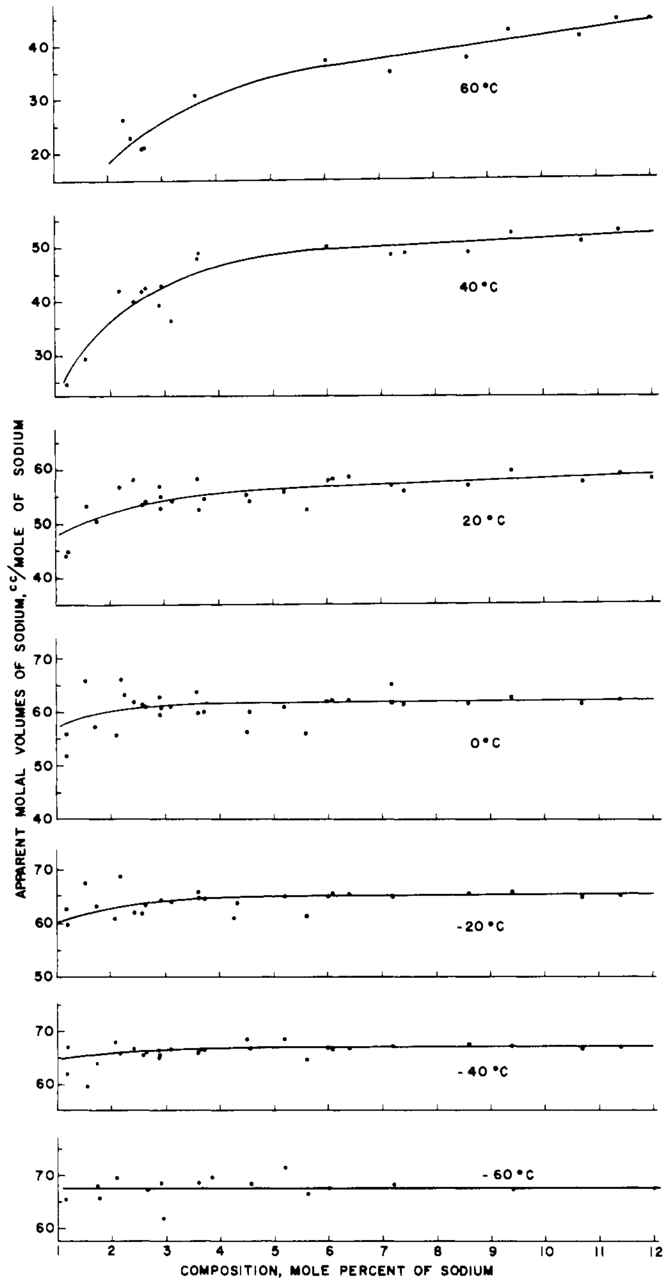

Figure 3. Apparent molal volume-composition isotherms

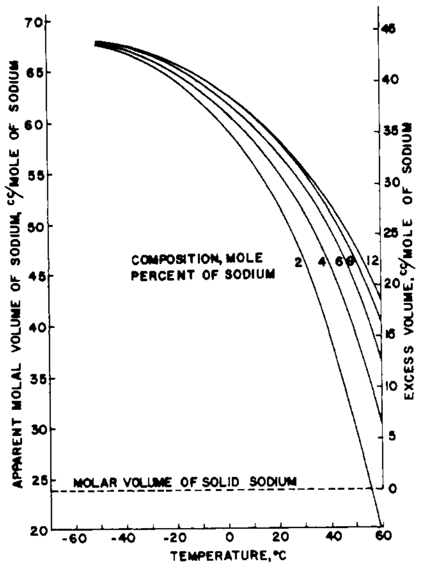

Figure 4. The behavior of excess functions as a function of temperature

NOMENCLATURE

ρ = solution density
K = ratio of solution vapor pressure to that of pure liquid ammonia at the same temperature
n_1 = number of moles of solvent in solution
n_2 = number of moles of solute in solution
v_{10} = molal volume of pure ammonia
v_{20} = molal volume of pure sodium
V_m = volume of solution at constant mass, i.e., in absence of loss by vaporization
V_x = measured volume of solution
V_c = increase in volume if all the ammonia vapor were condensed into the solution
V_a = apparent molal volume $V_a = (V_m - n_1v_{10})/n_2$
V_e = excess volume $V_e = (V_m - n_1v_{10} - n_2v_{20})/n_2$

Superscript

* = data at −33.8° C.

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