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LIQUID AMMONIA

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LIQUID AMMONIA

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Liquid Ammonia

I. Introduction

The chemistry of liquid ammonia has been studied so extensively that it cannot be adequately discussed in less than a book. In writing this chapter, we have decided not to attempt to cover all aspects of the solvent, but rather to discuss those aspects which are susceptible of quantitative treatment. We have emphasized the application of thermodynamics and kinetics to liquid ammonia chemistry. It should be recognized that this type of treatment is possible only as a result of many physical-chemical studies carried out in recent years. We hope, however, that it will be apparent that much remains to be done in the systematization of liquid ammonia chemistry.

In other books and review articles, liquid ammonia has normally been discussed in rather qualitative terms. The principal device for systematizing the chemistry has usually been analogy with aqueous chemistry. Some important literature sources are listed below. These chapters and articles are recommended as sources of information on topics not covered, or only touched on, in this chapter.

General

Chapters 3-6 in "Non-Aqueous Solvents", by Audrieth and Kleinberg (1953).
Chapter 4 in "Systematic Inorganic Chemistry", by Yost and Russell (1944).
"The Nitrogen System of Compounds", by Franklin (1935).
Chapter 2 in "Chemistry in Non-Aqueous Solvents", by Sisler (1961).
Chapter 3 in "Die Chemie in Wasserähnlichen Lösungsmitteln", by Jander (1949).

Review article: "Inorganic Reactions in Liquid Ammonia", by Fowles and Nicholls (1962).

Specific

Ammonolysis: Fernelius and Bowman (1940).

Alkali amides: Bergstrom and Fernelius (1933, 1937) and Levine and Fernelius (1954).

Metal-ammonia solutions: Kraus (1953), Jolly (1959), Symons (1959), and Lepoutre and Sienko (1964).

Reactions of metal-ammonia solutions: Watt (1950), Birch (1950), and Birch and Smith (1958).

Chemical thermodynamics: Jolly (1956).

II. Physical Properties of Ammonia

In this section, we tabulate the important physical properties of ammonia.

A. Vapor Pressure of Solid Ammonia (Armstrong)

(Based on 0°C = 273.16°K)

T°K	t°C	$P_{mm.}$
175	-98.16	4.85
180	-93.16	8.78
185	-88.16	15.42
190	-83.16	26.27
195	-78.16	43.57
195.46	-77.70	45.58 (triple point)

$$\log_{10} P_{(mm)} = 9.98379 - \frac{1627.22}{T}$$

B. Vapor Pressure of Liquid Ammonia (Armstrong)

(Based on 0°C = 273.16°K)

T°K	t°C	$P_{mm.}$	
195.46	-77.70	45.58	(triple point)
200	-73.16	64.92	
210	-63.16	133.21	
220	-53.16	253.97	
230	-43.16	454.28	
239.78	-33.38	760	(boiling point)
240	-33.16	768.43	
250	-23.16	1237.5	
260	-13.16	1914.8	
270	- 3.16	2857.1	
280	6.84	4130.0	
290	16.84	5804.2	
298.16	25.00	7520.5	
300	26.84	7956.6	
320	46.84	14028	
340	66.84	23089	
360	86.84	35973	
380	106.84	53597	
400	126.84	77334	
405.6	132.4	85400	(critical point)

$$\log_{10} P_{(mm)} = 9.95028 - \frac{1473.17}{T} - 0.0038603T \text{ (for } T < 250°K)$$

C. Heat of Fusion of Ammonia (Overstreet and Giauque, 1937)

$$\Delta H = 1351.6 \text{ cal./mole}$$

D. Heat of Vaporization of Ammonia at Boiling Point

(Overstreet and Giauque, 1937)

ΔH = 5581 cal./mole

E. Heat Capacity of Ammonia (Overstreet and Giauque, 1937)

(Based on 0°C = 273.10°K and a temperature scale appreciably different from the International Temperature Scale)

T°K	C_p	T°K	C_p	T°K	C_p
20	0.368	110	6.877	200	17.58 (ℓ)
30	1.033	120	7.497	210	17.75
40	1.841	130	8.102	220	17.90
50	2.663	140	8.699	230	18.03
60	3.474	150	9.272	240	18.12
70	4.232	160	9.846		
80	4.954	170	10.42		
90	5.612	180	11.03		
100	6.246	190	11.71 (s)		

F. Thermodynamic Functions for Ammonia Gas at 25°C

(Rossini <u>et al</u>, 1952)

ΔH°_f = - 11.04 kcal./mole

ΔF°_f = - 3.976 kcal./mole

S° = 46.01 e.u.

C°_p = 8.523 cal./deg. mole

G. Density of Liquid Ammonia (Cragoe and Harper, 1921)

t°C	density (g/ml)
-70	.7253
-60	.7138
-50	.7020
-40	.6900
-34	.6826
-33	.6814
-30	.6776
-20	.6650
-10	.6520
0	.6386
10	.6247
20	.6103
25	.6028
30	.5952

H. Viscosity of Liquid Ammonia

t°C	Viscosity, centipoises	Reference
-33.5	.2543	(a)
-26	.230	(b)
-10	.183	(b)
- 4	.170	(b)
5	.1618	(c)
10	.152	(b)
15	.1457, .1479	(c), (d)

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t°C	Viscosity, centipoises	Reference
20	.1411	(d)
25	.1350, .1345	(c), (d)
30	.138	(b)
50	.125	(b)

(a) Elsey (1920)

(b) Pinevich (1948)

(c) Plank and Hunt (1939)

(d) Shatenshtein et al. (1949)

I. Dielectric Constant of Liquid Ammonia (Grubb et al., 1936)

t°C	Dielectric Const.
-60 ± 10	26.7
-33	(23) interpolated
5	18.94
15	17.82
25	16.90
35	16.26

J. Surface Tension of Liquid Ammonia (Berthoud, 1918; Stairs and Sienko, 1956)

t°C	γ, erg/cm^2
11.10	23.38
34.05	18.05
58.98	12.95

where t = °C., $\gamma = 23.41 - 0.3371t - 0.000943t^2$ $(-75° < t < -39°)$

K. Crystal Structure (Vegard and Hillesund, 1942)

Cubic, 4 molecules per unit cell.

at -185°, a_o = 5.2253 kX

= 5.2358 Å.

Calculated density = 0.7881 g./cc.

L. Electrical Conductivity of Liquid (Hnizda and Kraus, 1949)

$L_o \sim 1 \times 10^{-11}$ ohm^{-1} cm^{-1} (very pure NH_3)

M. Refractive Index of Liquid (Franklin, 1935)

η = 1.325 at 16° for λ = 5899 Å.

N. Some Derived Constants

Freezing point constant, $K_f = \frac{RT_f^2}{1000\ \Delta H_f} = 0.9567$

Boiling point constant, $K_b = \frac{RT_b^2}{1000\ \Delta H_v} = 0.3487$

III. Physical Properties of Liquid Ammonia Solutions

A. Non-Electrolytes

Liquid ammonia is an excellent solvent for many non-electrolytes that are relatively insoluble in water. (See Section IV A 1.) Most research on these solutions has centered on practical problems such as the separation by extraction and crystallization of materials which are difficultly separable. We shall mention here only a few basic studies in the area of non-electrolytic solutions.

Phase studies have been performed on several hydrocarbon-liquid ammonia systems by Ishida (1957 a & b, 1958, 1960). It was found that the experimental data for both the critical composition and the activity coefficients are best interpreted by the solubility parameter theory if it is assumed that ammonia is associated nearly to a dimer as a liquid.

Some data are available on the heats of solution for non-electrolytes in liquid ammonia. It has been observed by Schmidt et al (1941) that the molar heats of solution of normal alcohols in liquid ammonia decrease from 1960 calories for methanol to -100 calories for normal butanol. Gunn and Green (1960) found that the molar heats of solution for water and methylamine are independent of concentration.

It is interesting that nitrogen (Wiebe and Tremearne, 1933), hydrogen (Ipat'ev and Teodorovich, 1932), helium and argon (Cseko and Cornides, 1960) all obey Henry's Law up to pressures of about 100 atmospheres when dissolved in liquid ammonia. The temperature dependence of the solubility of the mixture $N_2 + 3\ H_2$ in liquid ammonia was studied by Lefrancois and Vaniscotte (1960). They observed that the solubility follows a third order function of the temperature (°C).

The spectra, from 2500 to 6000 Å, of solutions of several nitrophenols and nitronaphthols in liquid ammonia have been interpreted by Dykhno and Shatenshtein (1948, 1951). Comparison was made with the spectra of these same molecules in 0.005 M NaOH solutions in water. General similarities were found in the spectra of both solvent systems, however the peaks were shifted to higher wavelengths in liquid ammonia. These shifts were attributed to the formation of acid-base complexes.

B. Electrolytes

Solutions of electrolytes in liquid ammonia have been subjected to extensive research. Nearly all the types of measurements which have been made with aqueous solutions of electrolytes have also been made with liquid ammonia solutions even though the handling of liquid ammonia is more difficult than that of water. It is not possible to present the results of all the work which has been carried out in determining the nature of electrolyte-liquid ammonia solutions. However, some of the more important data and conclusions will be covered.

1. Molar Volumes

The densities of the solutions of several alkali metal halides and ammonium halides have been measured at various temperatures and concentrations (Johnson and Martens, 1936; Kikuchi and Kudo, 1944). It was found (Johnson and Martens, 1936) that the densities vary linearly with the temperature and that the apparent molar volumes are a linear function of $c^{\frac{1}{2}}$ (in moles/liter). This behavior is entirely similar to that found in aqueous solutions.

In more recent work, Gunn and Green (1962 a) have determined the apparent molar volumes of several electrolytes in liquid ammonia at 0°C. They find that plots of V versus $c^{\frac{1}{2}}$ (in equivalents/liter) have almost the same shapes for several alkali metal halides, ammonium halides, and barium nitrate. Even at concentrations where considerable ion pairing would be expected, the ion additivity rule is obeyed. Using estimated association constants, Gunn and Green extrapolate their data to infinite dilution to obtain the volumes given in Table I. The table includes the volumes of the same salts in water at 25°C (Harned and Owen, 1958).

Table I.

Some Molar Volumes at Infinite Dilution in Ammonia and Water

Salt	V° in NH_3 at 0°C	V° in H_2O at 25°C
NaCl	-38 cc	16.4 cc
NaI	-55 cc	35.1 cc
KI	- 6 cc	45.4 cc

From the data it may be noted that

$$V^\circ_{NaI}(NH_3, 0°) - V^\circ_{NaCl}(NH_3, 0°) = 23 \text{ cc.}$$

$$V^\circ_{NaI}(H_2O, 25°) - V^\circ_{NaCl}(H_2O, 25°) = 18.7 \text{ cc.}$$

thus $V^\circ_{I^-}(NH_3) - V^\circ_{Cl^-}(NH_3) \approx V^\circ_{I^-}(H_2O) - V^\circ_{Cl}(H_2O)$

and $V^\circ_{KI}(NH_3, 0°) - V^\circ_{NaI}(NH_3, 0°) = 9 \text{ cc.}$

$$V^\circ_{KI}(H_2O, 25°) - V^\circ_{NaI}(H_2O, 25°) = 10.3 \text{ cc.}$$

thus $V^\circ_{K^+}(NH_3) - V^\circ_{Na^+}(NH_3) \approx V^\circ_{K^+}(H_2O) - V^\circ_{Na^+}(H_2O)$

Since there is no "absolute" way of finding the V° for any single ion, the ionic V° values still remain unknown. Ionic volumes obtained by assuming that $V^\circ_{K^+} = V^\circ_{Cl^-}$ have been given elsewhere (Jolly, 1959); a more detailed calculation will be given here. Using an expression similar to Hepler's (1957), one calculates a $V^\circ_{Na^+}$ (in ammonia at 0°C)

of - 41.5 cc. The expression of Couture and Laidler (1956) yields the value -34 cc. If we take the average of these two, we calculate

$$V^{\circ}_{Na+} = -37 \text{ cc}$$

$$V^{\circ}_{K+} = -28 \text{ cc}$$

$$V^{\circ}_{Cl-} = -1 \text{ cc}$$

$$V^{\circ}_{I-} = +22 \text{ cc}$$

2. Thermochemistry

The heats of solution of several electrolytes in liquid ammonia have been measured at 25°C and -33°C by Gunn and Green (1960). Table II gives the heats of solution of several salts in ammonia at 25°C and -33°C and in water at 25°C. The heats of solution are all for a mole ratio of solvent to solute of 500. It will be noted that the heats of solution are more negative in ammonia than in water, and are likewise more negative at 25°C than at -33°C.

