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The Reversibility of the Reaction of Alkali Metals with Liquid Ammonia

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Ammoniated electrons exist in solutions of the alkali metal amides in liquid ammonia which have reached thermodynamic equilibrium with hydrogen gas. By using both electron spin resonance and optical spectroscopy to measure the electron concentration, an equilibrium constant of 5 × 10^4 was measured for the reaction

$$e_{am}^- + NH_3 = NH_2^- + {}^1/_2H_2$$

and 3 × 10^9 for the reaction

$$Na^+ + e_{am}^- + NH_3 = NaNH_2(s) + {}^1/_2H_2$$

at 25°. From the temperature coefficients of these reactions, the approximate $\Delta H°$ values of -16 and -12 kcal/mole, respectively, were obtained.

Introduction

Solutions of alkali metals in liquid ammonia decompose slowly (rapidly in the presence of certain catalysts) to form the metal amides and hydrogen. For potassium, rubidium, and cesium, the reaction may be written as

$$e_{am}^- + NH_3 = NH_2^- + {}^1/_2H_2 \qquad (1)$$

For lithium and sodium (whose amides are sparingly soluble in ammonia) the reactions may be written as

$$Li^+ + e_{am}^- + NH_3 = LiNH_2(s) + {}^1/_2H_2 \qquad (2)$$

$$Na^+ + e_{am}^- + NH_3 = NaNH_2(s) + {}^1/_2H_2 \qquad (3)$$

These reactions can be useful for the preparation of the amides, but more often they are undesirable side reactions in the study and use of metal–ammonia solutions. Kraus[1] suggested that a systematic study of these reactions was a necessary prelude to the study of more stable solutions. No one has directly measured the equilibrium constants of these reactions, but it is possible to correlate thermodynamic data for electrolytes in liquid ammonia and thereby to calculate indirectly the equilibrium constants. In this way one can calculate, for 25°, the approximate values K = 1.2 × 10^6 for reaction 1,[2] K = 7 × 10^{12} for reaction 2,[2,3] and K = 1.3 × 10^{10} for reaction 3.[2,4] The purpose of this work was to demonstrate the reversibility of these reactions and to measure directly the equilibrium constants and their temperature coefficients.

The experiments were of two types, corresponding to two methods for determining the electron concentration. In one type of experiment, the electron concentration was determined spectrophotometrically. In the other type of experiment, the electron concentration was determined by electron spin resonance.

Experimental Section

Description of the Optical Cell.—The high pressure optical cell is shown in Figures 1 and 2. The heavy stainless steel body of the cell resisted attack by the solutions to be studied, contained the high pressures anticipated, and acted as an efficient heat reservoir to dissipate the heat absorbed from the infrared source by the sample. The windows were made of Pyrex glass and were approximately 1 cm thick. The O rings were of a special polyethylene–propylene composition (Porter Seal Co.) selected for resistance to attack by metal ammonia solutions. A stainless steel bellows seal valve was used as a master valve for the same reason. Stainless steel, V seated, packed valves were used in the manifold. Stainless steel tubing and Swagelock fittings were used in the construction of the manifold and gauge connections. When assembled, the unit could hold 136 atm of helium gas with no detectable leakage for a period in excess of 24 hr.

Temperature control was accomplished by circulating thermostated water through copper heat-exchange coils soldered to the body of the cell. The temperature was measured with a copper–constantan thermocouple located in a well a few millimeters from the sample cavity, in conjunction with a Rubicon potentiometer. The temperature was maintained at 25 ± 0.1°.

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(1) C. A. Kraus, *J. Chem. Educ.*, **30**, 83 (1953).

(2) W. L. Jolly in "Solvated Electron," Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 30.

(3) "Selected Values of Chemical Thermodynamic Constants," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C. The free energy of formation of $LiNH_2$ was calculated from the heat and an estimated entropy.

(4) L. V. Coulter, J. R. Sinclair, A. G. Cole, and G. C. Roper, *J. Am. Chem. Soc.*, **81**, 2986 (1959).

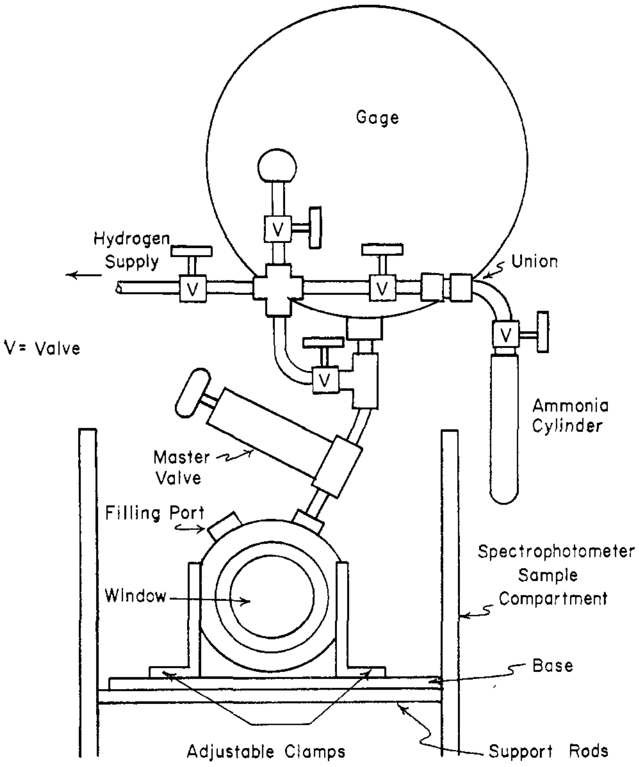

Figure 1.—Optical cell viewed along axis of the light beam.

