Note that (8) and (11) involve activated complexes which are tautomeric. Of the two, (8) is favored since the proton would be expected to be more strongly bound to OH^- than to the weak base $^-SO_3\text{–}SH$.

Either (8) or (11) requires nucleophilic attack at a tetra-coördinated atom which is surrounded by electronegative atoms. The existence of direct displacement reactions at such an atom has been reviewed.[13] The limited evidence available indicates that such S_N2 reactions can occur.[14]

Distinguishing between reaction 6 and 8 may be possible. The driving force for the decomposition of thiosulfate to sulfide and sulfate possibly can be provided by either high temperatures or by high proton activities at lower temperatues. Thiosulfates liberate variable amounts of H_2S on being dissolved in acid.[15] If reaction 1 occurs in, for example, concentrated sulfuric acid, then eq. 6 predicts the rate constant will depend on Hammett's acidity function and eq. 8 predicts dependence on the molar concentration of acid.[16]

A reaction which is formally similar to (1) occurs when OH^- is replaced by radioactive SH^-. Radioactive sulfide becomes incorporated in the thiosulfate. However, the reaction is faster than the one studied here and may have a different mechanism.[17]

In acid solution, Bunté salts decompose[18] in a manner analogous to $HS\text{–}SO_3^-$

$$RS\text{–}SO_3^- + H_2O \xrightarrow[10\text{ hours}]{HCl,\ 100°} RSH + HO\text{—}SO_3^-$$

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Ion Transport in Sodium–Ammonia Solutions

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The anion transference number was measured as a function of concentration for sodium-ammonia solutions at −37° by the moving-boundary method. Details of the apparatus are described. The ionic equivalent conductance of Na^+ was calculated from these data and existing conductivity data. Assuming that the conductance of free sodium ions follows the Shedlovsky equation, the degree of dissociation of ion-pairs (or monomers) and the concentration of dimers were calculated. A satisfactory fit of the data was obtained using two equilibrium constants, $K_1 = 9.2 \times 10^{-3}$ for the dissociation reaction, and $K_2 = 18.5$ for the dimerization reaction.

Introduction

Because of the bridge which they form between metals and non-metals, alkali metal–ammonia solutions are of great theoretical interest. Current theories of the dilute solutions are adequately covered elsewhere,[2–4] but a brief description of those features which are important for a discussion of conductance and activity behavior is in order.

It is clear that in very dilute solutions, ($<10^{-3}$ *M*), it is necessary to view the system in terms of alkali metal cations and solvated electrons. Even the "monomer–dimer" theory[2b] requires dissociation of the monomer in dilute solutions. The recent calculations of Jortner[3] which are refinements of the calculations of Ogg[5] and Lipscomb,[6] afford convincing arguments for the existence of cavities created by electronic polarization of the solvent. This view is supported by the thermal e.m.f. measurements of Dewald and Lepoutre.[7] The mobility of the negative species is too high to involve appreciable migration of solvent molecules along with the electron. Quantum tunnelling of the electron from a cavity to a properly oriented group of solvent molecules in the vicinity of the cavity probably occurs.

In the intermediate concentration range, (10^{-3} to 10^{-1} *M*), free ions are removed from the solution. Electrostatic considerations demand that, in a solvent of this dielectric constant, a considerable fraction of the ions form pairs or other neutral species. The theory of Becker, Lindquist and Alder[2b] proposes the formation of a monomer unit with a single electron in an expanded orbital about the solvated cation. Nuclear magnetic resonance data[8,9] for fairly concentrated solutions favor such a postulate, but recent spectral data of Clark, Hors-

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field and Symons[10] and Douthit and Dye[11] indicate that monomers are relatively unimportant in the intermediate and low concentration ranges. A normal ion-pair, represented by $M^+ \cdot e^-$, could form between the cation and the electron cavity. This could then be in equilibrium with a monomer unit. Since ion-transport data cannot distinguish between these alternatives, they are considered together in our equilibrium constant calculations.

Magnetic evidence[12,13] makes it clear that electron-pairing is important in the intermediate and high concentration ranges. The Becker–Lindquist–Alder theory[2b] postulates the formation of a dimer, M_2, with the bonding electrons in expanded orbitals outside of the ionic solvation sheath. Another explanation for the magnetic behavior, which was advanced in connection with the cavity model,[5] is the existence of centers in which two electrons occupy the same cavity. Ion-transport data can aid in deciding between these two possibilities.

The e.m.f. and conductance data of Kraus[14,15] have stood the test of time and are still among the best available. Conductance data have been extended by Gibson and Phipps[16] and by Fristrom.[17] The latter author has also measured the e.m.f. of cells with transference as a function of temperature. Recently, Evers and co-workers[18] have extended this type of measurement to solutions of alkali metals in methylamine.