Table II.

Some Heats of Solution in Water and Ammonia ($\Delta H°$ in kcal./mole)

	$H_2O(25°C)$ (a)	$NH_3(25°C)$ (b)	$NH_3(-33°C)$ (b)
$H_2O(\ell)$	0	- 3.32	- 2.81
$CH_3NH_2(\ell)$	-5.0	+ 0.50	—
HgI_2	—	(-20.8)	(-20.15)
NaCl	+1.02	- 6.75	- 1.57
KI	+4.95	- 9.44	- 7.89
CsI	+7.9	- 5.27	—
NH_4Cl	+3.71	- 8.23	- 6.95
NH_4I	+3.3	-16.10	-13.37
$Ba(NO_3)_2$	+9.96	-15.31	—

(a) Rossini *et al* (1952)

(b) Gunn and Green (1960)

The slope obtained from a plot of the heat of solution versus $c^{\frac{1}{2}}$ for KI solutions of low concentrations is 27 kcal mole $^{-3/2}$ liter$^{1/2}$. This is almost twelve times the calculated Debye-Hückel slope and undoubtedly is the result of a high degree of ionic association in liquid ammonia. Therefore the thermal effects accompanying dilution are principally due to dissociation of the ion pairs and solvation of the resulting ions; that is, KI in liquid ammonia is analogous to most "strong" 2-2 salts in water.

3. Electrochemistry

a. Conductance: The conductances of several salts and acids in liquid ammonia have been determined. Unfortunately, the agreement between equivalent conductances measured by different experimenters has seldom been as good as that found for aqueous solutions. Some of the better conductance data are presented in Table III. The data are not exactly self-consistent. Thus, using the data of Hnizda and Kraus at -34°,

$$\Lambda^{\circ}_{KBr} - \Lambda^{\circ}_{NaBr} = 32.5 = \lambda^{\circ}_{K^+} - \lambda^{\circ}_{Na^+}$$

while from the data of Monoszon and Pleskov at -33.5°,

$$\hat{}^{\circ}_{KNO_3} - \hat{}^{\circ}_{NaNO_3} = 39 = \lambda^{\circ}_{K^+} - \lambda^{\circ}_{Na^+}$$

Monoszon and Pleskov have used the transference data of Franklin and Cady (1904) to assign λ°_{+} to the alkali metal ions and λ°_{-} to the nitrate ion, but due to the lack of agreement in the nitrate and halide data, there is no advantage gained by assigning λ°_{-} values to the halide ions.

It will be noted that the association constants of the potassium halides follow the order expected from the relative sizes of the halide ions. However, it is surprising that the values for the closest distance of approach, å, of the potassium and halide ions which best fit the extended Onsager-Fuoss conductance theory are larger than they are in either water or methanol (Kay, 1960). The å values for aqueous solutions often agree closely with the sum of the ionic radii (Fuoss and Accascina, 1959). However, this is apparently not true for the alkali metal halides in liquid ammonia.

b. Polarography: Polarographic studies using the dropping mercury electrode have contributed much to our understanding of the nature of

Table III.

Conductances of Salt Solutions in Ammonia and Water

Electrolyte	Temperature °C	Λ° in NH_3	10^8 å	$K_{assoc.}$	Reference	Λ° in H_2O at 25°
KCl	-34	348.0	6.7	1060	(1)	149.9
KBr	-34	346.8	7.8	453	(1)	151.9
KI	-34	345.1	6.6	183	(1)	150.4
NaBr	-34	314.3	5.9	263	(1)	128.3
$LiNO_3$	-33.5	299			(2)	110.1
$LiNO_3$	-40	290			(2)	110.1
$NaNO_3$	-33.5	315			(2)	121.6
$NaNO_3$	-40	300			(2)	121.6
KNO_3	-33.5	354			(2)	145.0
KNO_3	-40	338			(2)	145.0
$RbNO_3$	-40	344			(2)	149.2
$CsNO_3$	-40	345			(2)	148.7
KNH_2	-33	343		13,700	(3)	

(1) Data are those of Hnizda and Kraus (1949). These data were recently treated by Kay (1960), using the extended form of the Onsager-Fuoss conductance theory (Fuoss and Accascina, 1959).

(2) Monoszon and Pleskov (1931).

(3) Hawes (1933).

solutions of electrolytes in liquid ammonia, in spite of the fact that the freezing point of mercury (-38.9°C) is very close to the boiling point of liquid ammonia (-33.4°C). Polarograms can indicate whether the reduction occurs in one or more steps and thereby also indicate the nature of intermediate species that are involved.

Thus Laitinen and Shoemaker (1950 a) showed that the oxidation product of the Hg pool anode during polarographic measurements in liquid ammonia is Hg^{2+}, and that the Hg-Hg^{2+} electrode behaves reversibly in liquid ammonia.

Table IV presents the half-wave potentials for several reduction processes in liquid ammonia at -36°. The half-wave potentials given are versus a Pb/0.1N$Pb(NO_3)_2$ electrode.

When the cation of the indifferent electrolyte is non-reducible, platinum and mercury electrodes act as electron electrodes in liquid ammonia. The standard potential of the electron electrode relative to the standard hydrogen electrode at -36°C is -1.9 volts.

Schaap et al (1961) have used a high-pressure polarographic cell for measurements at room temperature.

C. Metals

In spite of the large amount of work done on metal-ammonia solutions since they were first studied by Weyl (1864), there is still some uncertainty concerning the nature of the solutions. All metal-ammonia solutions are metastable and decompose to give hydrogen and the metal amide. Since this reaction is catalyzed by certain impurities, the need for extreme care and cleanliness when working with these solutions cannot be overemphasized. This could well be the

Table IV.

Polarographic Half-Wave Potentials in Ammonia at -36°

Species Reduced	$E_{\frac{1}{2}}$ (volts)	Reversibility	Reference
Li^+	-1.67	Rev.	(1)
Na^+	-1.31	Rev.	(1)
K^+	-1.24	Rev.	(1)
Rb^+	-1.21	Rev.	(1)
Cs^+	-1.15	Rev.	(1)
Tl^+	+0.15	Rev.	(2)
$Cu^{2+} \rightarrow Cu^+$	+0.16	Rev.	(2)
$Cu^+ \rightarrow$ amalgam	-0.21	Irrev.	(2)
NH_4^+	-1.37	Rev.	(2)
$Pb^{2+} \rightarrow$ Pb amalgam	-0.01	Rev.	(3)
$Ca^{2+} \rightarrow$ Cd	-0.45	Rev.	(3)
$Ni^{2+} \rightarrow$ Ni	-0.79	Irrev.	(3)
Zn^{2+}	-0.89	Irrev.	(3)
$Ca^{2+} \rightarrow$ Ca	-1.96	—	(4)
$Sr^{2+} \rightarrow$ Sr	-1.68	—	(4)
$Ba^{2+} \rightarrow$ Ba	-1.59	—	(4)

(1) Laitinen and Nyman (1948 a & b)

(2) Laitinen and Shoemaker (1950 b)

(3) McElroy and Laitinen (1953)

(4) Nyman (1949)

source of much of the disagreement found in the results obtained by various workers in these systems. It is generally agreed however, that when a metal is dissolved in liquid ammonia, it dissociates into a metal ion and electron(s), at least in very dilute solutions.

1. Phase Diagrams

The metals which dissolve in liquid ammonia are those with low ionization potentials and high solvation energies. Thus the alkali metals, the alkaline earth metals heavier than beryllium, and those rare earths which exhibit the +2 oxidation state are soluble.

The solubilities of the alkali metals are given in Table V. The alkaline earth metals europium and ytterbium do not exist in equilibrium with their solutions. These metals form solid hexammoniates. The hexammoniate of calcium separates out at a concentration of 10 mole percent calcium at -64°C. and 11 mole percent calcium at 0°C. The NH_3/hexammoniate ratio is about 4 to 5, which is about the same as the NH_3/metal ratio for the alkali metals.

A portion of the phase diagram for the sodium ammonia system is shown in Figure 1. The significant features of this diagram (which are general for metal-ammonia systems) are: (1) a steep solubility curve for the metal or its hexammoniate, (2) a low temperature eutectic point, and (3) a miscibility gap in the liquid region corresponding to the coexistence of two different metal solutions. In the region of the miscibility gap, the more concentrated phase is bronze colored and less dense than the blue phase, which is of considerably lower concentration at the lower temperatures. The alkali metals, except cesium, and the alkaline earth metals all show this behavior. Sienko (1964) has reviewed

Table V.

Solubilities of Metals in Liquid Ammonia

Metal	Temperature °C	Gram atoms of metal per 1000 g. NH_3	Moles NH_3 per gram atom of metal
Lithium	0	16.31	3.60
(1, 2)	-33.2	15.66	3.75
	-39.4	16.25	3.61
	-63.5	15.41	3.81
Sodium	22	9.56	6.14
(3, 4, 5)	0	10.00	5.87
	-30	10.63	5.52
	-33.8	10.72	5.48
	-33.5	10.93	5.37
	-50	10.89	5.39
	-70	11.29	5.20
	-105	11.79	4.98
Potassium	0	12.4	4.68, 4.74
(3, 4, 5, 6)	-33.2	11.86	4.95
	-50	12.3	5.05, 4.79
	-100	12.2	4.82
	-33.5	12.05	4.87
Cesium	-50	25.1	2.34
(7)			

(1) Johnson and Piskur (1933)
(2) Kraus and Johnson (1925)
(3) Johnson and Meyer (1932)
(4) Kraus and Lucasse (1921)
(5) Ruff and Geisel (1906)
(6) Johnson and Meyer (1929
(7) Hodgins (1949)

the subject of metal-ammonia systems, and has proposed an electron model which predicts consolute concentrations of 3.9 atom % metal in ammonia, in remarkable agreement with observed values.

There are other differences between the alkali metal- and alkaline earth metal-ammonia systems besides the difference in the solid species that exist in equilibrium with saturated solutions. Whereas the upper consolute temperature for the sodium-ammonia two liquid equilibrium is -41.6°, the upper consolute temperature for calcium-ammonia solutions is not yet reached at 50° (Jolly, Hallada and Gold, 1964). The concentration at which the second phase first begins to appear is much lower for calcium solutions than for sodium solutions (Hallada and Jolly, 1963). The eutectic temperatures are much lower for alkali metal-ammonia systems than for the alkaline earth metal-ammonia systems. The eutectic points of several systems are given in Table VI.

Table VI.

Metal-Ammonia Eutectics
(Birch and MacDonald, 1947; 1948)

Metal	t, °C	Mole Percentage Metal
Li	-185	22
K	-157	15
Cs	-118	—
Ca	-87	12
Sr	-89	7
Ba	-89	7.7

2. Molar Volumes

When a metal is dissolved in liquid ammonia, there is a large net increase in volume. Table VII presents the densities of saturated solutions of lithium, sodium and potassium at several temperatures.

Table VII.