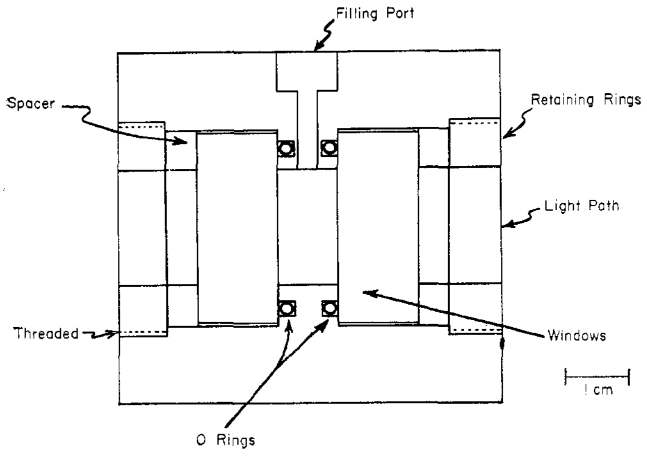

Figure 2.—Cross section of optical cell.

Pressure was determined with a stainless steel Bourdon gauge with a range of 0–2000 psig (136 atm) divided in increments of 20 psig (1.36 atm). By fitting the tip of the gauge pointer with a thin piece of flat metal mounted perpendicular to the gauge face, readings could be estimated to ±0.1 division (±0.14 atm).

The cell was mounted on a base plate with adjustable clamps designed to permit accurate, reproducible positioning of the unit in the sample compartment of a Cary Model 14 recording spectrophotometer. Once the proper position had been established, the cell could be repositioned by simply ensuring that two edges of the base plate were in firm contact with two walls of the compartment.

Calibration of the Optical Cell.—The light path length of the optical cell was mechanically measured with a micrometer caliper at various pressures. The path length at zero pressure was 0.992 cm and increased about 0.012%/atm increase in pressure. These measured values were used in the calculations. The light path length was checked against a cell of known path length using the 12,000 A absorption band of a solution of methanol in ethyl ether. A value of 0.996 cm was obtained which, considering the possible errors in this technique, is in good agreement with the mechanical measurement.

The cell was filled with liquid NH_3 and the effect of pressure on the spectrum was checked at several pressures up to about 130 atm. Hydrogen gas was used to pressurize the cell. The results indicated an increase in absorbance with pressure. At 100 atm this increase was 1.7%, which was larger than predicted from the increase in path length. Maybury and Coulter[5] measured the adiabatic compressibilities of liquid ammonia solutions, and from their data we estimate an increase in the density of liquid ammonia of 0.5% per 100 atm increase in pressure. We conclude that the measured increase in absorbance was the result of changes in both path length and density.

The volume of the cell was checked on a vacuum line by filling the cell to a known pressure of nitrogen and then pumping the nitrogen into a gas buret of known volume using a Toepler pump. The volumes of the gauge and the manifold were determined in the same manner.

The Bourdon gauge was calibrated on a dead weight tester and a calibration chart prepared. Above 10 atm the gauge read 0.1 atm high. All readings were corrected by the use of the calibration chart. Periodically the gauge was checked against a second calibrated gauge; the calibration did not change over the period the gauge was in use.

Procedure for Obtaining Optical Data.—Prior to use, the optical cell was carefully cleaned, the metal surfaces of the sample compartment coated with 0.05 *M* chloroplatinic acid, and the whole unit dried in an oven at 120°. This procedure left a thin coating of platinum in the cell to act as a catalyst. The cell was assembled and leak tested with helium at 136 atm.

The cell was attached to a vacuum line and evacuated. The entire system was wrapped with heating tape and the temperature raised to about 100°. Care was taken to loosen the retaining rings during the bake out to prevent cracking of the windows due to the different coefficient of expansion of steel and Pyrex. The cell was pumped out for a minimum of 8 hr and then filled with dry, oxygen-free nitrogen or argon. Ammonia, dried with sodium metal, was then distilled into a small steel cylinder (10 ml) equipped with a valve. This valve was closed; the cylinder was removed from the vacuum line, weighed, and then attached to the manifold of the optical cell. A small hole was cut in the end of a plastic glove bag (I^2R Co., Cheltenham, Pa.) and this was sealed to the filling port of the cell. The bag was continuously flushed with nitrogen or argon which had passed, successively, through a column packed with BTS catalyst (BASF Colors and Chemicals Inc.) to remove traces of oxygen and a column of magnesium perchlorate to remove traces of water. In a run involving sodium or potassium, a piece of metal was cleaned of all oxide and placed in an extrusion press in the dry bag. A length of wire was extruded and placed in a small tared weighing bottle which had been baked in an oven at 200° and then cooled in the dry gas atmosphere. The sample was weighed and returned to the dry bag, and the bag was thoroughly flushed with dry gas. The filling port of the cell was opened and a known amount of metal introduced.

Cesium was much more difficult to handle because of its semiliquid state and extreme reactivity. We found that we could deliver accurate volumes of clean cesium into the cell with a micropipet heated to 30°. The density of cesium at this temperature was estimated at 1.84 g/cc. The metal at 30° was drawn up into the pipet which was kept at the same temperature. The tip of the pipet was then placed into the filling port and dry nitrogen was used to force the metal from the pipet into the cell. When the pipet had been properly cleaned and dried, no reaction occurred, and the pipet emptied cleanly. The entire operation took place in a well-flushed glove bag.

After the introduction of metal, the port was closed, and the cell was evacuated. The valve to the vacuum line was closed; cold water was circulated through the cell heat exchanger, and ammonia was distilled into the cell from the small steel cylinder.

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(5) R. H. Maybury and L. V. Coulter, *J. Chem. Phys.*, **19**, 1326 (1951).

When the cell appeared full, the master valve was closed, and ammonia in the manifold was condensed back into the steel cylinder using liquid nitrogen. The manifold was again opened to the vacuum line, and the pressure was measured with a thermocouple gauge to check that no ammonia was left in the manifold. The cylinder was removed and weighed.

In the spectral range in which the electron absorption band occurs, ammonia has intense absorption bands. It was necessary to take readings at wavelengths between these bands, where the ammonia absorption is low. At zero hydrogen pressure, the concentration of the electron was zero. Therefore, the absorbance due to the electron was taken to be the difference in the total absorbance at pressure $P > 0$ and that at $P = 0$.

$$A_{e^-} = A_T(P > 0) - A_T(P = 0)$$

In early experiments the absorbance at zero hydrogen pressure was determined after removing the hydrogen produced by the reaction of the metal with ammonia. After the hydrogen pressure dependence of the reaction had been thoroughly established, this step was eliminated. Instead, the total absorbance was plotted against the square root of the hydrogen pressure and the line extrapolated to zero hydrogen pressure.