While transference numbers and individual ionic mobilities can be inferred from the e.m.f. measurements, this requires the assumption of unit activity coefficients. For such a complex system, this is perhaps too drastic an assumption, and independent mobility studies would be desirable. The only reported attempt to measure the transference number of the electron in liquid ammonia is by Meranda[19] who obtained a very low value ($\sim$0.01). In the light of the data reported here, the results of Meranda must be in error.

For the present research, it was desirable to establish an independent value for λ_+^0 the limiting ionic equivalent conductance of the sodium ion. Franklin and Cady[20] measured the transference numbers of a group of salts in liquid ammonia by the moving-boundary method using an autogenic boundary. When these measurements were made, and also at the time of a later review article by Kraus and Bray,[21] the available theory predicted a constant mobility for ions as a function of concentration. Re-examination of these data showed that the transference numbers were concentration-dependent. Table I gives the transference data of Franklin and Cady for sodium nitrate. These data were plotted *versus* $C^{1/2}$ and extrapolated to zero concentration to obtain a value of T_+^0 of 0.455 ± 0.002. Combination of this value with the conductivity data of Kraus and Bray[21] for sodium nitrate in ammonia gives a value of λ_+^0 of 137 ± 3 cm.^{2} ohm^{-1} equiv.$^{-1}$ for sodium ion.

TABLE I

TRANSFERENCE NUMBER OF SODIUM NITRATE IN LIQUID AMMONIA AT −33.5°[20]

(Molarity)$^{1/2}$	T_+
0.1267	0.4617[a]
.1294	.4451
.1926	.4451
.2890	.4385
.3237	.4352
.476	.4252
.491	.4252

[a] This point deviates considerably from the straight line through the others.

The determination of λ_+ and λ_- for sodium–ammonia solutions is of theoretical importance because the total equivalent conductance goes through a minimum at 0.05 molar. Presumably, the increase with concentration is due to the onset of increased electronic conductance. The separation of this effect from the normal decreasing conductance of the positive ion can be made only with the acquisition of transference number data. In addition to the direct use of mobility data, the determination of transference numbers permits calculation of activity coefficients by combination with the e.m.f. data of Kraus.[14] Both mobility and activity data provide useful tests of the theories concerning these solutions.

The moving-boundary method provides the most accurate tool for the measurement of transference numbers in aqueous solutions. A number of problems were encountered in adapting this method for use with metal–ammonia solutions. The most serious problems arose because of the reactive nature of the solutions, which readily decompose to form the amide and hydrogen. This reaction is catalyzed by many common impurities, including oxygen, water and most metals. It was necessary to develop a moving-boundary apparatus which could be evacuated prior to use and in which all of the solutions could be made up without exposure to the atmosphere. The apparatus which was finally evolved and the results obtained with sodium in liquid ammonia are the subject of this paper. The calculation of activity coefficients and their comparison with theory are the subject of a companion paper.[22]

Experimental

Materials.—Sodium metal (Baker's Analyzed) was purified by a modification of the method of Watt and Sowards[23] involving multiple distillations of the metal *in vacuo*. Before being introduced into the distillation apparatus, the metal was first melted under vacuum. After distillation, the molten metal was forced by helium pressure into thin-

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walled glass bulbs through capillaries. The helium was removed by evacuation and the tips of the capillaries were covered with sodium to protect the bulk of the metal from contamination during the seal-off operation. The weight of sodium in the bulbs was determined from the initial weight of the bulb with its attached capillary and the final weight of the bulb and sodium plus all glass residues. Anhydrous ammonia (Matheson) was stored over sodium in a steel cylinder and transferred by distillation to the glass purification system as needed. Mallinckrodt A. R. grade sodium bromide was used without further purification. Helium used to force molten sodium into the glass ampoules was also the covering gas during the transference run. It was purified by passage over copper and copper oxide at 600°, then over silica gel and activated charcoal at liquid air temperatures. The purified helium was stored in two liter flasks attached to the vacuum manifold.

Apparatus.—A constant temperature bath was constructed from a Pyrex cylinder 12″ in diameter by 18″ high surrounded by a sheet of copper to which $^1/_4$″ copper refrigeration coils were soldered. This assembly was surrounded by 2″ of Foam-glass insulation. Double windows were left on either side of the bath to permit observation of the boundary. Alcohol was used as a bath fluid and an auxillary refrigeration coil was immersed in the liquid. Two refrigeration units ($^1/_3$ and $^1/_4$ h.p.) employing Freon-22 permitted the attainment of temperatures down to −42°. The refrigeration units were run continuously and a 250 watt knife-heater connected to a variable transformer was used to balance most of the extra heat-loss. An infrared heat lamp, actuated by a mercury thermoregulator provided the temperature control. Efficient stirring was maintained by circulating the fluid with a centrifugal pump insulated with Styrofoam. The temperature could be controlled for long periods of time to ± 0.05° near the transference tube and differed by less than 0.1° from one region of the bath to another. The temperature was measured with a Mueller Bridge employing a platinum resistance thermometer which had been calibrated by the Bureau of Standards.