Densities of Saturated Solutions of Alkali Metals in Ammonia

Lithium (1)		Sodium (2)		Potassium (2)	
t, °C	Density	t, °C	Density	t, °C	Density
19	0.477	-31.6	0.576	-33.3	0.625
-80	0.495	-33.3	0.578	-39.0	0.627
		-40.7	0.581	-41.0	0.629
		-47.0	0.585	-46.4	0.636
		-51.0	0.587	-49.6	0.638

(1) Jaffe (1935)

(2) Johnson, Meyer and Martens (1950)

Gunn and Green (1962 a) found that the apparent molar volumes at 0°C. of alkali metals change only slightly over the concentration range 0.01 to 1.0 molar. They assign the following partial molar volumes at infinite dilution:

$$V^{\circ}_{Li} = 49 \text{ cc.}$$

$$V^{\circ}_{Na} = 57 \text{ cc.}$$

$$V^{\circ}_{K} = 65 \text{ cc.}$$

Using the values of the partial molar volumes at infinite dilution that were given earlier (section B-1) for KI and NaI, one obtains the molar volume of the solvated electron at infinite dilution:

$$V^\circ_K - V^\circ_{KI} = 65 - (-6) = 71 \text{ cc} = V^\circ_{e^-} - V^\circ_{I^-}$$

$$V^\circ_{Na} - V^\circ_{NaI} = 57 - (-15) = 72 \text{ cc} = V^\circ_{e^-} - V^\circ_{I^-}$$

Since $V^\circ_{I^-} = 22$ cc,

$$V^\circ_{e^-} = 94 \text{ cc per mole}$$

This volume corresponds to a sphere of radius 3.34 Å. Other calculations have also led to values around 3 Å for the elctron cavity radius (Jolly, 1959; Hutchison and O'Reilly, 1962 a).

3. Thermochemistry

The alkali metals, except lithium, have very low heats of solution, but the metals that form solid ammoniates evolve large amounts of heat when they are dissolved in liquid ammonia. The heats of solution of several metals are given in Table VIII.

The heat of dilution of sodium is endothermic, and when NaI is present, the heat of dilution is greater. (Gunn and Green, 1962 b)

The heat of ammonation of the electron (that is, the heat of transfer from the gas phase to ammonia) is of considerable interest. Coulter (1953) calculated an ammonation heat of -11 kcal./mole. This seems to be too positive compared to the experimental photoelectric threshold energy, 33 kcal./mole (Hasing 1940); a value for the heat of ammonation of the electron of about -40 kcal./mole seems more reasonable (Jolly, 1959). Jortner (1959) theoretically calculated

Table VIII.

Heats of Solution of Metals in Ammonia at -33°C

Metal	Concentration (Molarity)	$\Delta H°$ (kcal/mole)	Reference
Li	0.067	- 9.65	(1)
Na	0.4	+ 1.4	(2)
K	0.07	0.0	(2), (3)
Rb	0.13	0.0	(3)
Cs	0.19	0.0	(3)
Ca	0.023	-19.7	(4)
Sr	–	-20.7	(5), (6)
Ba	–	-19.0	(5), (6)

(1) Coulter and Monchik (1951)

(2) Kraus and Schmidt (1934)

(3) Schmidt, Studer and Sottysiak (1938)

(4) Wolsky, Zdanuk, and Coulter (1952)

(5) Coulter (1953)

(6) Wolsky (1952)

a heat of solution of -39 kcal./mole for the electron in a cavity of radius 3.2-3.4 Å.

4. Electrical Conductance

The equivalent conductances of metal solutions in liquid ammonia are greater than those for any other type of electrolyte in any

known solvent. The specific conductivities of concentrated solutions are of the same order of magnitude as the conductivities of metals, and the equivalent conductances of dilute solutions approach values near 1000, i.e. some five to ten times the values for salts in water. (Kraus and Lucasse, 1921) The equivalent conductances of lithium, sodium and potassium are given in Figure 2. It will be noticed that as the concentration increases from infinite dilution the equivalent conductance decreases to a minimum near 0.04 molar, and then increases very abruptly with increasing concentration.

Transference studies of sodium solutions have shown that the conductance of the electron, λ_-, has a minimum value at about 0.04 molar, whereas the conductance of the sodium ion, λ_+, decreases continuously as concentration increases. (Dye _et al_, 1960) The ratio T_-/T_+ varies from seven in dilute solutions to 280 at _ca_. 0.9 molar (Kraus, 1914). These transference data show that the behavior of the conductance curves is determined primarily by the mobility of the electron.

The temperature coefficient of specific conductivity for sodium

$$\frac{\Delta K}{\Delta t} \cdot \frac{100}{K_{-33.5°C}}$$

is 1.9% per degree for dilute solutions, reaches a maximum of about 4% per degree at _ca_ 1 molar, and falls almost to zero at higher concentrations (Kraus and Lucasse, 1922 and 1923). These data are not explicable by changes in viscosity, and must be due to quite different conduction mechanisms in the various concentration regions. A review of the many mechanisms that have been proposed for the low field conductance has been given elsewhere (Jolly, 1959).

In measurements of the Wien effect, fields of magnitude 15,000 volts/cm. gave a 4 per cent increase in the conductivity of alkali metal solutions (Lepoutre and Patterson, 1955). Comparable increases in aqueous solutions of electrolytes require fields of magnitude 100,000 volts/cm.

5. Magnetic Properties

The molar magnetic susceptibility of an alkali metal solution approaches that of a mole of free electron spins, $N\mu_o^2/kT$, at infinite dilution. As the concentration is increased, however, the molar susceptibility decreases rapidly. (Freed and Sugarman, 1943) Comparison of static susceptibilities of sodium and potassium and susceptibilities obtained from paramagnetic resonance measurements has been interpreted to indicate that the radius of the cavity in which the electron resides is 3.0 Å (Hutchison and Pastor, 1953). This agrees well with what we calculated earlier from partial molar volumes. The paramagnetic resonance line width for potassium solutions is only about 0.03 gauss. The line width varies directly with viscosity (Levy, 1956) and has been interpreted as due to motionally narrowed hyperfine interactions between unpaired electrons and the protons bordering the electron cavity (Kaplan and Kittel, 1953).

The spin-spin relaxation times, T_1, and spin-lattice relaxation times, T_2, are about equal in dilute solutions, and again in concentrated solutions, of potassium; in the middle concentration range, T_1 is larger than T_2. (Hutchison and O'Reilly, 1961 b) Within a limited concentration range, T_1 and T_2 are almost equal for solutions of lithium, sodium and calcium (Cutler and Powles, 1962). The equality

of T_1 and T_2 is interpreted as meaning that the electron interaction is with the nitrogen nucleus of the ammonia, not with the protons. The relaxation times vary from 1 to 3 microseconds depending on concentration and temperature (Pollak, 1961; Cutler and Powles, 1962).

It is now well known that the nuclear magnetic resonance absorption for a given species in metallic systems occurs at higher fields than normal (Knight, 1949). McConnell and Holm (1957) measured the Knight shifts of N^{14} and Na^{23} in sodium-ammonia solutions. They found that the average hyperfine contact density of Na^{23} and an unpaired electron is 3×10^{-3} to 5×10^{-3} as large as the contact density in an isolated sodium atom when the NH_3/Na ratio of the solutions is 50 to 400. At NH_3/Na ratios less than 50, the contact density increases markedly. On the other hand, the average hyperfine contact density of N^{14} and an unpaired electron is almost 0.1 that on a N atom at all solution concentrations. This supports the suggestion that the electron interaction is with the N nucleus (Pollak, 1961). The temperature dependence of the Knight shift for sodium solutions over a hundred-fold range of concentrations was measured by Acrivos and Pitzer (1962).

6. Absorption Spectra

The blue color of dilute metal solutions is due to the short wavelength tail of a broad absorption band that peaks at approximately 15,000 Å. The spectra of the alkali metals, and at least calcium of the alkaline earth metals, are essentially the same (Gold and Jolly, 1962; Hallada and Jolly, 1963). Furthermore, the alkali metals obey Beer's law at the lower wavelengths up to concentrations as high as 0.2 molar. At wavelengths beyond 20,000 Å, there may be a positive deviation from Beer's law at the higher concentrations.

Up to concentrations at which phase separation occurs, calcium solutions also obey Beer's law at all but the highest wavelengths. The molar extinction coefficients of the calcium solutions are very nearly twice the molar extinction coefficients of the alkali metal solutions at all wavelengths.

It has been reported that addition of NaI to sodium solutions produces a new band at 8000 Å (Clark, Horsfield and Symons, 1959); however, this peak was not observed in independent experiments (Gold and Jolly, 1962). It is entirely possible that the 8000 Å peak is due to a short-lived species which disappears after a few minutes.

Reflection spectra on sodium solutions with NH_3/Na ratios of 5 to 168 were measured at 1-20 microns (Beckman and Pitzer, 1961). Dilute solutions show a strong peak near 1.5μ. The concentrated solutions show high reflectivity over broad wavelength ranges.

6. Models

In the preceeding paragraphs on the physical properties of metal-ammonia solutions, we have occasionally interpreted the data in terms of particular models. Now, in conclusion, it will be instructive to briefly review some of the microscopic models that have been proposed for metal-ammonia solutions, especially those for low and intermediate concentrations.

The early conductivity work of Kraus led him to the conclusion that, in very dilute solutions, metals dissociate to give ammoniated cations and electrons.

$$M = M^+ + e^-$$

As the concentration is increased these species associate and the conductivity decreases. Eventually, incipient metallic behavior occurs and the equivalent conductance increases rapidly.

When magnetic data became available it was obvious that the model Kraus proposed from conductivity data was not adequate, since it did not account for the pairing of electrons. The magnetic data were explained by Huster (193) and Freed and Sugarman (1943) in terms of an equilibrium between the ionic species and diamagnetic metal atom dimers:

$$2\ M^{+} + 2\ e^{-} = M_2$$

Becker *et al* (1956) showed that the conductivity data and the susceptibility data can be explained by considering both of the above equilibria. Detailed models of the species involved in these equilibria have continually evolved.

All the data are fairly well explained by assuming that the electron-in-a-cavity retains its identity even when species such as M and M_2 are being formed. The M species may be described as an ion pair in which an ammoniated metal ion and an ammoniated electron are held together by coulombic forces with little distortion of the ammoniated electron, and the M_2 species may be pictured as a quadrupolar ionic assembly of two ammoniated ions and two ammoniated electrons. The wave functions for the two electrons in the dimer overlap sufficiently so that the singlet state is lower in energy than the triplet by more than kT. The highly concentrated metal solutions are like molten metals in which the metal cations are ammoniated. (Gold *et al*, 1962)

IV. Reactions in Liquid Ammonia

A. Comparison of Ammonia with Other Solvents

1. Solubilities

The most important function of a solvent is to dissolve other substances. Thus a knowledge of the kinds of substances which a solvent is capable of dissolving is of great importance. Hildebrand (1948) has discussed the properties of liquid ammonia which are significant in comparing solubilities in ammonia with solubilities in other solvents, and, in the following paragraphs, we shall cite solubility data to illustrate the effects of these properties.

The dielectric constant of ammonia (about 23 at the boiling point) is considerably lower than that of water (78.5), and yet significantly greater than that of acetic acid (6.4). As one might expect, the solubilities of ionic salts in ammonia lie, in general, between the values for the same salts in water and acetic acid. This generalization does not hold for salts whose anions are highly polarizable, because of London forces which are discussed in a later paragraph. Some typical solubilities for these three solvents are presented in Table IX. Salts with polynegative anions, such as sulfates, carbonates, and phosphates, are practically insoluble in liquid ammonia. In such salts, the solvation energy of the ions in ammonia is insufficient to compensate for the high lattice energy.

The abnormally high boiling point of ammonia is evidence of the tendency for ammonia to form hydrogen bonds. Substances which are capable of forming hydrogen bonds with ammonia have high solubilities

Table IX.

Solubilities of Some Ionic Salts in Water, Ammonia, and Acetic Acid[a]

(Grams per 100 g. of solvent at 25°)

	Water	Ammonia	Acetic Acid
$LiNO_3$	52.2	243.7	10.3 (30°)
$NaNO_3$	91.8	97.6	0.17
KNO_3	37.8	10.4	0.18
NH_4OAc	148 (4°)	253.2	39.3
NaCl	37	3.02	0.073 (30°)

[a] Solubilities taken largely from Jander (1949) and Audrieth and Kleinberg (1953).

in ammonia, just as they have in other hydrogen-bonding solvents such as water and hydrogen fluoride. Thus sugars, esters, amines, and phenols are very soluble in liquid ammonia.