Water at 25° was circulated through the heat exchanger, and the system was allowed to come to chemical equilibrium. This usually took 1–2 hr, depending upon the concentration of the alkali metal. The cell was positioned in the sample compartment of a Cary Model 14 spectrophotometer and the absorbance measured. Because of the sensitivity of the electron absorption band and the equilibrium constant to temperature, the sample was exposed to the light source for periods of less than 5 sec, and time was allowed to dissipate any heat absorbed before taking the next reading. To ensure that equilibrium had been reached, the procedure was repeated at 20-min intervals until three successive readings were identical.

At this point hydrogen gas at approximately 150 atm was added to the manifold. This in turn was carefully bled into the gauge section until a pressure near that desired was registered on the gauge. The valve to the manifold was closed; the master valve was opened, and the pressure was allowed to equilibrate. This normally took 5–10 min. The master valve was then closed and the system allowed to reach chemical equilibrium as established by three successive absorbance readings at 20-min intervals. This equilibration took from 1 to 3 hr, depending on the concentration of the amide and the pressure used. This over-all procedure was repeated until the desired data had been obtained. To test for reversibility in several runs, the process was reversed, that is hydrogen was removed from the system. It was impossible in this step to prevent some ammonia from coming off with the hydrogen and (with the exception of saturated solutions) increasing the amide concentration. This ammonia was collected by passing the gas being removed very slowly through two traps at liquid nitrogen temperature. The hydrogen was pumped away and the amount of ammonia determined by either condensing it into a gas bulb and weighing or by absorbing it in a known quantity of acid and titrating. The amide concentration was corrected accordingly.

Throughout the procedure, extreme care had to be taken to prevent liquid ammonia from condensing above the master valve in the gauge section, resulting in a change in the amide concentration. This was accomplished both by heating the gauge to a temperature about 5° greater than the cell and by keeping the master valve closed except when taking a pressure reading.

Determination of the Amide Concentration in the Optical Studies.—The concentrations of amide in the solutions in the optical cell were determined from the weights of the metals used and the volumes of the ammonia. The volume of the ammonia solution was determined from the weight of ammonia used, corrected for the amount of ammonia in the gas phase. Three approximations were made in this calculation: first, that the vapor pressure of the solution could be estimated using Raoult's law; second, that knowing the pressure and volume of the ammonia gas, the number of moles of gas could be calculated using van der Waal's equation for ammonia;[6] third, that the effect of the amide concentration on the volume of the solution could be estimated by adding the volume of the amide formed (calculated from the density of the solid amide[7]) to the volume of the liquid ammonia calculated from its weight and density.[8]

Preparation of the Esr Samples.—The esr samples were prepared by sealing measured amounts of alkali metal and ammonia in Pyrex glass tubes and allowing chemical equilibrium to be reached. In all of the samples studied, the intense blue color of the alkali metal completely faded and was replaced either by the yellow color of the amide ion (in the cases of potassium and cesium) or a precipitate of metal amide (in the cases of sodium and lithium).

The epr sample tubes consisted of 3-mm Pyrex tubing which had been selected for uniformity of wall thickness and bore. Each tube was fitted with a pyrex O ring joint and annealed. The cross section of each tube was determined gravimetrically using mercury. The tubes were thoroughly cleaned, rinsed with a 0.001 *M* solution of chloroplatinic acid, and placed in an oven at 200° for 2 hr. This procedure left a very fine coating of platinum on the walls to act as a catalyst for the preparation of the amide from the metal and liquid ammonia. The presence of the catalyst did not interfere with the spectrum, and without it the reaction to form the amide was extremely slow.

The tubes were placed on the vacuum line, evacuated, and flamed. They were then filled with dry nitrogen, removed, capped, and weighed. The tubes were transferred to a dry bag and charged with samples of the metal which had been extruded from a hand press. The tubes were carefully reweighed, placed back on the vacuum line, and evacuated. Dry liquid ammonia was then distilled onto the samples. From the weight of metal used and the cross section of the tube, the approximate level of ammonia to give a desired concentration could be determined. The tubes were sealed off, and both sections were weighed to determine the weight of ammonia used. The tubes were set aside and allowed to reach chemical equilibrium.

Certain experiments called for the addition of sodium bromide, potassium bromide, or both salts to the solution. The salts were dried for several hours at 180° and allowed to cool in a desiccator. Short lengths, 2–3 cm, of melting point capillary were weighed on a microbalance, filled with an estimated amount of the desired salt, and reweighed. The capillary with the salt was placed in the esr sample tube and the whole unit evacuated and gently flamed. The sample tubes were filled with dry gas, and the samples were prepared as described above.

Method for Determining the Esr Spectrum.—After the reaction had reached equilibrium (usually a few days after the blue color of the metal solution had disappeared) the spectrum was recorded on a Varian V-4502 epr spectrometer. A small crystal of diphenylpicrylhydrazyl (DPPH) was placed in the cavity near the sample to act as a reference and intermediate standard. The temperature was controlled to ±0.1° by passing dry air through a heat exchanger and then through a small dewar in which the sample was positioned. Figure 3 shows the arrangement. The temperature could be varied by changing the temperature of the heat exchanger bath and by controlling the flow of air. The temperature was measured with a copper–constantan thermocouple.

The electron concentration was determined by indirectly comparing the sample signal with that of a solution of recrystallized vanadium(IV) oxyacetylacetonate of known concentration.

The *Q* value of the microwave cavity is seriously affected by the introduction of samples of varying dielectric strength. A lowering of the *Q* value decreases the sensitivity of the spectrometer and results in a reduced signal intensity. Such sensitivity

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(6) "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Co., Cleveland, Ohio, 1966.

(7) R. Levine and W. C. Fernelius, *Chem. Rev.*, **54**, 449 (1954).