A schematic diagram of the essential apparatus is shown in Fig. 1. Prior to each run the entire system was evacuated for at least 24 hr., using a mercury diffusion pump, to a pressure below 1×10^{-5} mm. as indicated by an ionization gauge. Ammonia from a steel tank was distilled into vessel *A* containing degassed sodium and allowed to stand at −40 to −60° for at least 2 hr. It was then forced by its own vapor pressure through the frit in A into flask B. From this container it could be distilled into the make-up vessel directly, or a definite volume of ammonia could be condensed in C if desired.

The solution make-up vessel consisted of a jacketed 100 ml. graduated cylinder with a coarse frit sealed on the bottom. The sodium ampoule was held near the top until needed by means of a magnet sealed in glass. Condensation of ammonia was effected by circulating cold alcohol with a Gorman-Rupp #210 centrifugal pump through the jacket and through coils immersed in a dry ice–acetone bath. The incoming ammonia gas stream prevented liquid from flowing through the frit and served to stir the solution vigorously. Both the sodium bromide following solution and the sodium metal leading solution were prepared in this make-up vessel.

The transference tube was made from a two ml. graduated pipet. Before construction of the cell, the volume between marks in this tube was calibrated with mercury. A silver–silver chloride cathode and a platinum anode were employed. Since the electrode reaction at the cathode produced no bubbles, this compartment was chosen to be the closed side of the cell. The hollow-bore, boundary-forming stopcock and the other stopcocks below the bath level were lubricated with Dow–Corning silicone high vacuum grease. This proved to be sufficiently fluid above −40° to allow the stopcocks to be turned and also was apparently inert to sodium in liquid ammonia. Bulbs F and E were provided for collecting a rinse and the anode solution, respectively. A very important feature of the transference cell, which was incorporated after a number of unsuccessful runs, was the pair of conductance electrodes sealed into the tube above the calibration marks. At first, platinum electrodes of #28 wire were sealed through lead glass which was then sealed into the Pyrex transference cell using a pair of graded seals. While this design proved to be vacuum tight, it involved considerable strain at the graded seals and at the electrode seals, and a number of runs were ruined by breakage of the cell. Finally, a seal was made which proved to be suitable for our purposes. Ball electrodes were formed on #34 platinum wires which were then sealed through 3 mm. Pyrex tubing and into the Pyrex transference tube. The wires were protected from the bath with the 3 mm. tubing. The small leaks left at the wire seals were eliminated by partially filling the electrode tubes with Apiezon N vacuum grease. Preliminary attempts to seal the leaks using a silicone fluid in the tubes were unsuccessful because of "creep" of the fluid through the seal. A number of runs with both sodium and potassium have been made with the present apparatus without breakage and the seals appear to be completely satisfactory.

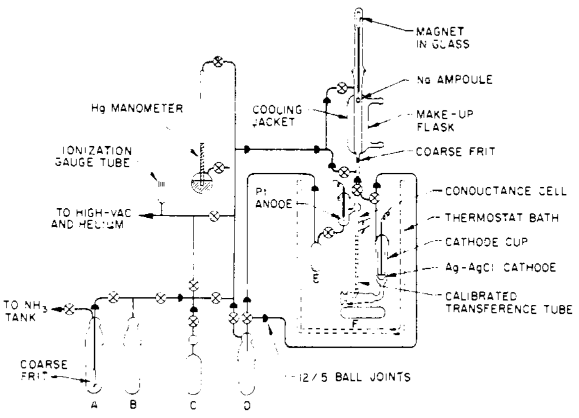

Fig. 1.—Schematic diagram of the essential apparatus.

A constant current was supplied by an electronic device described elsewhere[24] and was measured by the e.m.f. developed across a standard resistor. Current was controlled to better than ± 0.1%. Time of rise of the boundary was measured with a pair of calibrated stopwatches.

Conductance measurements were made at 400, 600, 1000, 2000 and 4000 cycles and proved to be practically independent of frequency (<0.2%). The conductance equipment used has been previously described.[24] Because bright platinum electrodes were used, calibration of the cell was done using a potassium iodide-iodine mixture as recommended by Kraus.[15] The specific conductance of the mixture was measured in a Leeds and Northrup Type A conductance cell calibrated with aqueous potassium chloride.