The basic character of ammonia is largely responsible for the high solubility of carboxylic acids, alcohols, and phenols in ammonia. In many cases, it may be difficult to distinguish the effects of ammonia's basicity from the effects of its tendency to hydrogen bond. A characteristic closely related to the basicity of ammonia is its tendency to coordinate to transition metal ions such as

Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, etc. Salts of such metal ions usually have high solubilities in ammonia. This coordinating characteristic of ammonia is clearly shown by the high solubilities of the silver halides in ammonia. At 25°, the solubilities (in grams per 100 g. of ammonia) are 0.83, 5.92 and 206.8 for AgCl, AgBr, and AgI, respectively. (Jander, 1949)

Molecules which do not react chemically with one another nevertheless are attracted by London, or van der Waals, forces which arise from a coupling of the motion of the electrons in the separate atoms. The London interaction energy between two molecules may be approximated by the relation

$$E_{AB} = - \frac{3\,\alpha_A \alpha_B}{2\,R^6} \quad \frac{I_A I_B}{I_A + I_B}$$

where α_A and α_B denote the polarizabilities of the molecules, R their distance apart, and I_A and I_B their ionization potentials. In the case of molecules which not only have high dipole moments, but also have enough electrons to be highly polarizable, the London forces may outweigh the dipole orientation effect. In Table X, the London and orientation potentials for water and ammonia are compared. It will be noted that the attractive potential for water depends mainly on its dipole moment, whereas that for ammonia depends almost equally on its dipole moment and its polarizability. Thus, although ammonia is generally a poorer solvent than water for ionic salts and highly polar molecules, it is a better solvent for non-polar molecules, particularly those with many electrons. The higher polarizability of the thiosulfate ion as compared with that of the sulfate ion is

Table X.

	Dispersion Potential	Orientation Potential
H_2O	47	190
NH_3	93	84

probably the cause of the fact that sodium thiosulfate dissolves to the extent of 0.17 g. per 100 g. of ammonia, whereas sodium sulfate has no detectable solubility in ammonia. Similarly, the increase in anionic polarizability on going from chloride to iodide is probably the main cause of the increase in solubility on going from AgCl to AgI, for which the data are quoted above.

The "solubility parameter", or the square root of the energy of vaporization per cc., is a useful criterion of solubility. In the absence of strong dipole and acid-base effects, substances are most soluble in one another when their solubility parameters are of the same order of magnitude. The solubility parameters for several substances, and their solubilities in ammonia, are presented in Table XI.

2. Available Oxidation Potential Range*

If all reactions in liquid ammonia were thermodynamically controlled (as opposed to kinetically controlled), no oxidizing agent more

* A table of oxidation potentials in ammonia and a discussion of their application to liquid ammonia chemistry is given by Jolly (1956).

Table XI.

Solubility Parameters and Solubilities in Ammonia[a]

	$(\Delta E_v/V)^{\frac{1}{2}}$	Solubility in Liq. NH_3
n-hexane	7.3	5.1% at 20°[b] (compare with 0.014% at 15.5° for H_2O)
carbon tetrachloride	8.6	soluble
benzene	9.2	moderately soluble
yellow phosphorus	13.1	soluble
ammonia	13.1	
water	23.8	infinitely miscible because of hydrogen-bonding, etc.
mercury	30.7	practically insoluble

[a] Solubility parameters from Hildebrand and Scott (1962).

[b] Ishida (1958)

powerful than nitrogen, and no reducing agent more powerful than hydrogen, would be capable of existence in liquid ammonia. The NH_3-N_2 and H_2-NH_3 couples, and their potentials in volts at 25°, in both acid and basic solutions are given below.

ACID SOLUTIONS (1 M NH_4^+):

$$\tfrac{1}{2} H_2 + NH_3 = NH_4^+ + e^- \qquad E° = 0$$

$$4NH_3 = \tfrac{1}{2} N_2 + 3NH_4^+ + 3e^- \qquad E° = -0.04$$

BASIC SOLUTIONS (1 $\underline{M}$ NH_2^-):

$$\tfrac{1}{2} H_2 + NH_2^- = NH_3 + e^- \qquad E^\circ = 1.59$$

$$3NH_2^- = \tfrac{1}{2} N_2 + 2NH_3 + 3e^- \qquad E^\circ = 1.55$$

Obviously with only a 0.04 volt range available, hardly any species are thermodynamically stable in ammonia. Fortunately, however, both the hydrogen couple and the nitrogen couple usually exhibit "overvoltages" of about one volt. So in acid solutions, the practical range of potentials for dissolved species is from 1.0 volt to -1.0 volt. In basic solutions, where the hydrogen and nitrogen couples have potentials of about 1.6 volt, the practical range extends from 2.6 to 0.6 volts. Thus it is possible to work in liquid ammonia with species which are extremely strong reducing agents (such as the alkali metals) and with species which are extremely strong oxidizing agents (such as permanganates, ozonides, and superoxides).

In Figure 3, the oxidation potentials for several couples are plotted against pH. (pH = 0 corresponds to 1 $\underline{M}$ NH_4^+, and pH = 27 corresponds to 1 $\underline{M}$ NH_2^-.) The dotted lines in Figure 1 correspond to the approximate boundaries of the stability zones for redox couples. Thus we see that the ammoniacal electron is thermodynamically unstable with respect to hydrogen evolution at all pH values; however, in alkaline solutions and in the absence of catalysts, the decomposition reaction is slow. In general, solid metals show negligible overvoltage effects in the reduction of ammonia. Thus, although the zinc couple falls within the dotted line boundaries, metallic zinc causes hydrogen evolution both in acid solutions and in alkaline solutions. (Bergstrom and Fernelius, 1933) The probable net reaction

in alkaline solutions is

$$Zn + 2\ NH_2^- + 2\ NH_3 = Zn(NH_2)_4^{2-} + H_2$$

Metallic thallium is, of course, inert toward ammonia at all pH values, and it happens that neither Tl^+ nor $Tl(NH_2)_2^-$ reacts with ammonia. (Bergstrom and Fernelius, 1933) The nitrate ion is essentially inert toward ammonia in acid solutions, but in alkaline solutions nitrogen evolution slowly occurs: (Bergstrom, 1940)

$$3\ K^+ + 3NH_2^- + 3NO_3^- = 3KOH + N_2 + 3NO_2^- + NH_3$$

3. Available Acid-Base Range

The basicity of ammonia is about 10^{12} times greater than that of water, and the acidity of ammonia is about 10^{-25} times smaller than that of water. Consequently acids for which pK $\lesssim$ 12 in aqueous solutions are "strong" acids in liquid ammonia, and acids for which pK $\gtrsim$ 39 in aqueous solutions have practically no acidity in liquid ammonia. Acids of intermediate strength are weak acids in ammonia, and they may be differentiated according to their acid strengths. In Figure 4, the aqueous pK ranges in which differentiation of acid strength is possible are indicated for the solvents acetic acid, water, ammonia, and benzene. On the same graph the aqueous pK values of several acids are indicated. It will be noted that, because of the smaller ionization constant of ammonia, a wider range of acid strengths may be studied in ammonia than in the other protonic solvents. In addition, because ammonia is more basic than either acetic acid or water, the pK values of the acids which can be differentiated are higher for ammonia than for acetic acid and water. Finally it may be

noted that inasmuch as benzene is an aprotic solvent, it is possible in principle to study any acid in benzene. In practice, however, difficulty is often encountered in dissolving ionic species in benzene.

Acids for which aqueous pK < 12 react completely with ammonia to form the corresponding ammonium salts. However, it must not be thought that these acids (or ammonium salts) are strong in the sense that they are completely dissociated to independent ions in liquid ammonia. All salts, ammonium salts included, are weakly dissociated in ammonia. The "strength" of an acid is best measured in terms of the equilibrium constant of the reaction

$$HX + NH_3 = (NH_4^+)(X^-)$$

However, rather than always indicate the formation of ion-pairs when these are the principal species, it is customary to write the ions as independent species, keeping in mind that considerable ionic aggregation takes place in moderately concentrated solutions. Thus we write

$$HOAc + NH_3 \longrightarrow NH_4^+ + OAc^-$$

even though the ion-pair dissociation constant for ammonium acetate is 7.7×10^{-5} (Gur'yanova and Pleskov, 1936)

Bases whose conjugate acids have aqueous pK values $\gtrsim$ 39 undergo essentially complete ammonolysis in liquid ammonia to form the amide ion. Two examples of such ammonolysis are given below.

$$KH + NH_3 \longrightarrow K^+ + NH_2^- + H_2$$

$$Na_2O + NH_3 \longrightarrow NaNH_2 + NaOH$$

The aqueous ionization constants of H_2 and OH^- have been estimated to be 10^{-38} and $< 10^{-36}$, respectively (Latimer, 1952). Thus the criterion for basic ammonolysis is just barely satisfied in these cases.

Some oxidizing agents react with liquid ammonia to form nitrogen-containing products which can be looked upon either as oxidation-reduction products or as ammonolysis products. Consider, for example, the reactions of chlorine, bromine, and iodine:

$$X_2 + 2NH_3 = NH_4^+ + X^- + NH_2X$$

(The halamine NH_2X reacts further at a lower rate to form species such as hydrazine and nitrogen.) The initial reaction can be looked upon as a self-oxidation-reduction of the halogen to the +1 and -2 oxidation states, but it is equally valid to consider the reaction as the ammonolytic cleavage of the X-X bond. Similarly, consider the following reaction (Franklin, 1934):

$$3K^+ + 3NH_2^- + NO_3^- = N_3^- + 3KOH + NH_3$$

This reaction corresponds to the oxidation of amide to azide by nitrate, but it may also be looked upon as the basic ammonolysis of the nitrate ion. (The $O{=}\overset{+}{N}\begin{smallmatrix}\nearrow O^- \\ \searrow O^-\end{smallmatrix}$ ion is converted to the $\overset{-}{N}{=}\overset{+}{N}{=}\overset{-}{N}$ ion by replacing the $O{=}\overset{+}{N}$ bond by an $\overset{-}{N}{=}\overset{+}{N}$ bond and by replacing the $\overset{+}{N}\begin{smallmatrix}\nearrow O^- \\ \searrow O^-\end{smallmatrix}$ bonds by an $\overset{+}{N}{=}\overset{-}{N}$ bond.)

4. Ease of Handling

The low boiling point of ammonia (-33.4°) is an obvious disadvantage when working with this solvent. However, in many types of

work it is not necessary to use any refrigeration when handling liquid ammonia. Because of the high heat of vaporization, the liquid may be kept at its boiling point in open containers such as beakers, flasks, etc. without too rapid boiling of the ammonia. The rate of evaporation of ammonia in dewar flasks (even when unsilvered for ease in observation) is practically negligible. The vapor pressure of the liquid at room temperature (8-10 atm.) is low enough so that it may be handled in sealed glass ampules without much danger of explosion. Techniques for handling liquid ammonia are discussed by Audrieth and Kleinberg (1953), Franklin (1935), Jolly (1960), and Sanderson (1948).

The viscosity of ammonia at its boiling point is only one-quarter that of water at room temperature. The low viscosity of ammonia is a definite advantage when filtering ammonia solutions and when carrying out heterogeneous reactions which require the diffusion of solutes through the liquid.

B. Ionic Solvation

1. Thermodynamic Functions for Ammonation and Hydration Processes

The free energies of formation of pairs of oppositely-charged ions are found to be of approximately the same magnitude in ammonia as they are in water, if one restricts the comparison to ions which do not form abnormally strong ammonia complexes. (Jolly, 1953, 1956) The data for a few pairs of ions of this type are presented in Table XII. We shall claim as a reasonable approximation for ions of the type given in Table XII, that the free energy of transfer of an individual ion from water to ammonia is zero. We shall therefore assume that the free energy of transfer of an ion which forms strong ammonia complexes

Table XII.