(8) C. Cragoe and D. Harper, National Bureau of Standards Scientific Papers No. 420, U. S. Government Printing Office, Washington, D. C., 1921, p 313.

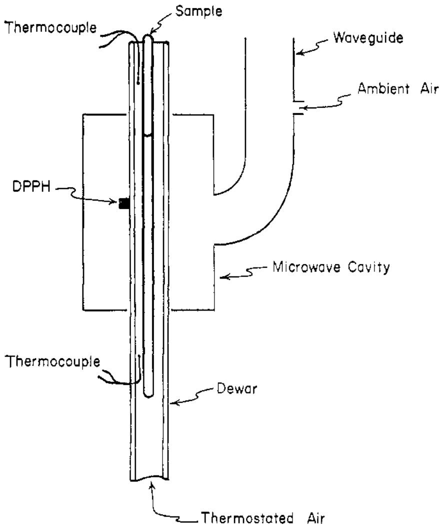

Figure 3.—Schematic drawing of esr microwave cavity, showing arrangement of the sample and the DPPH intermediate reference standard.

changes were compensated for by means of the DPPH intermediate standard. When the spectra of each sample and the standard sample were recorded, the spectrum of the DPPH was also recorded. One of the samples was selected as a reference, and the ratio of the signal intensity of each of the other samples ($I_{(obsd)}$) to that of the reference ($I_{R(obsd)}$) was corrected by the ratio of the DPPH signal intensities (D_R/D) according to the equation $I/I_R = (I_{(obsd)}/I_{R(obsd)})D_R/D$. Then by determining the concentration of spins in the reference sample by means of the vanadium(IV) solution, the electron concentration of all of the samples could be calculated. This technique also accounts for any change in cavity match or radiofrequency power level.[9] Readings on a given sample could be duplicated to within ±10%.

The temperature-dependence studies were carried out with the sample left in place in the spectrometer. After establishment of thermal equilibrium, the spectrum was taken at 10-min intervals. Equilibrium was considered to have been reached when three successive readings were of the same intensity. The temperature was then changed slightly in a direction opposite to the main direction in which the temperature had been shifted, and the change in intensity noted. A signal change in the direction predicted by this temperature change indicated that we had been at equilibrium.

Determination of the Hydrogen Pressure and Amide Concentration of the Esr Sample.—The total volume of each prepared sample tube was determined from its internal length and cross section. An adjustment (~0.2%) was made for the rounded ends. The volume of liquid was determined either by directly measuring the height in the tube or by determining the weight and estimating the density of the solution. When possible, both methods were used, and they agreed within 2%.

After the spectrum had been recorded, the sample tube was placed in a specially built glass vessel which could be evacuated and which permitted breaking the tube and determining the hydrogen volumetrically. Using the solubility data of Wiebe and Tremearne[10] and the volume data, the pressure of hydrogen in the tube was calculated. For every 0.5 mole of hydrogen formed, 1 mole of amide forms, and therefore for the potassium and cesium runs it was possible to calculate the amide concentrations.

Results of the Optical Study

The optical spectra of solutions of $NaNH_2$, KNH_2, and $CsNH_2$ were recorded at 13,650 A and at hydrogen pressures up to approximately 100 atm. Some of the results are shown in Table I. As previously stated, readings had to be taken at a wavelength where the

Table I

Equilibrium Data from Optical Studies at 13,650 A

Molarity of amide	Hydrogen press, atm	Total absorbance	Net absorbance	Concn of absorbing species, $10^5 M$
2.01	0	0.325	...	...
	12.5	0.585	0.260	2.37
	25.9	0.730	0.405	3.69
	40.8	0.835	0.509	4.62
	50.3	0.900	0.573	5.20
	72.1	1.000	0.672	6.10
	87.2	1.061	0.732	6.62
	100	1.125	0.796	7.20
1.80	100.0	1.045[a]	0.770	6.98
1.70	0	0.340	...	...
	15.0	0.640	0.300	2.75
	38.1	0.800	0.459	4.18
	64.0	0.928	0.585	5.30
	88.5	1.020	0.676	6.12
	99.7	1.043	0.698	6.32
1.85[b]	64.5	0.940	0.599	5.42
1.99[b]	42.2	0.817	0.475	4.32
2.13[b]	17.0	0.680	0.340	3.12
1.41	100.0	0.994[a]	0.652	5.90
1.21	100	0.898	0.572	5.18
1.00	0	0.216	...	...
	4.0	0.329	0.113	1.04
	11.6	0.415	0.199	1.83
	25.2	0.495	0.278	2.53
	49.0	0.618	0.401	3.65
	82.7	0.720	0.502	4.54
	99.6	0.775	0.556	5.02
	100	0.776[a]	0.557	5.05
0.93	100	0.778[a]	0.542	4.91
0.80	100	0.740	0.537	4.87
0.72 ($CsNH_2$)	100	0.700[a]	0.447	4.05
0.68	0	0.270	...	...
	8.85	0.402	0.132	1.21
	28.6	0.488	0.218	1.99
	49.6	0.525	0.254	2.31
	68.4	0.640	0.368	3.34
	88.0	0.660	0.388	3.51
	100	0.688	0.416	3.77
0.73[b]	72.0	0.644	0.372	3.37
0.79[b]	47.0	0.591	0.320	2.91
0.90[b]	18.3	0.503	0.233	2.14
0.58	100	0.641[a]	0.394	3.57
0.55	0	0.300[a]	...	...
	0.7	0.330	0.030	0.28
	18.4	0.465	0.165	1.51
	45.2	0.557	0.276	2.51
	73.5	0.640	0.339	3.07
	95.0	0.691	0.388	3.52
	100	0.705	0.403	3.65
0.50	100	0.665	0.363	3.29
0.40	100	0.613	0.333	3.01
0.28	100	0.552	0.281	2.54
0.26	100	0.558[a]	0.289	2.62
0.20 ($CsNH_2$)	0	0.260[a]	...	...
	0.8	0.270	0.010	0.09
	11.6	0.345	0.085	0.78
	25.9	0.400	0.140	1.28
	60.5	0.462	0.201	1.83
	100	0.520[a]	0.259	2.34
	104	0.522	0.260	2.35
0.19	100	0.540[a]	0.247	2.23
0.16	100	0.611	0.298	2.70
0.15	100	0.496[a]	0.185	1.67
0.067	100	0.438[a]	0.167	1.51
0.027 ($NaNH_2$)	0	0.256[a]	...	...
	25.8	0.263	0.007	0.06
	49	0.270	0.014	0.13
	67	0.276	0.020	0.18
	100	0.277	0.021	0.19
	58[b]	0.274	0.018	0.17
	24.5[b]	0.260	0.004	0.04

[a] Determined by extrapolation of the measured absorbance.