The amount of ammonia in the solution in *E* of Fig. 1 was determined by distilling the ammonia into a weighed steel pressure vessel which was then re-weighed at room temperature. The sodium residue in E was taken up with alcohol and water and analyzed for sodium by the zinc-uranyl acetate method.[25]

Steps Involved in a Transference Run.—(1) The transference cell and make-up flask are cleaned with alcoholic potassium hydroxide and hot sulfuric–chromic acid cleaning solution and thoroughly rinsed with distilled water. (2) Sodium bromide dried at 200° is weighed into the make-up vessel and the sodium ampoule inserted. The entire apparatus is assembled and evacuated for at least 24 hr. or until the pressure is less than 1.0×10^{-5} mm. as registered by an ionization gauge. (3) Ammonia is distilled into the purification train and allowed to stand over sodium at −40 to −70° for several hours. During this time the thermostat bath is filled with absolute ethanol and cooled to −37°. (4) Ammonia is distilled into the make-up vessel and the sodium bromide indicator solution is made up and transferred to the closed side of the cell. Excess solution is run into container D and the small amount of ammonia remaining in the make-up flask and lead tubes is distilled into D. From this point on, close temperature control of the bath is required to prevent pressure build-up in the cell. (5) Ammonia is condensed in the make-up vessel two or three times and run into D to serve as a rinse. The sodium ampoule is lowered into the liquid to rinse off any sodium bromide which might have splashed onto it. (6) The make-up vessel is re-evacuated overnight and the pressure

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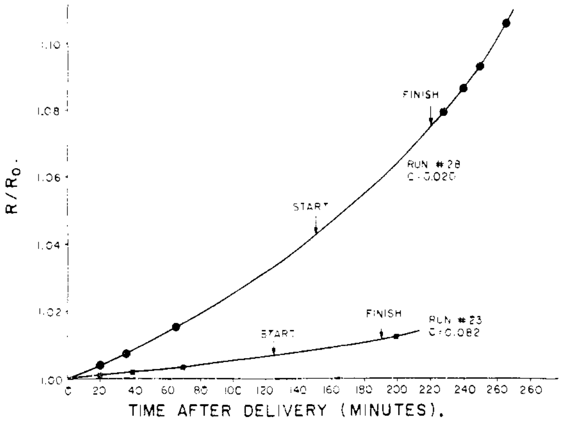

Fig. 2.—Resistance divided by resistance at the time of transfer *versus* time for two sodium–ammonia solutions.

checked again to insure that no leaks have developed and then the glass ampoule containing the sodium is broken. (7) The desired amount of leading solution is prepared in the make-up vessel and a portion of the solution is discarded to the waste vessel D. (8) The sodium solution is forced by helium pressure into the transference cell. The boundary-forming stopcock is opened to F and some solution is allowed to flow into F thus rinsing the tube. The stopcock is closed and the cell is filled. Excess solution is discarded as before. (9) After allowing the make-up vessel to warm to room temperature and adjusting the helium pressure to slightly below atmospheric pressure, the two stopcocks above the transference tube are opened alternately to equilibrate the pressure on the closed and open sides. The stopcock above the metal solution is left open during the run while the stopcock above the cathode compartment is closed. (10) The resistance of the solution is measured as a function of time for about 1 hr. before the boundary is formed. The boundary-forming stopcock is opened to form a junction between the sodium and the sodium bromide solutions and the current is turned on. (11) The motion of the boundary, which is made easily visible by the high absorption of light by the metal solution, is observed as a function of time until it traverses all of the marks. (12) After the current is turned off, the resistance is again measured as a function of time. (13) Some solution is drained into F bringing fresh solution into contact with the electrodes. The resistance is again noted. (14) The anode solution is drained into *E* for analysis. (15) Ammonia is distilled from the cell and the cell is disassembled and removed from the bath for cleaning.

Special Precautions Required.—In accord with the suggestions of Dewald and Lepoutre[26] the mercury manometer was used only when the system contained an appreciable pressure of ammonia vapor. When breakage occurred with ammonia in the system, it was necessary to wash the entire system out with water to remove the ammonium carbonate formed. A covering gas such as helium was required to prevent bubble formation in the transference tube during a run. Also the current had to be kept below about 50 *C* mamp; where *C* is the molarity of the solution. Due to ohmic heating, higher currents caused bubble formation near the stopcock. It was necessary to disconnect the conductance electrodes from the bridge during the transference run to eliminate a secondary current path through the conductance bridge. Very close temperature control was necessary because the closed side of the cell behaved like a thermometer, giving erratic readings of the boundary speed if temperature fluctuations were allowed to occur. When the temperature was controlled to ±0.05° such fluctuations were negligible.