Free Energies of Formation in Water and Ammonia

Ion Pair	ΔF_f°, kcal./mole (25°) in water	in ammonia
$Na^+ + F^-$	-128.7	-124.4
$Li^+ + I^-$	- 82.6	- 83
$Rb^+ + NO_3^-$	- 93.9	- 90.3
$NH_4^+ + Br^-$	- 43.6	- 42.6
$Na^+ + ClO_3^-$	- 63.2	- 61.3

can be equated to the sum of the free energies of transfer of that ion and an equivalent number of non-ammonia-complexing counter-ions. We shall call such ionic free energies of transfer "experimental" free energies of transfer. It is interesting to compare such "experimental" free energies of transfer with the free energies of the aqueous reactions of type

$$M(H_2O)_x^{z+} + xHN_3 = M(NH_3)_x^{z+} + xH_2O$$

The free energy (in kcal./mole) of such a reaction, using the 1 M solution as the standard state for both water and ammonia, is given by the expression

$$\Delta F_K^\circ = -1.36 (\log K + x \log 55)$$

where K is the usual equilibrium constant for aqueous solutions. In Table XIII, values for ΔF_K° may be compared with the corresponding "experimental" free energies of transfer, ΔF_t°. It can be seen that the correspondence is very close. Hence we may estimate the standard

Table XIII.

Calculated and "Experimental" Free Energies of

Transfer from Water to Ammonia

(kcal./mole at 25°)

Ion	x	$-\Delta F^{\circ}_{K}$	$-\Delta F^{\circ}_{t}$
Hg^{2+}	4	36	40
Cu^{2+}	5	29	29
Zn^{2+}	4	22	22
Cu^{+}	2	20	20
H^{+}	1	15	16
Ag^{+}	2	14	17

free energy of formation of an ion in liquid ammonia from the relation

$$\Delta F^{\circ}_{f_{NH_3}} = \Delta F^{\circ}_{f_{H_2O}} + 16\ Z - 1.36\ (\log K + x \log 55)$$

where $\Delta F^{\circ}_{f_{NH_3}}$ and $\Delta F^{\circ}_{f_{H_2O}}$ are the standard free energies of formation in ammonia and water, respectively, and Z is the charge (taking account of sign) of the ion. The term 16 Z arises from the fact that $\Delta F^{\circ}_{f} = 0$ for the hydrogen ion in both solvents, and $\Delta F^{\circ}_{t} = -16$ kcal./mole for the hydrogen ion. Similar equations have been given for estimating ionic entropies and heats of formation in ammonia. (Jolly, 1956)

2. Kinetics of Ammonia Exchange Reactions

The ammoniated hydrogen ion, or ammonium ion, is the simplest ion one can have in liquid ammonia. The rate at which protons move from ammonium ions to ammonia molecules (or the rate at which solvent ammonia molecules displace ammonia molecules from ammonium ions) is much too great to measure by classical chemical techniques. (Nyman et al, 1950) However Ogg (1954) has shown that it is possible to measure this rate by n.m.r. techniques. The proton magnetic resonance spectrum of pure liquid ammonia consists of three peaks, due to the spin-spin coupling of the protons with the N^{14} nucleus. A trace of ammonium salt causes the signal to change to a single line. The change is attributed to the reaction

$$NH_3 + NH_4^+ \rightleftharpoons NH_4^+ + NH_3,$$

and from a rough estimate of the ammonium ion concentration required to cause collapse of the triplet, Ogg calculated a rate constant of about 5×10^8 ℓ. mole^{-1} sec.$^{-1}$ He estimated rate constants of the same order of magnitude for the reactions

$$NH_3 + NH_2^- \rightleftharpoons NH_2^- + NH_3$$

and

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Wiesendanger, Jones, and Garner (1957) have shown, using N^{15}, that the exchange of ammonia molecules between the solvent and the ions $Ag(NH_3)_2^+$, $Cu(NH_3)_4^{2+}$, and $Ni(NH_3)_6^{2+}$ is too fast to measure by classical methods, but they were able to show that the ions $Cr(NH_3)_6^{3+}$ and $Co(NH_3)_6^{3+}$ exchange their ammonia molecules relatively slowly with the solvent. In the case of $Cr(NH_3)_6^{3+}$, a bimolecular rate constant 1.3×10^{-6} ℓ. $mole^{-1}$ $sec.^{-1}$ was measured. Hunt et al (1963) measured the rate of exchange of N^{14} between $Ni(NH_3)_6^{2+}$ and the solvent ammonia molecules by n.m.r. line broadening measurements. Because the rate of the corresponding exchange reaction in water was found to be independent of the ammonia concentration and to be of practically the same magnitude as that for the exchange in anhydrous ammonia, they propose that the reaction is unimolecular and report the rate constant $k = 4.7 \times 10^4$ $sec.^{-1}$ at 25°.

C. Acid-Base Reactions

1. The Nature of the Ammonium and Amide Ions

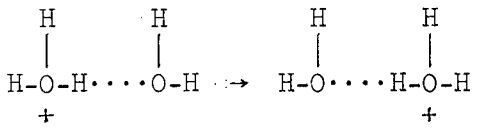
The ammonium ion and amide ion are analogs of the oxonium ion and hydroxide ion, respectively. Thus the neutralization of a strong acid with a strong base in ammonia is represented by the equation

$$NH_4^+ + NH_2^- \rightarrow 2\ NH_3$$

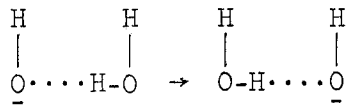
whereas the analogous reaction in water is usually written as

$$H^+ + OH^- \rightarrow H_2O$$

The analogy breaks down, however, when one considers the mobilities of the ions. The aqueous oxonium ion and aqueous hydroxide ion have ionic conductances which are several times as large as the conductances of ordinary +1 and -1 ions. (See Table XIV.) These abnormally high conductances are explained in terms of a mechanism, the essentials of which were first described by deGrotthuss (1806). Oxonium ion migration is accomplished when the proton of an oxonium ion moves the small distance necessary to partially break its bond to the oxygen atom and to form a bond to the oxygen atom of the adjacent hydrogen-bonded water molecule:



Hydroxide ion migration is quite similar:



Analogous processes do not contribute appreciably to the mobilities of the NH_4^+ and NH_2^- ions in ammonia because of the much weaker hydrogen bonds in this solvent. (The weaker a hydrogen bond, the higher the barrier between the two equilibrium positions for the proton.) It is clear from the data in Table XIV. that the mobilities of the ammonium and amide ions in ammonia are similar to the mobilities of ordinary univalent ions in the same solvent. We have noted above that the rate constants for the reactions

$$NH_4^+ + NH_3 \rightarrow NH_3 + NH_4^+$$

$$NH_2^- + NH_3 \rightarrow NH_3 + NH_2^-$$

are of the order of magnitude 5×10^8 ℓ. mole^{-1} sec.$^{-1}$. The rate

Table XIV.

Ionic Conductances in Ammonia and Water

Ion	Equivalent Ionic Conductance ($cm.^2\ ohm^{-1}\ eq.^{-1}$)	
	Liquid NH_3, -33.5°	Water,[c] 25°
Na^+	158[a]	50.1
NH_4^+	142[a]	73.4
H^+		349.8
NO_3^-	177[a]	71.4
NH_2^-	166[b]	
OH^-		198

[a] Laitinen and Shoemaker (1950).

[b] Hawes (1933).

[c] Mac Innes (1939).

constants for the corresponding aqueous reactions

$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+$$

$$OH^- + H_2O \rightarrow H_2O + OH^-$$

are 1.1×10^{10} and 5×10^9 $\ell.\ mole^{-1}\ sec.^{-1}$, respectively. (Loewenstein and Szöke, 1962)

2. Determination of Ammonium Ion Concentration

Platinum black electrodes show very little hydrogen overvoltage in liquid ammonia and, when equilibrated with hydrogen, may be used as

reversible hydrogen electrodes. Pleskov and Monoszon (1935) used the hydrogen electrode in ammonia at -50° to determine the activity coefficients for NH_4NO_3 and NH_4Cl. By studying the cell pt, H_2 | 0.1 M NH_4NO_3 | satd. KNO_3 | KNH_2 (C) | Pt, H_2, they determined the self-ionization constant for liquid ammonia.

$$2\ NH_3 = NH_4^+ + NH_2^- \qquad K = 1.9 \times 10^{-33} \text{ at } -50°$$

Using the heat of reaction, $\Delta H° = 26.1$ kcal./mole (Mulder and Schmidt, 1951), one calculates $K = 5.1 \times 10^{-27}$ at 25°. This is to be compared with the value 2.2×10^{-28} calculated from the free energy of solution of sodium amide. (Coulter et al, 1959) For most purposes, the value $K = 10^{-27}$ is sufficiently accurate. If we set up a pH scale using the relation pH = - log (NH_4^+), we calculate that pure liquid ammonia has a pH of 13.5 at 25°.

Zintl and Neumayr (1930) were unsuccessful with the hydrogen electrode, but they did find the quinhydrone electrode to be reproducible. They obtained self-consistent results with the concentration cell Pt|quinhydrone (C_1), NH_4Cl (c_1)|| quinhydrone (C_2), NH_4Cl (c_2)| Pt at -50°.

Heyn and Bergin (1953) attempted the use of glass electrodes in liquid ammonia solutions. Their cells were of the type Pb|0.1 M $Pb(NO_3)_2$, NH_4NO_3 (C)|glass membrane|0.1 M $Pb(NO_3)_2$, 0.1 M NH_4NO_3|Pb. Each of the several glasses tried failed to show glass electrode response. It appears that the ammonium ions in liquid ammonia are not in equilibrium with ions on the surface of the glass electrode. Perhaps the ammonia dehydrates the glass to such an extent that protons are no longer mobile in the glass. It would be interesting to try a

sheet of cation exchange resin in the ammonium form as a pH-sensitive membrane.

A number of acid-base indicators, including some that are used in aqueous solutions, have been studied in liquid ammonia. (Shatenshtein, 1939, and Franklin and Kraus, 1900) Some of these are listed in Table XV with their colors in acid and basic solutions.

Table XV.

Acid-Base Indicators in Liquid Ammonia

Indicator	Color of Solution in pure NH_3	Basic Solution	Acidic Solution
Phenolphthalein	pale red	deep red	colorless
Carmine	dirty red	blue	red
Saffranine	crimson	blue	crimson
n-nitroaniline	yellow	green	yellow
p-nitroaniline	yellow	orange	yellow
o-nitroaniline	yellow	red	yellow

Cuthrell, Fohn, and Lagowski (1963) have determined the ionization constants and dissociation constants for the weak acids o- and p-nitroacetanilide by a spectrophotometric method. These compounds are colorless in acidic solutions and yellow-brown in alkaline solutions. The ionization, to form an ion pair, may be represented by the general equation

$$HX + NH_3 = NH_4^+X^- \qquad K_i = (NH_4^+X^-)/(HX)$$

and the dissociation by the equation

$$NH_4^+X^- = NH_4^+ + X^- \qquad K_d = (NH_4^+)(X^-)/(NH_4^+X^-)$$

The equilibrium constants, corrected to infinite dilution, are

	K_i	K_d
o-nitroacetanilide	2.2×10^{-2}	2.2×10^{-4}
p-nitroacetanilide	9.3×10^{-2}	0.89×10^{-4}

In solutions of very high pH, the concentration of amide ion may be determined spectrophotometrically. The amide ion absorbs at 3410 Å. (Ogg et al, 1933)

Watt et al (1955) have potentiometrically titrated several acids in liquid ammonia with potassium amide. A "difference indicator" electrode system was used, in which one electrode is immersed in the solution being titrated, and the other is immersed in a solution having a composition the same as the initial composition of the titrated solution but separated from the bulk of the solution by a capillary tube. (Zintl et al, 1931, and Watt and Sowards, 1955) From the positions of the inflection points in the titration of mixtures of acids, the following order of acid strengths was determined: $NH_4^+ > H_2NC(NH)NH_3^+ > H_2NC(S)NH_2 > H_2NC(O)NH_2 > H_2NC(NH)NH_2 > H_2NC(S)NH^- > H_2NC(O)NH^- > H_2NC(NH)NH^- > NH_3$. Unfortunately this method is not suitable for the quantitative measurement of acid strengths.