[b] The hydrogen pressure was reduced to test the reversibility of the equilibrium. When necessary, the amide concentration was adjusted for loss of ammonia.

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(9) Varian Technical Information Publication 87-114-000, pp 5-7–5-11.

(10) R. Wiebe and T. H. Tremearne, *J. Am. Chem. Soc.*, **56**, 2357 (1934).

ammonia absorbance exhibits a minimum. It was desirable that this minimum be fairly broad (about 500 A) and at a wavelength for which the extinction coefficient of the electron is high. We found that the minimum at 13,650 A satisfied both of these conditions and gave the most reproducible results. Some measurements were made at 11,200, 12,500, 16,000, and 17,500 A; the results were similar, but the data were more scattered.

The concentration of the electron was calculated by substituting the values of the net absorbance A_{e^-}, the extinction coefficient ϵ, and the path length d (Table I) into the Beer-Lambert equation, $(e_{am}^-) = A_{e^-}/\epsilon d$. We used an extinction coefficient of 1.1×10^4 M^{-1} cm^{-1} at 13,650 A, taken from the data of Corset and Lepoutre.[11,12] Figure 4 shows the relationship between the electron concentration and the hydrogen pressure for several amide concentrations. The data for all concentrations studied exhibited the same linear dependence on the square root of the hydrogen pressure. To determine that it was specifically the hydrogen gas pressure which caused the increase in absorbance, the following experiment was performed. The spectrum at 25 atm hydrogen pressure was recorded, and then, using argon, the pressure was increased by 25 atm and the spectrum again recorded. The experiment was repeated using helium and nitrogen. No increase in absorbance other than that due to changing path length and density was detected. To ensure that nothing had affected the samples during the experiments, hydrogen was again added to the system and the spectrum recorded. An increase in absorbance was detected in every case.

From the data in Table I at 100 atm of hydrogen pressure, assuming the amide to be completely dissociated, we calculated equilibrium quotients for reaction 1 from the equation

$$K_c = \frac{[NH_2^-]P_{H_2}^{1/2}}{[e_{am}^-]}$$

The values of K_c are plotted against amide concentration in Figure 5. Obviously K_c is not constant with changing amide concentration. To try to resolve this difficulty we treated the data in two ways. First, a modified Debye-Hückel treatment was employed combining the properties of KNH_2 in liquid ammonia calculated by Fuoss and Kraus[13] with the calculations for an alkali metal made by Arnold and Patterson.[14] This treatment required a series of approximations, not the least of which was that the Debye-Hückel theory was valid at these concentrations. Unfortunately this treatment failed to produce a significant improvement in the data.

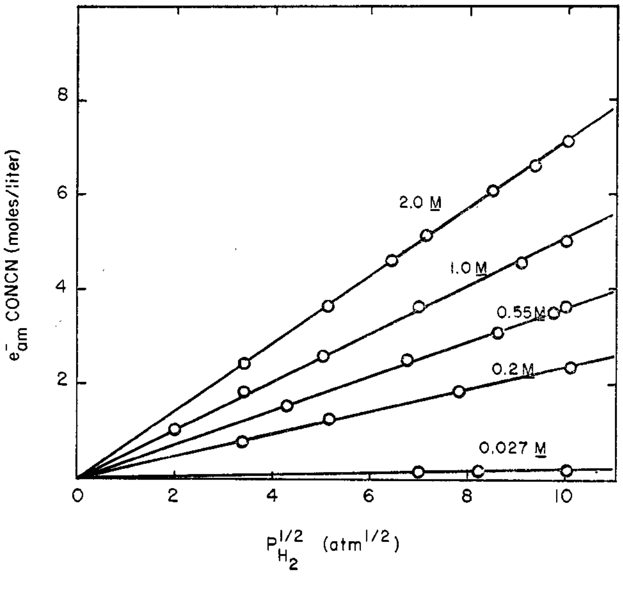
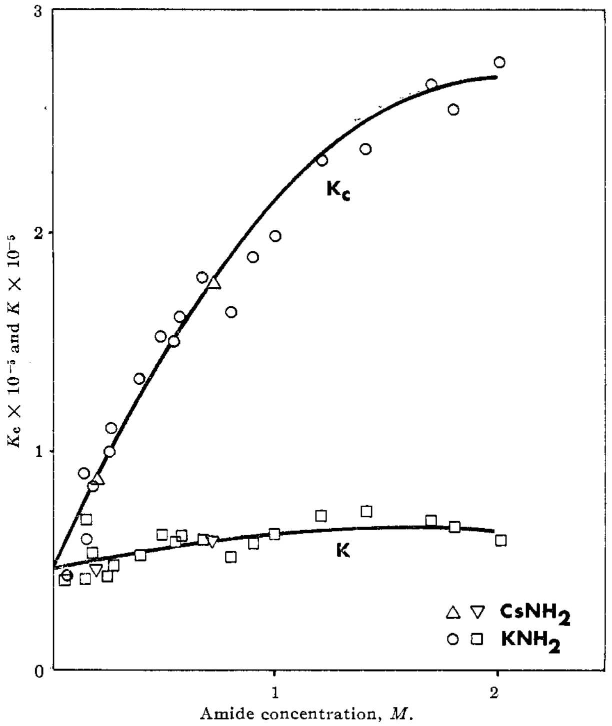


Figure 4.—Electron concentration (as determined by optical measurements) *vs.* the square root of the hydrogen pressure at several amide concentrations.