Results

Sharp, clearly visible boundaries were obtained whose speed could be easily measured. Since decomposition was the greatest problem encountered, the determination of the concentration at the time of the measurement was essential to the method. A number of early runs gave stable boundaries, but meaningless results because the concentration during the run was unknown. The incorporation of conductance electrodes in the transference tube permitted determination of the solution concentration as a function of time before and after a transference run. The concentration at any time during the run could then be obtained by interpolation. Relative decomposition rates were found to be dependent upon concentration. Figure 2 shows graphs of the resistance ratio R/R_0 *versus* time for two concentrations. It is to be noted that the lower concentration has the higher relative decomposition rate and that the rate of decomposition increases with time. Table II gives the relative initial decomposition rate as a function of concentration as well as the absolute decomposition rate. While the data show some scatter, there appears to be a zero order dependence of the decomposition rate upon concentration. This is what might be expected if the slow step in the decomposition occurred at a catalytic surface. Earlier studies confirmed the necessity for the thorough degassing and the rinsing procedure finally employed.

Table II

Initial Decomposition Rate of Sodium Solutions at −37°

Run no.	Initial molarity	Decomp. per hour, %	Absolute rate mole l.$^{-1}$ hr.$^{-1}$ × 10^4
28	0.02052	1.0	2.0
32	.03983	0.28	1.1
25	.0477	.68	3.2
23	.0818	.24	1.9
29	.1172	.22	2.6
26	.1436	.05	0.7

A critical test of the method was the negligibly small change in resistance which normally occurred when fresh solution was allowed to come into contact with the electrodes after the run. This indicated that the decomposition rate was also reasonably uniform throughout the tube, at least to within about two centimeters of the boundary.

The experimental parameters measured were: (1) solution resistance *versus* time, (2) bath temperature *versus* time, (3) current, (4) time for the boundary to sweep out known volumes.

Several preliminary runs were used to test the effect of current on the speed of motion of the boundary. It was found that the speed was proportional to the current as required for satisfactory transference measurements. The boundary was found to have excellent self-sharpening qualities. The current could be shut off for several minutes until diffusion was clearly present. Upon resumption of the current the boundary was observed to sharpen quickly. The fact that metal solutions are less dense than salt solutions, and the great difference in mobility between the solvated electron and the bromide ion make for favorable self-sharpening qualities.

In order to convert the raw data into corrected transference numbers, it was necessary to calculate the concentration of the solutions as a function of time from the resistance measurements. For this

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[26] J. F. Dewald and G. Lepoutre, This Journal, **76**, 3369 (1954).

purpose, the data of Kraus[15] were used. Since his data were obtained at −33.5° and the transference number measurements were done at about −37°, a temperature correction was made using the temperature coefficient data of Fristrom.[17] From the known cell constant and the solution resistance, the specific conductance of the solution could be calculated. Calculated equivalent conductances could then be used to compute the concentration. It was necessary to correct for the conductance of the amide ion formed upon decomposition of the solution. This was done by extrapolating the specific conductance back to the time of transfer of the solution assuming no prior decomposition. A value of 40 cm.^{2} ohm^{-1} equiv.$^{-1}$ was used for the equivalent conductance of the amide ion. Since this correction cancels out when making the solvent conductance correction, the value chosen is not critical and is needed only for comparison with the gravimetric analysis. Detailed data and calculations for a particular run are given in Table III and a summary of all data is given in Table IV. The data for the completed runs prior to No. 23 were obtained without the benefit of a sealed-in conductance cell and so the variation of concentration with time was unknown. Runs 24, 27, 30 and 31 were not completed because of equipment failure. For run No. 26 the conductance cell was broken before it could be calibrated, so that the analysis had to be used to determine the initial concentration, although the relative decomposition rate was known from resistance readings. In addition, for runs 23 and 28 analyses were made by the zinc uranyl acetate method[25] for comparison with those from conductance. The values of the initial sodium concentration obtained were

Run #23: analysis, 0.0826; conductance, 0.0818
Run #28: analysis, 0.0205; conductance, 0.0205

TABLE III

SUMMARY OF RUN NO. 23

Bath temp. −37.03°C. $R_{\text{av}} = 775.4$ ohms
Cell constant 28.40 cm.$^{-1}$
NaBr conc. 0.04 *M* $\dfrac{\text{d}\log\Lambda}{\text{d}t} = \dfrac{-\text{d}\log R}{\text{d}t} - \dfrac{\text{d}\log C}{\text{d}t}$
Current 3.100 mamp. $\dfrac{\text{d}\log\Lambda}{\text{d}t} = 0.0062 + 0.00077$

$\Lambda = 454$ for $\Lambda_{-33.5} = 481$

Time	Remarks and resistance (ohms)
5:30	Transfer
7:45	768
7:50	768.7
8:10	769.8
8:40	770.7
8:45	Current on
9:25	First mark
10:40	Current off
10:50	777.6

$C_{\text{av}} = 0.0807$ *M*
$R_{\text{transfer}} = 763.8$ ohms
$C_{\text{transfer}} = 0.0818$
C_{transfer} by analysis = 0.0826
Correction for volume changes:

$$T_- = (T_-)_{\text{app}}\left[1 + \left(\frac{65.9\,T_- - 10.2}{1000}\right)C\right] = 0.922$$