3. Base-Catalyzed Exchange Reactions

Weak acids exchange their hydrogen for deuterium when they are dissolved in liquid ND_3. The exchange rate constants for several hydrocarbons are given in Table XVI. It will be noted that the more acidic a hydrocarbon, the more rapidly it exchanges its hydrogen with

ammonia. Probably these rate constants correspond to the rate constants for the ionization of the hydrocarbons.

Extremely weak acids such as benzene do not undergo exchange in deuteroammonia in the absence of a catalyst. However, in the presence of a strong base such as potassium amide, exchange takes place. The mechanism for exchange is probably of the following type:

$$RH + ND_2^- \rightarrow R^- + NHD_2$$

$$R^- + ND_3 \rightarrow RD + ND_2^-$$

Some experimental rate constants for benzene are presented in Table XVII.

Table XVI.

Comparison of Deuterium Exchange Rate Constants at 120° with Aqueous pK Values (No Amide Catalyst Added)

Hydrocarbon	Rate Constant[a] (sec^{-1})	Aqueous pK[b]
Indene	4×10^{1}	~ 21
Fluorene	2×10^{-2}	~ 31
Triphenylmethane	2×10^{-7}	~ 40
Diphenylmethane	7×10^{-9}	~ 42

[a] Shatenshtein (1962)

[b] Cram (1963)

Table XVII.

Deuterium Exchange Rate Constants for Benzene in Potassium Amide Solutions

(from Shatenshtein, 1962)

(Constants, in sec^{-1}, calculated assuming rate = k[benzene].)

temp. °C	Molarity of Potassium Amide					
	0.010	0.014	0.021	0.059	0.19	0.43
-30				4×10^{-7}		
0	4×10^{-6}		7.3×10^{-6}			8.9×10^{-5}
25	4.4×10^{-5}	5.7×10^{-5}	8.6×10^{-5}	1.8×10^{-4}	4.2×10^{-4}	
40	1.6×10^{-4}	3.1×10^{-4}				

These constants are pseudo first-order rate constants, calculated assuming (for convenience) that the rate is independent of the potassium amide concentration. It can be seen that in dilute solution the rate is approximately proportional to the potassium amide concentration, and that at higher concentrations the apparent rate constant falls off. This fall in catalyst activity is probably attributable to the formation of ion pairs.

It has been found that the rate of exchange of a deuterium atom in the ortho position of a substituted benzene is highly sensitive to the electronegativity of the substituent group. Thus the rate constant for fluorobenzene is more than 10^7 times greater than the rate constant for toluene. If we plot the logarithm of the relative exchange rate constants for substituted benzenes against the aqueous pK values for the corresponding substituted acetic acids, a straight line is obtained, as shown in Figure 5. This is further evidence that the rate of exchange parallels the acidity of the hydrocarbon.

The exchange of hydrogen between organic compounds and ammonia can be used for the preparation of deuterated compounds. Some compounds which have been fully deuterated in this way are benzene, naphthalene, phenanthrene, biphenyl, triphenylmethane, diphenylmethane, bibenzyl, and pyridine. (Shatenshtein, 1962)

Wilmarth and Dayton (1953) observed that the conversion of parahydrogen to orthohydrogen is catalyzed by liquid ammonia solutions of potassium amide. The exchange of deuterium gas was found to proceed at approximately the same rate in these solutions, and the initial product was found to be HD. In each case, the rate was found to be proportional to the concentrations of amide ion and hydrogen (parahydrogen or deuterium).

They reported a rate constant at -50° of 130 ℓ. mole^{-1} sec.$^{-1}$. The data are consistent with the following type of mechanism:

$$D_2 + NH_2^- \rightarrow D^- + NH_2D$$

$$D^- + NH_3 \rightarrow HD + NH_2^-$$

A study of the deuterium exchange reaction over a wide concentration range at various temperatures indicated that the reaction is catalyzed both by the free amide ion and by the undissociated potassium amide. (Bar-Eli and Klein, 1962) The calculated rate constants at -61° are $k_{NH_2^-} = 36$ ℓ. mole^{-1} sec^{-1} and $k_{KNH_2} = 1.7$ ℓ. mole^{-1} sec^{-1}. The activation energy for the amide ion reaction was found to be 7.5 kcal./mole. From the exchange rates for D_2, HD, and HT, and from the parahydrogen conversion rate, the following isotope effects were calculated:

$$2\ k_{HD}/k_{D_2} = 1.28 \pm 0.03$$

$$k_{HD}/k_{HT} = 1.64 \pm 0.07$$

$$2\ k_{H_2}/k_{D_2} = 2.36 \pm 0.30$$

The amide-catalyzed exchange of hydrogen with ammonia is under serious consideration as the basis of a method for concentrating deuterium in ammonia. (Haul <u>et al</u>, 1961; Dirian and Grandcollot, 1961; Bourke and Lee, 1961; Brown and Roberts, 1961; Rebora, 1962)

4. Acid-Catalyzed Reactions

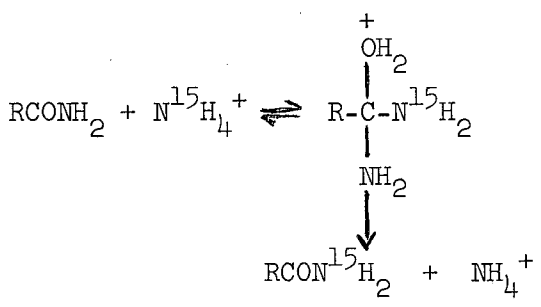
Many esters undergo ammonolysis when treated with liquid ammonia.

$$RCO_2R + NH_3 \rightarrow RCONH_2 + ROH$$

Ammonium salts catalyze such ammonolyses, just as aqueous acids

catalyze the corresponding hydrolyses. The order of catalytic activity for ammonium salts is, however, the reverse of the order of acid strengths based on conductance studies. For example, in the ammonolysis of ethyl benzoate, Fellinger and Audrieth (1938) found the catalytic effect to decrease in the following order: ammonium benzoate > NH_4Cl > NH_4Br > NH_4ClO_4. It was later observed that sodium salts are also capable of catalyzing ester ammonolysis. Such electrolytes are not as effective as the ammonium salts, but it seems clear that all these catalyzed ester ammonolyses are best looked upon as examples of electrolyte catalysis. (Audrieth and Kleinberg, 1953)

The exchange of nitrogen between carboxylic acid amides and liquid ammonia has been studied by the use of N^{15}- labelled ammonia. (Heyns et al, 1958) The exchange is catalyzed by ammonium chloride, and the following mechanism has been proposed:



D. Reactions of Metal Solutions

1. Systematics

An enormous number of synthetic reactions involving metal-ammonia solutions have been carried out. These reactions have been reviewed by Birch (1950), Birch and Smith (1958), Watt (1950 and 1957), and Fowles and Nicholls (1962). Practically nothing is known of the

mechanisms of these reactions; nevertheless some systematization is possible by considering the products of the reactions. Most reactions involving metal-ammonia solutions may be considered as being initiated by one of the following three steps:

(1) simple electron addition without bond cleavage,

$$e^-_{am} + X \rightarrow X^-$$

(2) bond cleavage by the addition of one electron,

$$e^-_{am} + X\text{-}Y \rightarrow X\cdot + Y^-$$

or(3) bond cleavage by the addition of two electrons,

$$2\ e^-_{am} + X\text{-}Y \rightarrow X^- + Y^-$$

<u>Electron addition without bond cleavage</u>.- The reactions of the electron with molecular oxygen and the nitrite ion involve the formation of products which have reasonable kinetic stabilities in liquid ammonia:

$$e^-_{am} + O_2 \rightarrow O_2^-$$

$$e^-_{am} + NO_2^- \rightarrow NO_2^{2-}$$

The rates of these reactions in liquid ammonia are unknown. Thus it is interesting that, even though the electron and the O_2^- and NO_2^{2-} ions are extremely short-lived species in water, the rates of these reactions in water have been measured. (Czapski and Schwarz, 1962; Dorfman, 1963)

Some very interesting reductions of transition metal ions appear to involve the simple addition of one or more electrons:

$$e^-_{am} + MnO_4^- \rightarrow MnO_4^{2-}$$

$$2\ e^-_{am} + Ni(CN)_4^{2-} \rightarrow Ni(CN)_4^{4-}$$

$$2\ e^-_{am} + Pd(CN)_4^{2-} \rightarrow Pd(CN)_4^{4-}$$

$$2\ e^- + Pt(NH_3)_4^{2+} \rightarrow Pt(NH_3)_4$$

$$2\ e^- + Pt(en)_2^{2+} \rightarrow Pt(en)_2.$$

Bond cleavage by the addition of one electron.- The reactions of the electron with protonic acids fall in this category. The kinetics and mechanisms of the following three examples are discussed in the following sections.

$$e^-_{am} + NH_3 \rightarrow NH_2^- + 1/2\ H_2$$

$$e^-_{am} + NH_4^+ \rightarrow NH_3 + 1/2\ H_2$$

$$e^-_{am} + EtOH \rightarrow EtO^- + 1/2\ H_2$$

The reaction of the electron with organic sulfides may be interpreted in terms of the intermediate formation of R· radicals:

$$e^-_{am} + R_2S \rightarrow RS^- + 1/2\ R_2.$$

The following reaction is an unusual case in which a stable radical is formed:

$$e^-_{am} + (C_2H_5)_3SnBr \rightarrow (C_2H_5)_3Sn^{\bullet} + Br^-.$$

Bond cleavage by the addition of two electrons.- When a bond is broken by the addition of two electrons, either two anions or a "di-anion" form:

$$2\ e^-_{am} + Ge_2H_6 \rightarrow 2\ GeH_3^-$$

$$2\ e^-_{am} + C_6H_5NHNH_2 \rightarrow C_6H_5NH^- + NH_2^-$$

$$2\ e^-_{am} + C_6H_5{-}N{=}O \rightarrow C_6H_5{-}N^-{-}O^-$$

However, one of the anions usually undergoes ammonolysis, as in the following examples.

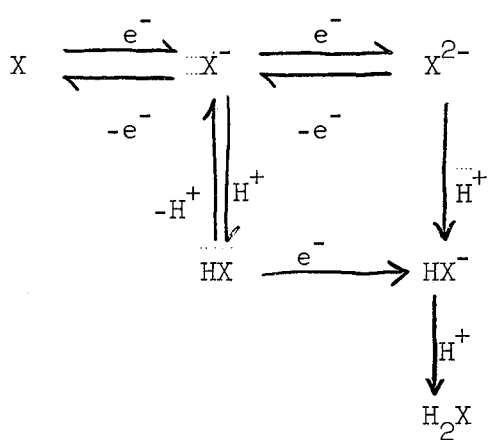
$$2\ e^-_{am} + N{\equiv}N^+{-}O^- \rightarrow N{\equiv}N + O^{2-} \xrightarrow{NH_3} OH^- + NH_2^-$$

$$2\ e^-_{am} + N{\equiv}C{-}O^- \rightarrow N{\equiv}C^- + O^{2-} \xrightarrow{NH_3} OH^- + NH_2^-$$

$$2\ e^-_{am} + Br\text{-}C_2H_5 \rightarrow Br^- + C_2H_5^- \xrightarrow{NH_3} C_2H_6 + NH_2^-$$

$$2\ e^-_{am} + RCH{=}CH_2 \rightarrow RCH\text{-}CH_2^{2-} \xrightarrow{2NH_3} RCH_2CH_3 + 2\ NH_2^-.$$

It has been observed that many reductions which take place in liquid ammonia solutions containing both an alkali metal and a protonic acid such as an alcohol or water do not occur at all in the absence of the protonic acid. (Birch, 1950; Birch and Smith, 1958) Thus benzene does not appreciably react with sodium in ammonia. However, in the presence of alcohol, reduction to 1,4-dihydrobenzene takes place. Behavior of this type is probably best explained in terms of the buffering action of the alcohol or other protonic acid. The reduction of a species X to H_2X may be considered to proceed by the following type of mechanism:



In most cases, the intermediate X^{2-} is thermodynamically very unstable; consequently practically no reaction proceeds via this intermediate. The ratio between the concentrations of HX and X^- depends on the pH of the solution. In the absence of any added protonic acid, the pH will

soon reach quite high values as a consequence of the reaction proceeding to a slight extent; hence, unless HX is an exceedingly weak acid, the HX concentration will drop, and the reaction will essentially stop. In the presence of an added protonic acid, the solution will be buffered at a pH depending on the strength of the acid. If the added acid is sufficiently strong, the $(HX)/(X^-)$ ratio will be high, and the reduction will proceed steadily.