Amide concentration, *M*.

Figure 5.—K_c and K *vs.* amide concentration for reaction 1. Data from optical measurements.

Second, an equilibrium constant was calculated from the equation

$$K = \frac{P^{1/2}[NH_2^-]\gamma_\pm^2(KNH_2)}{[e_{am}^-]\gamma_\pm^2(K)} = K_c\frac{\gamma_\pm^2(KNH_2)}{\gamma_\pm^2(K)}$$

in which $\gamma_\pm(KNH_2)$ and $\gamma_\pm(K)$ are the empirically determined mean ionic activity coefficients for potassium amide and potassium, respectively. Since no activity coefficient data have been reported for any of the alkali amides, values were estimated from the measurements on NH_4Cl at 25° by Ritchie and Hunt.[15]

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[11] J. Corset and G. Lepoutre in "Solutions Metal-Ammoniac: Propriétés Physico-Chimiques," G. Lepoutre and M. J. Sienko, Ed., W. A. Benjamin, New York, N. Y., 1964, p 186.

[12] G. Lepoutre, private communication. Errata to ref 11: Figure 3, p 188; the abscissa reads 13,000 under the 1 of 13,000 and 10,000 under the 1 of 10,000. Page 188, line 3, second paragraph; change 13,000 cm^{-1} to 12,000 cm^{-1}.

[13] R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.*, **55**, 476 (1933).

[14] E. Arnold and A. Patterson, *J. Chem. Phys.*, **41**, 3089 (1964).

[15] H. W. Ritchie and H. Hunt, *J. Phys. Chem.*, **43**, 407 (1939).

The activity coefficients for potassium were taken from the work of Marshall.[16] The latter values were measured at −33° and were left uncorrected. The principle of ionic strength was assumed valid. The results of this calculation appear in Table II, and the calculated values of K are plotted in Figure 5. Clearly the K values are much more constant than the K_c values.

The value of K for reaction 1 obtained by extrapolation to zero concentration is approximately 5×10^4. A value of $K = 3 \times 10^9$ was calculated for reaction 3 from the data for a saturated $NaNH_2$ solution, using the expression

$$K = \frac{P_{H_2}^{1/2}}{[Na^+][e^-]\gamma_\pm^2(Na)}$$

The $\gamma_\pm(Na)$ value was estimated from the data of Marshall.[16]

Table II

Calculated Values of the Equilibrium Constant Using Estimated Activity Coefficients; P_{H_2} = 100 atm

Amide concn, M	$10^2\gamma_\pm$ of amide[15]	$10^2\gamma_\pm$ of metal[16]	Electron concn, $10^5 M$	$K \times 10^{-4}$
2.0	1.35	2.90	7.20	6.0
1.8	1.50	2.95	6.98	6.7
1.7	1.57	3.00	6.32	7.3
1.4	1.82	3.25	5.90	7.5
1.2	1.97	3.55	5.18	7.2
1.0	2.25	4.00	5.05	6.3
0.93	2.37	4.25	4.91	5.9
0.80	2.65	4.70	4.87	5.2
0.72[a]	2.91	5.05	4.05	5.9
0.68	3.03	5.25	3.77	6.0
0.58	3.55	5.75	3.57	6.2
0.55	3.75	6.05	3.68	5.8
0.50	4.05	6.35	3.29	6.2
0.40	4.45	7.05	3.01	5.3
0.28	6.10	9.25	2.54	4.8
0.26	6.35	9.50	2.62	4.4
0.20[a]	7.72	10.5	2.34	4.6
0.19	8.70	11.0	2.23	5.3
0.16	9.80	11.7	2.70	4.1
0.15	10.5	12.0	1.67	6.9
0.067	18.0	18.5	1.51	4.2
0.027[b]	...	27.0	0.18	300,000

[a] $CsNH_2$. [b] $NaNH_2$.

Results of the Esr Measurements

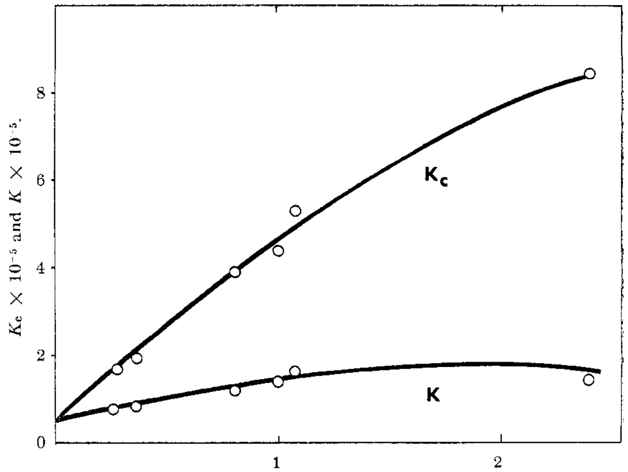
Determination of the Equilibrium Constant.—In an earlier study,[17] using electron spin resonance to determine the total concentration of unpaired electrons, we observed that the equilibrium quotient (K_c) for reaction 1 varied markedly with the concentration of potassium amide. At the time it was believed that a change in the sensitivity of the esr spectrometer was responsible for the inconstancy of K_c. More recently we have used smaller diameter sample tubes in an attempt to correct the problem. Table III shows the results. Obviously the K_c values are still not constant with changing amide concentration. However, a marked improvement in the data is achieved by calculating equilibrium constants (K) using activity coefficients of potassium and potassium amide (as estimated for the constants obtained from optical data). The values for K_c and K are plotted against amide concentration in Figure 6. Extrapolation to zero concentration yields a value of approximately 5×10^4, which is fortuitously in agreement with the value obtained from optical data.

