

SOLUTION PHENOMENA IN LIQUID AMMONIA

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ABSTRACT

An extended discussion of solution phenomena in anhydrous liquid ammonia is presented. The solvent properties of ammonia for various classes of compounds is discussed in terms of its hydrogen bonding ability, moderate dielectric constant, relatively high basicity, and high dipole moment. In general, ammonia is a better solvent than water for covalent molecules, but a poor solvent for ionic species. Conductivity and spectral data is presented to support the contention that species in liquid ammonia undergo ion association, the aggregates being predominantly ion-separated ion-pairs in dilute solution. A brief discussion of the chemical properties of metal-ammonia solutions is presented. Electrochemical behavior as exemplified by static potential measurements and polarographic techniques is discussed. A detailed discussion of acid-base phenomena including proton transfer reactions and complexation reactions is presented with a summary and discussion of the quantitative data available for these systems.

INTRODUCTION

Liquid ammonia, the prototype basic water-like solvent, has received continuing attention as a reaction medium by chemists since 1864 when Weyl reported on the solubilities of a variety of substances in this solvent. With such a long time base for experimentation, the casual observer might assume that the significant areas available for study might have been exhausted. On the contrary, the results of each new investigation open unexpected facets of this unusual solvent. Perhaps the greatest deterrent to the potential investigator of liquid ammonia solutions arises from the experimental difficulties associated with handling an extremely hygroscopic liquid that boils at -33° . Working at ambient pressures requires the use of low temperature thermostats, whereas performing experiments under the usual temperature conditions leads to the use of pressure equipment. Thus it is not surprising that, except for the work of a few earlier investigators, reliable quantitative data on liquid ammonia solutions was not available until relatively recently.

The past twenty years have seen an increasing number of papers describing a variety of techniques for handling and for measuring properties of solutions of low-boiling substances. These have been summarized in a recent review¹. In addition, a rather detailed discussion of the methods which can be used to

prepare solvent grade ammonia from the commercial product as well as the factors which affect solvent purity in a reaction system has been presented².

SOLVENT PROPERTIES

It has been often said that liquid ammonia is, in general, a better solvent than water, although for specific classes of compounds, e.g. ionic compounds, the latter substance may have superior solvent characteristics. The bases for this generalization stem from the fact that liquid ammonia has a moderate dielectric constant and a high dipole moment, has a relatively high basicity, and can form hydrogen bonds. Each of these factors contributes to different aspects of solute-solvent interactions which must be relatively high to overcome the usual solvent-solvent and solute-solute interactions that oppose the solution of one substance in another.

Solubility of covalent molecules

The extent of solubility of covalent substances in liquid ammonia is affected by the polarity of the ammonia molecule, its ability to form hydrogen bonds, and the magnitude of the dispersion forces which exist between the solvent and solute. Considering each of these factors in turn, it is possible to understand the fundamental reasons for the general observation that ammonia is a better solvent for covalent substances than is water.

The interaction between two molecules possessing permanent dipole moments depends upon their relative orientation, the most favourable orientation occurring when the dipoles are parallel. At any temperature, the most favoured orientation is opposed by thermal motion and a statistically preferred orientation occurs. The potential energy of this system is expressed by equation 1, where μ_1 and μ_2 are the magnitude of the permanent dipoles at a distance r from each other.

$$E_p = \frac{-2\mu_1^2\mu_2^2}{3r^6kT} \quad (1)$$

The fact that ammonia (1.49 Debye) has a dipole moment about 80 per cent of that of water (1.84 Debye) suggests that it should be nearly as good a solvent as is water for polar molecules.

Two molecules can attract each other even if they do not possess permanent dipole moments. The fluctuating dipoles in a given molecule can induce dipoles in neighboring dipoles leading to relatively weak dipole-dipole interactions that were first described by London³ as dispersion forces. The magnitude of the dispersion energy is given by equation 2

$$E_D = - \left(\frac{3}{2} \right) \frac{\alpha_1\alpha_2}{r^6} \frac{I_1I_2}{I_1 + I_2} \quad (2)$$

where α and I represent the polarizability and ionization potential of the respective species [$\alpha(\text{H}_2\text{O}) = 1.48$, $\alpha(\text{NH}_3) = 2.21$, $I(\text{H}_2\text{O}) = 12.62$ ev, $I(\text{NH}_3) = 10.15$ ev]. Thus, because of its larger polarizability and small ionization potential, the dispersion effect is nearly twice as great for ammonia molecules as for water, although the reverse is true for the orientation effect

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which is dependent upon the dipole moment of the molecule. It is, therefore, not surprising that ammonia is not as good a solvent for less polar systems.