Mark	Volume (cm.^{3})	Average molarity	Time (sec.)	T_-
0.4–1.2	0.8064	0.08082	2224	0.912
.5–1.3	.8026	.08079	2207	.915
.6–1.4	.8032	.08077	2211	.914
.7–1.5	.8025	.08075	2195	.919
.8–1.6	.8040	.08072	2183	.926
.9–1.7	.8041	.08069	2181	.923
1.0–1.8	.8012	.08066	2188	.919

TABLE IV

SUMMARY OF TRANSFERENCE NUMBER DATA

Run no.	Molarity		Av. resistance during run (ohms)	Cell const. (cm.$^{-1}$)	T_-	
	Av. during run	At transfer			Obsd. (includes solvent corr.)	After volume corr.
28	0.01906	0.02052	3920	35.62	0.881	0.882
32	.03948	.03983	1515.6	25.85	.895	.897
25	.04636	.0477	1395.4	28.40	.940	.943
23	.0806	.0818	775.4	28.40	.918	.922
29	.1168	.1172	622.6	34.82	.915	.921
26	.1427	.1436	505.0	...	.933	.941

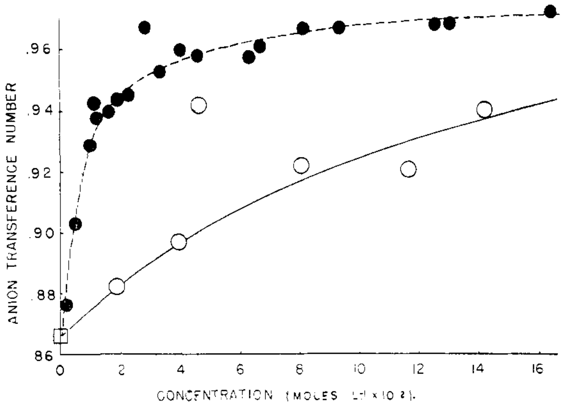

Fig. 3.—Anion transference number of sodium in liquid ammonia: ○, this Laboratory; ●, calculated from e.m.f. data of Kraus assuming activity coefficients of unity; □, intercept required by independent transference number data for $NaNO_3$ and conductances.

A solvent conductance correction was made, based upon the amount of amide ion formed by the decomposition of sodium. Approximate volume corrections were made using density data for sodium,[27] sodium iodide[28] and silver iodide.[29]

The corrected transference number as a function of concentration is shown in Fig. 3, along with the earlier estimates based upon the e.m.f. data of Kraus[14] and the assumption of unity activity coefficients. The intercept shown at $C = 0$ in Fig. 4 ($T_-^0 = 0.866$) is obtained using $\lambda_+^0 = 137$ as required by data on sodium nitrate[21] and using $\Lambda^0 = 1020$ for sodium metal as recommended by Kraus.[30] Using the data of Kraus[15] for the total conductivity corrected to −37° by the temperature coefficient data of Fristrom[17] and the smoothed transference number values from this research, λ_+ and λ_- were calculated. The values are given in Table V and shown graphically in Fig. 4. It is seen that the negative ion conductance has a minimum at $C = 0.04$ *M* and that the sodium ion conductance decreases continuously throughout this range of concentration. An extension of the λ_+ curve, together with the measured total conductivity, was used to calculate T_+ at concentrations above the range of measurement for use with e.m.f. data to compute activity coefficients.[22]

In considering the possible sources of error in these measurements, it can be safely concluded that all

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[27] W. C. Johnson and A. W. Meyer, THIS JOURNAL, **54**, 3621 (1932).
[28] W. C. Johnson and R. F. Martens, *ibid.*, **58**, 15 (1936).
[29] F. F. Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).
[30] C. A. Kraus, *J. Chem. Educ.*, **30**, 83 (1953).

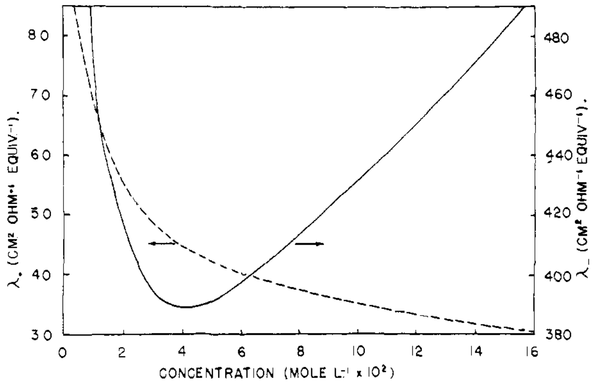

Fig. 4.—Anionic and cationic conductances for sodium–ammonia solutions.

parameters in the transference number equation are precise to at least ±0.2% except for the concentration of the metal during the run.