2. The Reaction of Metals with Ammonia

All metal-ammonia solutions are metastable. If they are allowed to stand for long periods, or if suitable catalysts are present, decomposition to hydrogen and the metal amide occurs:

$$M + x\ NH_3 \rightarrow x/2\ H_2 + M(NH_2)_x.$$

In dilute solutions of sodium or potassium (the amides of which are soluble), the net reaction is

$$e^-_{am} + NH_3 \longrightarrow NH_2^- + 1/2\ H_2.$$

If pure reagents and clean apparatus are used, and if the solutions are kept cold, decomposition may be held to 0.1% per day. (Dewald and Lepoutre, 1954) Warshawsky (1963) has pointed out that an initial hydrogen evolution from metal-ammonia solutions in glassware is attributable to reaction of the metal with a strongly adsorbed layer of water on the glass surface. This water may be removed from a Pyrex surface by baking at 400° for 200 hours <u>in vacuo</u>.

The reaction of potassium with liquid ammonia at room temperature has been followed spectrophotometrically by Chou <u>et al</u> (1963). These investigators found that the reaction was first order in metal for the first 75% of reaction and reported half-times of 9-13 hrs. for initial

concentrations in the range 2×10^{-4} - 1.13×10^{-3} M. Because the reaction was observed to take place at different rates in different reaction vessels, and because other investigators have observed entirely different rates, it is believed that the reaction is wall-catalyzed. Warshawsky (1964) has observed that the decomposition of dilute ($< 10^{-4}$ M) solutions of sodium in ammonia at -78° in the presence of platinum foil is zero order in sodium. A rate constant of 1.5×10^{-9} moles of H_2 cm^{-2} hr^{-1} was reported. The first-order and zero-order behaviors observed in the above studies indicate that the rates are independent of the ammonium ion concentration and the amide ion concentration (in the concentration ranges under study).

A reaction of more fundamental interest than the surface-catalyzed reactions described above is the homogeneous reaction of the electron with ammonia. It may be that this reaction is too slow to observe directly. If we assume that the rate of the homogeneous reaction is less than that of the presumably heterogeneous reaction observed by Chou et al, we calculate, for the first-order rate constant, $k < 1.5 \times 10^{-5}$ sec^{-1}. This may be compared with the rate constant $k < 4.4 \times 10^{4}$ sec^{-1} for the relatively fast reaction of the aqueous electron with water (Dorfman and Taub, 1963):

$$e^-_{aq} + H_2O \rightarrow H + OH^-$$

The large difference in the reactivity of the electron in water and ammonia is not unexpected. A higher activation energy for the liquid ammonia process,

$$e^- + NH_3 \rightarrow H + NH_2^-,$$

than for the aqueous process is consistent with the estimated heats of reaction, + 33 kcal./mole for the liquid ammonia process, and -10

kcal./mole for the aqueous process.

The mechanism of the homogeneous reaction is, of course, unknown. One can postulate that the atomic hydrogen formed in the initial step dimerizes,

$$2\ H \rightarrow H_2,$$

or that it reacts further with electrons to form the hydride ion,

$$H + e^-_{am} \rightarrow H^-$$

$$H^- + NH_3 \rightarrow H_2 + NH_2^-.$$

3. The Reaction of Metals with the Ammonium Ion

The ammonium ion reacts very rapidly with the electron in ammonia.

$$NH_4^+ + e^-_{am} \rightarrow NH_3 + 1/2\ H_2$$

The half-time for the reaction of 10^{-4} M electrons with 10^{-4} M ammonium ions is less than 1 second. This observation places a lower limit of 10^4 ℓ. mole^{-1} sec^{-1} on the second-order rate constant. We believe that the rate constant for the $NH_4^+ + e^-_{am}$ reaction cannot be greater than the rate constant of the exchange of protons between NH_4^+ and NH_3, for which the value 5×10^8 ℓ. mole^{-1} sec^{-1} has been reported. Therefore we place the $NH_4^+ + e^-$ rate constant between the limits of 10^4 and 5×10^8 ℓ. mole^{-1} sec^{-1}.

The rate constant for the corresponding reaction of the aqueous electron and the aqueous proton is 2.3×10^{10} ℓ. mole^{-1} sec^{-1} (Dorfman and Taub, 1963):

$$e^-_{aq} + H^+_{aq} \rightarrow H$$

There are at least two ways in which it should be possible to determine the rate of reaction of the electron with the ammonium ion in liquid

ammonia. First, it should be possible to utilize the same techniques of pulse radiolysis (Dorfman, 1963) and photolysis (Swenson et al, 1963) which have been used to study reactions of the aqueous electron. Second, it should be possible to study the decomposition of metals in solutions which are buffered at an ammonium ion concentration such that the reaction proceeds at a conveniently measurable rate. We have interpreted data on the reaction of sodium in ethanol-ethoxide solutions in this way in the following section.

4. The Reaction of Sodium with Ethanol

Kelly et al (1962) followed the reaction of sodium with ethanol in liquid ammonia at -33.4° by measuring the evolved hydrogen as a function of time.

$$e^-_{am} + EtOH \rightarrow EtO^- + 1/2\ H_2$$

They obtained data over a remarkably wide time interval. The data for a run in which the sodium was in excess are presented in Table XVIII in the form of the fraction of the alcohol reacted as a function of time. The investigators noted that, during the first 25% of reaction, the reaction was first-order in alcohol and essentially zero-order in sodium. During the second 25% of reaction, the reaction did not appear to be of definite kinetic order, but for the last half of the reaction, the reaction was first-order in both alcohol and sodium, or second-order overall. We believe that the data are most easily explained in terms of the following mechanism:

$$EtOH + NH_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_4^+ + EtO^-$$

$$NH_4^+ + e^-_{am} \xrightarrow{k_3} NH_3 + 1/2\ H_2$$

If we assume a low, steady-state concentration for the ammonium ion, we calculate the rate law

$$-\frac{d(EtOH)}{dt} = \frac{k_1(EtOH)(e^-_{am})}{(k_2/k_3)(EtO^-) + (e^-_{am})}$$

Qualitatively the data fit this rate law. At the beginning of the reaction, when the EtO^- concentration is very low, the rate law reduces to

$$-\frac{d(EtOH)}{dt} = k_1(EtOH).$$

Under these conditions, the rate-determining step is the ionization of the ethanol. During the last stages of the reaction, when $(k_2/k_3)(EtO^-) \gg (e^-_{am})$, the rate law reduces to

$$-\frac{d(EtOH)}{dt} = \frac{k_1(EtOH)(e^-_{am})}{(k_2/k_3)(EtO^-)}$$

Under these conditions, the rate-determining step is the reaction of the ammonium ion with the electron. The accuracy with which the data may be quantitatively represented by the complete rate law can be seen from the "Powell plot"[1] in Figure 6. Here we have plotted the fraction of reaction, f, against the logarithm of time, t. The circles correspond to the experimental points, and the solid curve has been calculated from the complete rate law, using the constants $k_1 = 0.0303\ sec^{-1}$ and $k_2/k_3 = 460$. The discrepancy between the experimental points and the calculated curve in the region f = 0.10 to f = 0.40 is not understood. It does not appear that the discrepancy may be accounted for by ion-pairing, by assuming an initial reaction of the sodium with the ammonia, or by a

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[1] This method of treating data, due to R. E. Powell is described by Frost and Pearson (1961).

Table XVIII

The Reaction of Sodium with Ethanol

(from data of Kelly *et al*, 1962)

Initial sodium: 0.96 M

Initial ethanol: 0.34 M

t (sec.)	f (fraction reaction)	t (sec.)	f (fraction reaction)
~3	0.012	1200	.495
10	.065	1680	.565
30	.141	2400	.620
60	.198	3600	.687
120	.254	4800	.760
240	.315	7200	.840
480	.377	10800	.910
720	.425	18000	.975
		28800	1.000

rate-law term first order in ethanol and first order in sodium.

The pK_a of ethanol in water is ~ 17. (Cram, 1963) If we use the rule that pK values in ammonia are 12 units lower than those in water, and estimate an ion-pair dissociation constant of 10^{-4} for NH_4OEt in ammonia, we may calculate an over-all ionization and dissociation constant for ethanol (k_1/k_2) in ammonia of 10^{-9}. From our values for k_1 and k_2/k_3 we may then calculate the rate constant for

the reaction of the electron with the ammonium ion, $k_3 \sim 10^5$ ℓ. mole^{-1} sec^{-1}. It will be noted that this value lies within the limits which we imposed above.

5. Comparison with Other Metal Solutions

Solutions of alkali metals in aliphatic amines are extensively used by organic chemists as reducing agents. (Birch, 1950; Birch and Smith, 1958) The advantages of amines over ammonia include higher boiling points, higher solubilities for organic compounds, and stronger reducing power in their metal solutions. The metal-amine solutions, however, are much more unstable with respect to decomposition to amide and hydrogen.

Down et al (1959) found that potassium and NaK dissolve slightly (of the order of 10^{-4} M) in certain ethers to give unstable blue solutions. The ethers which show the highest solubilities are the "glyme" solvents (dimethyl ethers of ethylene glycols), 1-methoxymethyl-tetrahydrofuran, and the cyclic tetramer of propylene oxide. The solubility of potassium in such ethers accounts for the successful use of these solvents in various reactions of potassium, such as the reactions with transition metal carbonyls to form potassium "carbonylates".

$$2\ K + Mn_2(CO)_{10} \rightarrow 2\ Mn(CO)_5^- + 2\ K^+$$

¶ Aromatic hydrocarbons such as naphthalene react with potassium and sodium in glyme ethers to form green solutions of electron addition compounds: (Scott et al, 1936)

$$K + C_{10}H_8 \rightarrow K^+ + C_{10}H_8^-.$$

These relatively stable solutions are very useful as strong

reducing agents in circumstances in which it is necessary to avoid solvolysis by protonic solvents. Thus Chatt and Watson (1962) have prepared zero-oxidation-state transition-metal complexes of the type $M[(CH_3)_2PCH_2CH_2P(CH_3)_2]_3$ by the reduction of higher-valent complexes with sodium naphthalenide in tetrahydrofuran.