Like water, ammonia is an associated liquid, the association occurring through the formation of hydrogen bonds. Water molecules have an equal number of hydrogen atoms and electron pairs which lead to a beautifully symmetrical continuous structure in the solid state. In the case of ammonia molecules, which possess one electron pair, it might appear that only limited hydrogen bonding would be possible. However, the cubic structure of solid ammonia (*Figure 1*) also exhibits a continuous hydrogen bonded system.

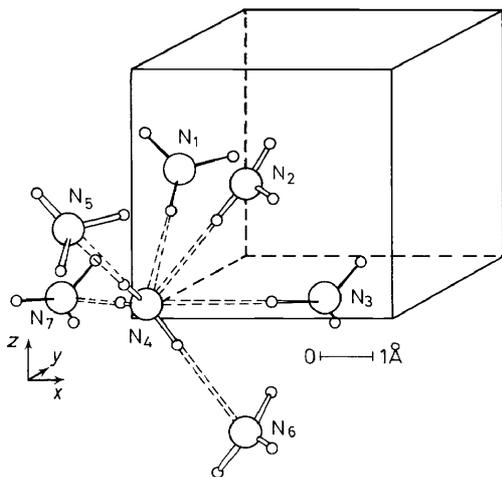


Figure 1. Crystal structure of cubic ammonia

Each nitrogen atom is surrounded by six hydrogen atoms, three of which are formally bound (short N-H distances) and three that are more loosely held (long N-H distances). It would appear that each unshared electron pair on a nitrogen atom can accommodate three hydrogen bonds. Although there is no claim that the solid state structure persists as such in the liquid phase, it does provide an insight into the probable basis for association in the liquid phase. Thus, ammonia molecules can be involved in hydrogen bonding either through its hydrogen atoms or unshared pair of electrons.

Table 1 illustrates the remarkable range of compounds that are soluble to a reasonable extent in liquid ammonia. Only representative compounds are listed. As might be expected, the aliphatic hydrocarbons are virtually insoluble, however, the more polarizable unsaturated hydrocarbons are markedly more soluble. Introduction of functional groups which are polarizable, which increase the polarity of the molecule, or which provide sites for hydrogen bonding leads to compounds that are very soluble in ammonia. Thus it is not difficult to see why ammonia has found use as a reaction medium, and why it is potentially a very useful solvent for physical chemical investigations.

Covalent molecules possessing acidic hydrogen atoms can react with liquid ammonia to form products, e.g. ammonium salts, which are soluble in this

Table 1. Qualitative solubility of some covalent substances in liquid ammonia

	Substance	Solubility	Ref.	
Hydrocarbons	CH ₃ CH ₂ CH ₃	Insoluble	a	
	CH ₃ (CH ₂) ₄ CH ₃	Insoluble	b	
	C ₆ H ₆	Moderately soluble	b	
Substituted hydrocarbons	C ₆ H ₅ CH=CH ₂	Soluble	b	
	CHBr ₃	Miscible	b	
	C ₂ H ₅ I	Soluble	b	
	BrCH ₂ CH ₂ Br	Soluble	b	
	Cl ₂ C=CH ₂	Miscible	b	
	CH ₃ NO ₂	Miscible	b	
	C ₆ H ₅ NO ₂	Solubility, 24%	c	
Carbonyl derivatives	(CH ₃) ₂ CO	Miscible	a	
	CH ₃ CHO	Miscible	a, d	
	CH ₃ (CH ₂) ₃ CHO	Easily soluble	b	
	CH ₃ CO—NH ₂	Very easily soluble	b, e	
	CH ₃ CS—NH ₂	Easily soluble	f	
	(H ₂ N) ₂ CS	Solubility, 37%	c	
	CH ₃ CH ₂ CO ₂ CH ₃	Miscible	b, g	
	C ₆ H ₅ CH ₂ CO ₂ CH ₃	Miscible	c	
	Alcohols	CH ₃ OH	Miscible	b
		CH ₃ (CH ₂) ₆ OH	Miscible	b
C ₆ H ₅ CH ₂ OH		Miscible	b, c	
1,2—C ₆ H ₄ (OH) ₂		Very easily soluble	b	
Amines	CH ₃ NH ₂	Miscible	b	
	(CH ₃) ₃ N	Miscible	b	
	CH ₃ (CH ₂) ₄ NH ₂	Miscible	b	
	C ₆ H ₅ N	Miscible	b	
Ethers	(C ₂ H ₅) ₂ O	Miscible	b, d	
	[CH ₃ (CH ₂) ₃] ₂ O	Soluble	h	
	C ₆ H ₅ OCH ₃	Miscible	b	