The error in concentration can be due to nonuniformity of concentration in the transference tube, error in the measurement of the specific conductance and errors in the published conductance and temperature coefficient data. The transference number is roughly linear in $C^{1/2}$, and a least-squares treatment of the data was made, excluding run No. 25, but including the intercept at $C = 0$. The estimated standard deviation was ±0.68%. An estimate of the error in the published conductances and temperature coefficients raises this value to ±0.94% giving a probable error of ±0.63%.

Table V

Λ, λ_+ and λ_- *Versus* Concentration at −37.0° (Smoothed Values)

Molarity	T_-	Λ	λ_+	λ_-
0.000	0.866	936	125	811
.010	.874	546	68.8	477
.020	.883	473	55.4	418
.030	.890	443	48.7	394
.040	.897	434	44.7	389
.060	.908	437	40.2	397
.080	.917	453	37.6	415
.100	.925	468	35.1	433
.120	.931	483	33.3	450
.140	.937	503	31.7	471
.160	.942	526	30.5	495

Discussion

As Fig. 3 shows, the extrapolation of the T_- data to the zero concentration value of 0.866 demanded by independent measurements is certainly reasonable. Previously accepted values of T_- based upon the e.m.f. data of Kraus[14] which are also shown in Fig. 3 are high. A companion paper[22] shows that this difference can be accounted for on the basis of the activity coefficient behavior. Making use of the conductance data of Kraus permits the evaluation of λ_+^0 as a function of concentration. In contrast to the total equivalent conductance, the cation conductance is a monotonically decreasing function of concentration and the increase in total conductance is caused solely by the negative species. Because the factors which cause this increase are undoubtedly present at lower concentrations as well, the cation conductance should be a better measure of the free ion concentration than is the total conductance.

The difficulty which is encountered in any treatment of this type concerns the use of a theoretical conductance function. If we could assign a theoretical conductance function to the free cations, then a comparison of observed and calculated conductances would permit evaluation of α, the degree of dissociation of ion-pairs. If we were dealing with the conductance of sodium ions in an ordinary salt solution in ammonia, the proper function to use would be the Fuoss–Onsager function[31] so successfully applied to 1–1 salts in a variety of solvents. However, an essential part of this treatment requires that the negative ion move as a unit with a definite radius and a characteristic mobility correlated with λ_-^0, the limiting equivalent conductance. The electron in ammonia undoubtedly migrates by a quantum tunnelling mechanism to which this theory is not applicable. Calculations made using the Fuoss–Onsager treatment resulted in high values for the degree of dissociation which could not be correlated with any pairing equilibrium.

Evers and Frank[32] used the Shedlovsky function[33]

$$\Lambda = \Lambda^0 - \frac{\Lambda}{\Lambda^0}(\alpha^*\Lambda^0 + \beta^*)\sqrt{C_i} \qquad (1)$$

which has been widely employed as an empirical conductance function for the free ions in the calculation of association constants. In view of the difficulties involved with the Fuoss–Onsager function for this system, the Shedlovsky function was assumed to describe the equivalent conductance of the *free* sodium ions as a function of concentration.

The degree of dissociation α, is given by

$$\alpha = \frac{C_i}{C} = \frac{\lambda}{\lambda_i} \qquad (2)$$

where λ is the measured equivalent conductance, λ_i is the equivalent conductance of the free ion, C is the stoichiometric concentration and C_i is the concentration of the free ion. Since from this equation, $C_i\lambda_i = C\lambda$, one can make a graph of any function of $C_i\lambda_i$ *versus* any convenient function of C_i to determine C_i from data on λ and C. In the present case $(C_i\lambda_i)^{1/2}$ was plotted *versus* $(C_i)^{1/2}$ on a large sheet of graph paper. From the measured values of C and λ, $(C\lambda)^{1/2}$ was computed and C_i was determined from the graph.

The values of C_i and α thus obtained were used to compute the dissociation and pairing constants. The reactions which were assumed to take place are

$$M^+{\cdot}e^- \rightleftarrows M^+ + e^-;\ K_1 = \frac{(M^+)(e^-)f_\pm{}^2}{(M^+{\cdot}e^-)} \qquad (1)$$

$$2M^+{\cdot}e^- \rightleftarrows M_2;\ K_2 = \frac{(M_2)}{(M^+{\cdot}e^-)^2} \qquad (2)$$

in which $f_\pm$ is the mean molar ionic activity coefficient and was calculated from the Debye–Hückel equation

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(31) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); R. M. Fuoss, This Journal, **79**, 3301 (1957).

(32) E. C. Evers and P. W. Frank, Jr., *J. Chem. Phys.*, **30**, 61 (1959).