Table III

Equilibrium Data from Epr Experiments

Concn of amide, M	Hydrogen press, atm	Concn of electrons, $10^6 M$	$K_c = \frac{P_{H_2}^{1/2}[NH_2^-]}{[e^-]}$	$K^a = K_c \times \frac{\gamma_\pm^2(KNH_2)}{\gamma_\pm^2(K)}$
0.269	7.52	4.50	1.65×10^5	0.7×10^5
0.361	18.9	8.05	1.96×10^5	0.8×10^5
0.815	19.2	9.24	3.87×10^5	1.2×10^5
1.00	19.4	9.92	4.44×10^5	1.4×10^5
1.08	16.8	8.45	5.26×10^5	1.6×10^5
2.40	21.5	13.0	8.55×10^5	1.4×10^5

[a] $\gamma_\pm(KNH_2)$ estimated from ref 15; $\gamma_\pm(K)$ from ref 16.



KNH_2 concentration, M.

Figure 6.—K_c and K *vs.* amide concentration for reaction 1. Data from esr measurements.

Two sets of experiments were made using esr to verify the hydrogen pressure dependence results found by optical methods. In the first, 1 M KNH_2 solutions were prepared in such a way as to vary the hydrogen pressure. This was accomplished by simply keeping the weight of potassium and the volume of ammonia in each sample constant and varying the total volume of the tube. The second set of experiments was run using saturated $NaNH_2$ solutions. Here the volume of the tubes and the quantity of ammonia were kept constant and the quantity of metal varied. The results of the two sets of experiments are shown in Table IV. In both cases the intensity of the spectrum was linearly dependent on the square root of the hydrogen pressure.

Temperature Dependence of the Equilibrium.—The temperature dependences of the equilibrium constants of reactions 1 and 3 were obtained by measuring signal intensities for systems equilibrated at various temperatures. We did not calculate absolute equilibrium constants for each temperature, but rather calculated the ratios of the equilibrium constant at room

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TABLE IV

HYDROGEN PRESSURE DEPENDENCE

Hydrogen press, atm	Signal intensity	Electron concn, $10^6 M$	10^{-5} × equilibrium constant
	1.0 M KNH_2 Solution		
35.5	5.70	13.1	1.4[a]
29.0	4.92	11.3	1.5[a]
19.4	4.32	9.92	1.4[a]
16.8	3.68	8.43	1.5[a]
10.0	2.87	6.60	1.5[a]
	Saturated $NaNH_2$ Solution (0.027 M)		
38	0.418	0.94	33,000[b]
34	0.382	0.87	34,000[b]
25	0.310	0.71	36,000[b]
22	0.316	0.71	34,000[b]
19	0.281	0.64	34,000[b]
14	0.243	0.56	34,000[b]

[a] From the expression $K = [NH_2^-]\gamma_\pm^2 P_{H_2}^{1/2}/[e^-]\gamma_\pm^2$. [b] From the expression $K = P_{H_2}^{1/2}/[Na^+][e^-]\gamma_\pm^2$. The activity coefficients were estimated from ref 15 and 16.

temperature to that at each temperature, K_{rt}/K. The signal intensity value had to be corrected for the change in the Boltzmann distribution of the energy levels with changing temperature. At a given temperature the distribution ratio is given by the expression $N_2/N_1 = \exp(-\Delta E/kT)$. By expanding and neglecting higher order terms we obtain the relation $N_2 - N_1 = -N_1\Delta E/kT$. The quantity $N_2 - N_1$ is proportional to the signal intensity so we corrected the relative intensity values S/S_{rt} by multiplying by the ratio T/T_{rt}.

The ratio of the equilibrium quotients for reaction 1

$$\frac{K_{rt}}{K} = \frac{[e_{am}^-]}{[e_{am}^-]_{rt}} \frac{[NH_2^-]_{rt}}{[NH_2^-]} \frac{P_{rt}^{1/2}}{P^{1/2}}$$

had to be corrected for the change in the hydrogen pressure with temperature and the change in the NH_2^- concentration due to the change in the density of the solution. The pressure correction was made by assuming that hydrogen gas behaves ideally and by taking into consideration the change in solubility of hydrogen in liquid ammonia with changing temperature and pressure.[10] The NH_2^- concentration is directly proportional to the density of the solution; therefore, density was substituted for the NH_2^- concentration in the above expression for K_{rt}/K. As a fair approximation for the density of the solution we used the density of liquid ammonia.[8] The complete expression for reaction 1 was

$$\frac{K_{rt}}{K} = \frac{S}{S_{rt}} \frac{T}{T_{rt}} \frac{D_{rt}}{D} \left(\frac{P_{rt}}{P}\right)^{1/2}$$

The ratio K_{rt}/K is plotted against $1/T$ in Figure 7. It will be noted that all the points for several different amide concentrations fall fairly well on one straight line. From the slope we calculate $\Delta H° = -15.7$ kcal/mole for reaction 1.

The ratio of the equilibrium constants for reaction 2 is

$$\frac{K_{rt}}{K} = \frac{[e_{am}^-][Na^+]P_{rt}^{1/2}}{[e_{am}^-]_{rt}[Na^+]_{rt}P^{1/2}}$$

We approximated the terms involving the electron and sodium ion as shown above and obtained

$$\frac{K_{rt}}{K} = \frac{S}{S_{rt}} \frac{T}{T_{rt}} \frac{D}{D_{rt}} \left(\frac{P_{rt}}{P}\right)^{1/2}$$

This ratio is plotted against $1/T$ in Figure 8; the slope yields $\Delta H° = -12.3$ kcal/mole for reaction 3.