^a C. A. Kraus and G. F. White. *J. Am. Chem. Soc.* **45**, 768 (1923).^b E. C. Franklin and C. A. Kraus. *Am. Chem. J.* **20**, 820 (1898).^c F. de Carli. *Gazz. Chim. Ital.* **57**, 347 (1927).^d G. Gore. *Proc. Roy. Soc. (London)* **20**, 441 (1872).^e R. V. Fulton, Thesis, Stanford University, 1925.^f E. C. Franklin and O. F. Stafford. *Am. Chem. J.* **28**, 83 (1902).^g E. Chablay. *Compt. Rend.* **154**, 364 (1912).^h F. A. White, A. B. Morrison and E. G. E. Anderson. *J. Am. Chem. Soc.* **46**, 961 (1924).

solvent. The apparent acidity of many types of compounds is more noticeable in ammonia than in water since the former solvent is distinctly more basic than water. Thus, carboxylic acids, phenols or imides form very soluble ammonium salts when dissolved in liquid ammonia.

The solubility of ionic substances

The solubility of an ionic substance in any solvent depends upon the polarity and dielectric constant of the solvent as well as the lattice energy of the solute. A comparison of the solubilities of ionic substances in two different solvents, leads to a consideration of the differences in solvent properties. The interaction between an ion of charge Ze and a molecule with a dipole moment μ separated by a distance r is given by

$$E = \frac{Ze\mu}{r^2} \quad (3)$$

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Accordingly, ion-dipole interactions should be weaker in ammonia than in water because of the larger dipole moment of the latter substance.

The solvation energy of a gaseous ion of charge Ze and radius r in a solvent of dielectric constant D is given by the Born expression

$$\Delta E = \frac{Z^2 e^2}{2r} \left(1 - \frac{1}{D} \right) \quad (4)$$

Table 2. Lattice energies of some sodium salts

	Solubility, moles/1000 g		Lattice energy Kcal/mole
	NH ₃ (-0.1°)	H ₂ O(0°)	
NaCl	2.20	6.10	180
NaBr	6.21	7.71	175
NaI	8.80	10.72	161
NaNO ₃	15.00	8.62	176

It is apparent that ions should be more readily solvated in water than ammonia because of the difference in dielectric constants of these solvents. Although extensive data are not available to verify these arguments, a comparison of the solubilities of a limited series of sodium salts under the same experimental conditions (Table 2) gives an insight into the validity of the previous discussion. In each case the solubility of a given salt is greater in water than in ammonia. Within a given solvent, the solubility of the halides falls in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$ which is the order expected on the basis of the relative lattice energies. An interesting inversion occurs in the case of sodium nitrate. The magnitude of the lattice energy of this substance suggests that its solubility in each solvent should be similar to that of sodium bromide, which is more nearly true in aqueous solution than in ammonia. Normally, dispersion forces are neglected when discussing ion-dipole interactions, however, the greater dispersion effect found for ammonia compared with water may be important for ions that have relatively high polarizabilities.

The moderate dielectric constant of ammonia suggests that ionic species in this solvent would be appreciably associated. Conductivity data for solutions of salts indicate that ion-pairing occurs at low concentrations and that higher ion aggregates are formed at higher concentrations.

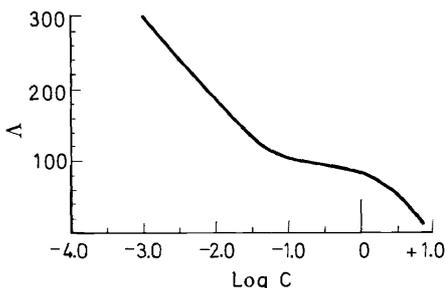
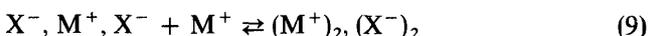
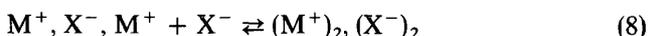
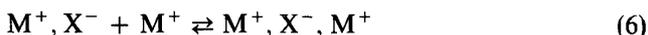