(33) T. Shedlovsky, *J. Franklin Inst.*, **225**, 738 (1938).

$$\log f_{\pm} = \frac{-A\sqrt{C_i}}{1 + B\,\mathring{a}\sqrt{C_i}} \qquad (3)$$

using an ion size parameter of 5.5 Å. This value was chosen somewhat arbitrarily as the mean distance from the center of the sodium ion to the center of the cavity in an ion-pair. The final result is not very sensitive to the value of $\mathring{a}$ used but the value of 5.5 Å. was used from the beginning and was *not* used as an adjustable parameter. It is felt that any reasonable value of $\mathring{a}$ is better than using only the limiting law.

The calculations were performed by first neglecting reaction 2, resulting in an approximate value of K_1 given by

$$K_1^{(a)} = \frac{\alpha^2 C f_{\pm}^2}{1 - \alpha} \qquad (4)$$

A series of $K_1^{(a)}$ values were obtained in this manner as a function of concentration. $K_1^{(a)}$ was then plotted *versus* concentration and a test value of the true constant $K_1^{(t)}$ was obtained by extrapolation. K_2 was obtained from $K_1^{(a)}$ and $K_1^{(t)}$ through the relationship

$$K_2 = \left[\frac{(K_1^{(t)} - K_1^{(a)})}{2(C\alpha f_{\pm})^2} \cdot \frac{K_1^{(t)}}{K_1^{(a)}}\right]^{1/2} \qquad (5)$$

For a series of values of $K_1^{(t)}$, K_2 was calculated as a function of concentration. Table VI gives the results obtained for three values of $K_1^{(t)}$. The most constant value of K_2, 18.5, was obtained for $K_1^{(t)} = 9.2 \times 10^{-3}$. These calculations show that the data obtained can be fit with the type of equilibria postulated by the "monomer–dimer" theory.[2] However, either a spherical monomer unit or an ion-pair between sodium ion and the electron in a cavity could be the important unit. Of course these data provide no information concerning the structure of the dimer. An uncharged dimer rather than an $e_2^=$ unit was considered in this treatment. A treatment based upon the assumption of dimerization to $e_2^=$ centers has not been made but would be more complex because of additional ion-pairing equilibria. The values of K_1 and K_2 are to be compared with 7.2×10^{-3} and 27 obtained by Evers and Frank from the total conductance up to concentrations of 0.04 molar. On the basis of both sets of calculations, the dimerization constant K_2 appears to be smaller than the corresponding constant for potassium calculated[2b] from the magnetic resonance data of Hutchison.[13] Unfortunately the paramagnetic resonance data for sodium are not as extensive nor as internally consistent as the potassium data. It would be of interest to extend the magnetic data for sodium and also to evaluate λ_+ for potassium from transference number measurements. On the basis of our results and the magnetic evidence, one would expect more dimerization for potassium than for sodium and therefore a larger value of K_2. Transference number data for potassium are currently being obtained in this Laboratory.

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The Activity Coefficient of Sodium in Liquid Ammonia

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Transference number data from moving-boundary measurements and data from the e.m.f. of cells with transference were used to calculate the activity of sodium in liquid ammonia as a function of concentration. Consideration of ion-pairing and dimerization equilibria allowed extrapolation of the data to infinite dilution and resulted in values of 9.6×10^{-3} and 23, respectively, for the equilibrium constants of the two reactions

$$Na^+{\cdot}e^- \rightleftarrows Na^+ + e^- \qquad (1) \qquad\qquad 2Na^+{\cdot}e^- \rightleftarrows Na_2{\cdot} \qquad (2)$$

The results were combined with published vapor pressure data for the high concentration region and with calorimetric data to give a partial molar entropy of 16.9 ± 1.8 cal. deg.$^{-1}$ mole^{-1} for the solvated electron in the hypothetical ideal one molal solution.

Introduction

The activity coefficients of alkali metals in liquid ammonia can be determined in the high concentration range from data on the vapor pressure of ammonia above such solutions. Since the precision in this method is poor at low concentrations, it is necessary to use pure sodium as the standard state or simply to compute relative activity coefficients.[2a] Such data are useful for comparing the behavior of different metals and for studying phase equilibria but do not help to determine the nature of the ionized species in dilute solutions. Calorimetric data are available[2b,3] for the heat of solution of the metal to form dilute solutions, so that ΔH^0 for the process

$$NH_{3(l)} + Na_{(s)} \longrightarrow Na_{(am)}^+ + e_{(am)}^- \qquad (3)$$

can be calculated. The data of Pleskov[4] on the e.m.f. of cells were used by Jolly[5] and by Coulter[2b] to calculate ionic enthalpies and entropies for the alkali ions and to estimate the heat of solvation of

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(2) (a) P. R. Marshall and H. Hunt, *J. Phys. Chem.*, **60**, 732 (1956). (b) L. V. Coulter, *ibid.*, **57**, 553 (1953).

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