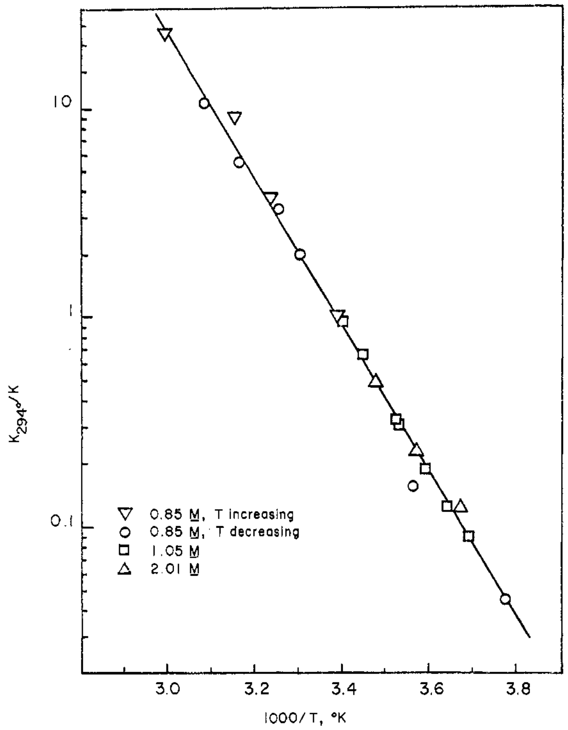

Figure 7.—Logarithm of the ratio $K_{294°}/K$ vs. 1000/T for solutions of KNH_2 in equilibrium with hydrogen.

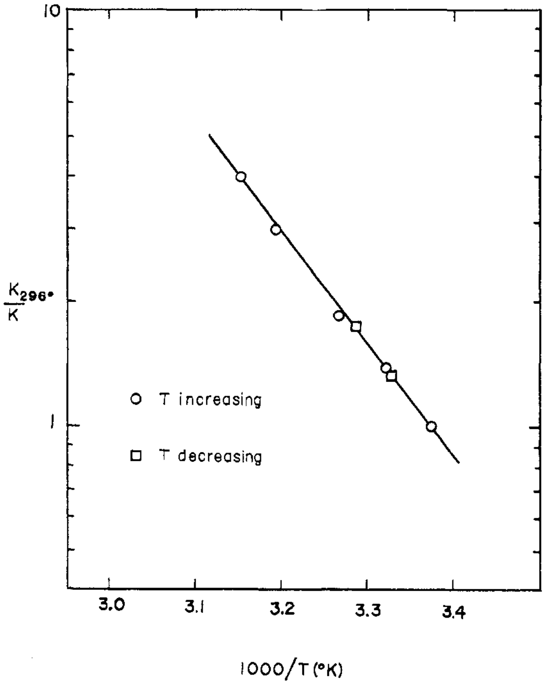

Figure 8.—Logarithm of the ratio $K_{296°}/K$ vs. 1000/T for a saturated solution of $NaNH_2$ in equilibrium with hydrogen.

Discussion

It seems certain that chemical equilibrium was achieved in our studies of reactions 1 and 3. For systems in which the amide concentration was held constant, the concentration of electrons (whether determined optically or by esr) was proportional to the square root of the hydrogen pressure.

Equilibrium quotients calculated from data for reaction 1 were found to increase markedly with increasing concentration of amide ion. However when these quotients were corrected to "constants" by use of estimated activity coefficients, the values were reasonably constant with changing amide concentration. The equilibrium constant at 25° corresponding to the most dilute solutions, $K = 5 \times 10^4$, is in fair agreement with that calculated indirectly from the known free energies of formation[2] of the species in reaction 1, $K = 1.2 \times 10^6$. Our experimental value of the heat for reaction 1, $\Delta H° = -15.7$ kcal/mole, is probably in reasonable agreement with that calculated indirectly from calorimetric data,[2] $\Delta H° = -11.5$ kcal/mole, particularly in view of the inaccuracies associated with heats determined from temperature coefficients. An equilibrium constant of 3×10^9 was calculated from data for reaction 3, using estimated activity coefficients. This value may be compared with the value 1.3×10^{10} calculated indirectly from the known free energies of formation of the species in reaction 3.[2,4] In view of the fact that our experimental value of the heat for reaction 3, $\Delta H° = -12.3$ kcal/mole, was obtained from data in a very narrow temperature interval, it is in remarkably good agreement with the heat calculated indirectly from calorimetric data, $\Delta H° = -11.7$ kcal/mole.[2,4]

Of the various species in reactions 1 and 3, that for which the free energy of formation is least accurately known is the electron, e_{am}^-. Using the tabulated[2,4] free energies for the other species and our directly determined equilibrium constants for reactions 1 and 3, we calculate the values 44.1 and 45.1 kcal/mole, respectively, for $\Delta F_f°(e_{am}^-)$ at 25°. We recommend use of the average value, 44.6 kcal/mole.

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Liquid Ammonia Solutions. V. Solutions of Hydrogen Sulfide

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The results of spectrophotometric experiments and potentiometric titrations on anhydrous liquid ammonia solutions of H_2S and the alkali metal sulfides suggest that the former undergoes ionization to give a hydrogen-bonded species, $SH^- \cdots NH_3$ or $S^{2-} \cdots HNH_3^+$. The ionization constant for the process $H_2S + 2NH_3 \rightleftarrows SH^- \cdots NH_3 + NH_4^+$ has been estimated as $(1.04 \pm 0.19) \times 10^{-2}$. The hydrogen-bonded product formed in this ionization does not have the same characteristics as sulfide ions arising from the dissolution of alkali metal sulfides in liquid ammonia.

Introduction

The band at 230 mμ in the electronic spectrum of aqueous solutions containing hydrosulfide ion (HS^-),[1] which has been attributed[2] to a charge-transfer-to-solvent electronic transition and shows the environmental dependence associated with this type of transition,[3] has been used to estimate the first and second dissociation constants of hydrogen sulfide in this medium.[1c] The band at 360 mμ in the spectrum of solutions containing the sulfide ion (S^{2-})[3,4] has also been characterized[3] as arising from a charge-transfer-to-solvent transition.

We present here the results of a study on the nature of the species present in anhydrous liquid ammonia solutions of hydrogen sulfide, which bear on the questions of (a) the relative acidity of substances in liquid ammonia and (b) the constitution of solutions of sulfur in liquid ammonia.[5]

Experimental Section

The spectra of liquid ammonia solutions were determined with the equipment and using the rinsing techniques described in previous publications from this laboratory.[6] Assuming that the vapor pressure lowering for the very dilute solutions studied ($\sim 10^{-4}$ *m*) was negligible, the temperatures of the solutions were conveniently estimated from their vapor pressures; initial experiments using a calibrated thermistor probe indicated that the

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