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Figure Captions

Figure 1. Sodium-ammonia phase diagram. (Reproduced with permission from Jolly, 1959)

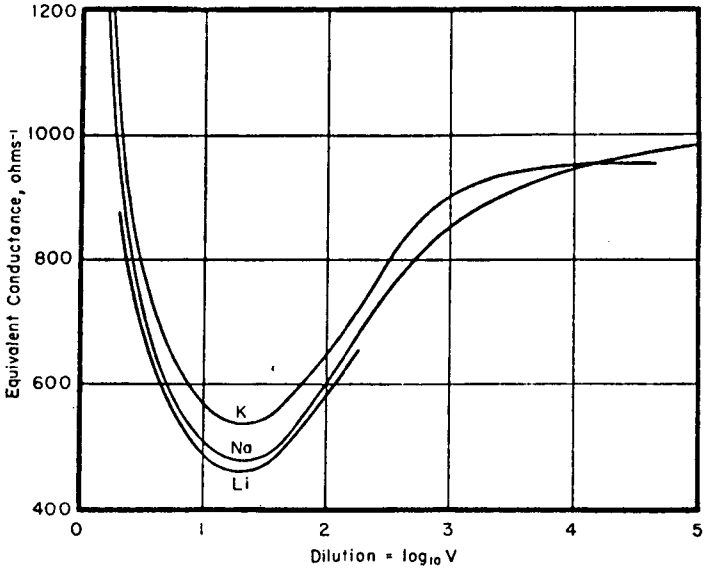
Figure 2. Equivalent conductance of metal-ammonia solutions at -33.5°. V = liters of ammonia of density 0.674 in which one gram atom of metal is dissolved. (Reproduced with permission from Jolly, 1959)

Figure 3. Oxidation potentials in ammonia at 25° as a function of pH.

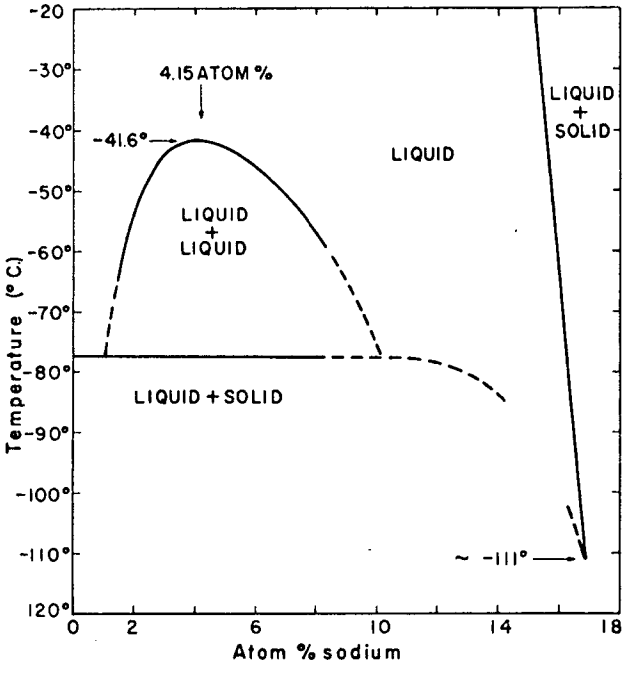
Figure 4. Ranges of acidity differentiation for several solvents. Most of the pK values were taken from Cram (1963). The values for HCl and HI taken from Pauling (1960).

Figure 5. Correlation between exchange rate constants for substituted benzenes and aqueous pK values for the corresponding substituted acetic acids.

Figure 6. Plot of fraction reaction *vs.* logarithm of time for sodium-ethanol reaction. (Data of Kelly *et al*, 1962)


1200
1000
800
600
400
Equivalent Conductance, ohms⁻¹
K
Na
Li
0
1
2
3
4
5
Dilution = log10 V

MU-33326


-20
-30°
-40°
-50°
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-70°
-80°
-90°
-100°
-110°
120°
Temperature (°C)
4.15 ATOM %
-41.6°
LIQUID
LIQUID
+
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~ -111°
0
2
6
10
14
18
Atom % sodium

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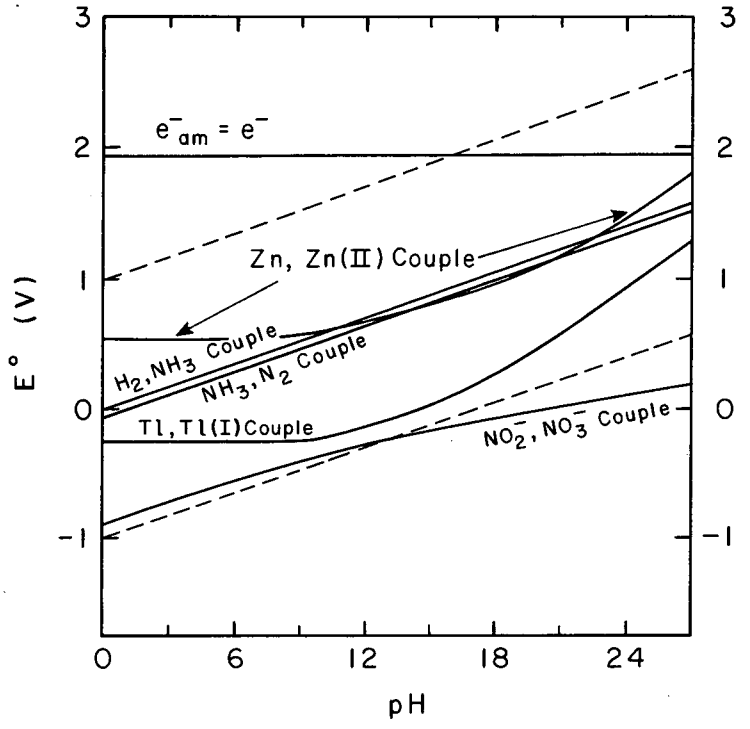
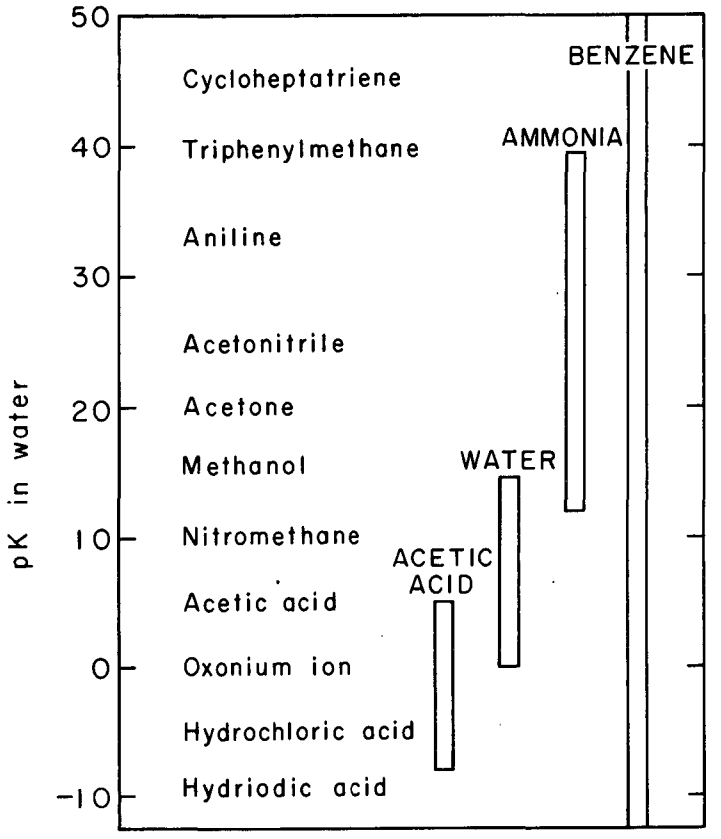
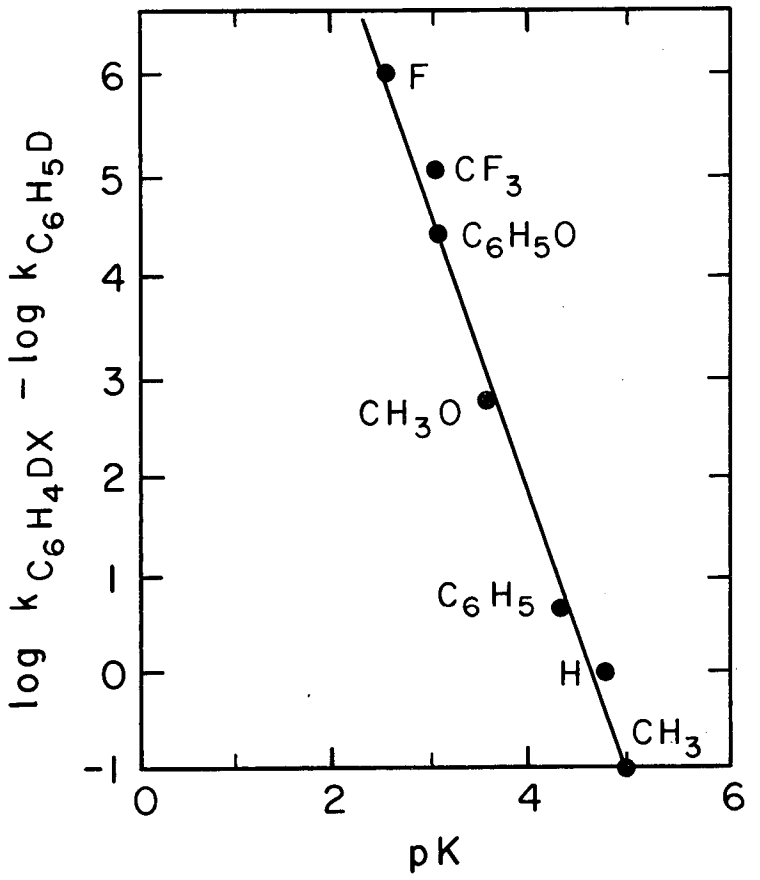

3
2
1
0
-1
E° (V)
$e^-_{am} = e^-$
Zn, Zn(II) Couple
H_2, NH_3 Couple
NH_3, N_2 Couple
Tl, Tl(I) Couple
NO_2^-, NO_3^- Couple
0
6
12
18
24
pH

MU-33390


50
40
30
20
10
0
-10
pK in water
Cycloheptatriene
Triphenylmethane
Aniline
Acetonitrile
Acetone
Methanol
Nitromethane
Acetic acid
Oxonium ion
Hydrochloric acid
Hydriodic acid
BENZENE
AMMONIA
WATER
ACETIC ACID

MU-33391


log $k_{C_6H_4DX}$ − log $k_{C_6H_5D}$
pK
F
CF_3
C_6H_5O
CH_3O
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CH_3
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-1
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2
4
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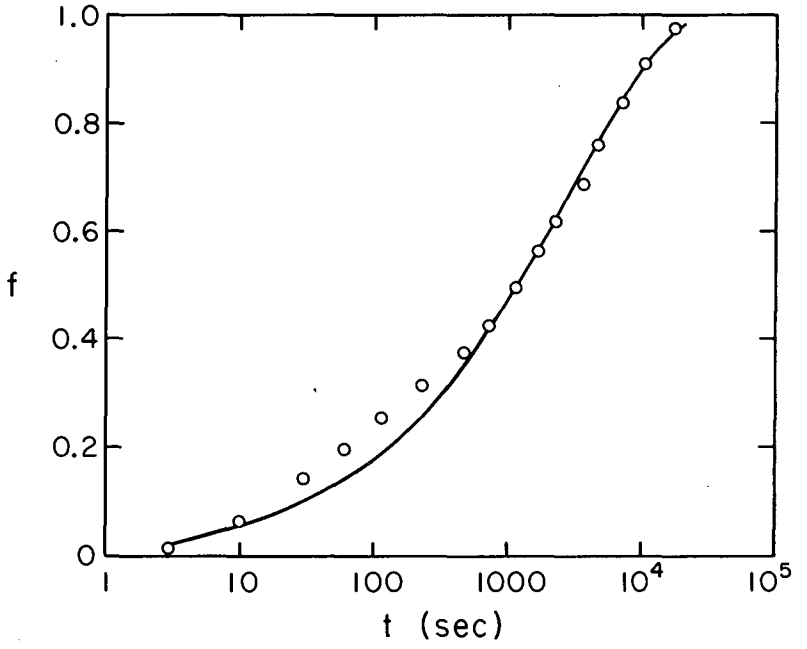
MU-33392



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