Figure 2. The equivalent conductances of NaNO₃ in liquid ammonia at -33.5°. [E. C. Franklin, *Z. Physik. Chem.* **69**, 272 (1910)]

In general, the equivalent conductance of solutions of completely ionized substances like NaNO_3 decreases rapidly with increasing concentration which has been interpreted as the formation of ion-pairs (*Figure 2*). However, after a point, as the concentration of electrolyte is increased, the conductivity decreases less rapidly; indeed, in a few cases there is a slight increase in conductivity. It has been suggested that higher ion-aggregates which are conducting, such as ion-triplets, are formed in this concentration range. The continued decrease in conductivity at very high concentrations reflects the formation of non-conducting ion-aggregates. The equilibria that have been proposed to account for the conductivity experiments are given by equations 5-10.



Conducting species are consumed at the expense of non-conducting species in equilibria 5, 8, and 9 whereas the reverse is true for equilibria 6 and 7.

Conductivity data for a variety of substances dissolved in liquid ammonia have been interpreted in terms of ion-pair formation for solutions less concentrated than about 10^{-3}M (*Table 3*). Substances that are obviously

Table 3. Electrolytic parameters for some salts in liquid ammonia

Solute	t, °C	A°	$a \times 10^8$	$K \times 10^4$	Ref.
KI	-34	345.1	6.6	54.64	a, b, c
NaBr	-34	314.3	5.9	38.02	a, c
LiNO_3	-40	277	5.04	36.5	c, d
$\text{Na}[\text{SC}_6\text{H}_5]$	-33	275.1	4.95	36.0	e
NaCl	-34	314.45	—	28.98	b, c
AgNO_3	-33	287	—	28.0	c
NH_4NO_3	-33	301.8	—	28.0	c
KBr	-34	346.8	7.8	22.07	a, b, c
KNO_3	-33	339	—	15.5	c, d
NH_4Cl	-33	310	—	12.0	e
AgI	-33	287	—	2.9	c
$\text{Na}[\text{CH}_2\text{NO}_2]$	-33	278	—	0.78	c
$\text{NH}_4[\text{CH}_2\text{NO}_2]$	-33	278	—	0.53	c

^a R. L. Kay. *J. Am. Chem. Soc.* **82**, 2099 (1960).

^b V. F. Hnizda and C. A. Kraus. *J. Am. Chem. Soc.* **71**, 1565 (1949).

^c C. A. Kraus and W. C. Bray. *J. Am. Chem. Soc.* **35**, 1315 (1913).

^d R. M. Fuoss and C. A. Kraus. *J. Am. Chem. Soc.* **55**, 1019 (1933).

^e C. A. Kraus and E. G. Johnson. *J. Am. Chem. Soc.* **55**, 3542 (1933).

ionic such as the alkali metal halides exhibit ion-pair formation constants which are of the order of 10^{-3} . The data in *Table 3* also illustrate the difficulty in interpreting conductivity data for liquid ammonia systems containing

weakly ionized substances. For example, nitromethane is sufficiently acidic in liquid ammonia to give a conducting solution and the conductivity data have been interpreted in terms of an equilibrium between ions and unpaired species. The reported value of the equilibrium constant in this system is more than two orders of magnitude smaller than that of NH_4NO_3 , the ions of which might be expected to exhibit similar conductivity as those in the compound $[\text{NH}_4]^+ [\text{CH}_2\text{NO}_2]^-$. A possible solution to the problem occurs if it is assumed that nitromethane is not completely ionized (equation 11).



In this case the conductivity data will give a lower value for the apparent equilibrium constant because this method relates the relative concentrations of conducting and non-conducting species (equation 12).

$$K = \frac{[\text{NH}_4^+] [\text{CH}_2\text{NO}_2^-]}{[\text{NH}_4^+, \text{CH}_2\text{NO}_2^-] + [\text{CH}_3\text{NO}_2]} \quad (12)$$

If an unknown fraction of the non-conducting species is associated into ion-pairs, equilibrium constants measured by conductivity methods are not necessarily directly comparable, nor do they have the same implications as those determined by other methods in ammonia or by the same method in solvents with a higher dielectric constant.

The nature of the ion-pairs found in liquid ammonia solutions which have been inferred from conductivity methods can be elucidated in some instances using spectroscopic data. For example, liquid ammonia solutions containing iodide ions possess⁴ an absorption band at about 2500 Å characteristic of charge-transfer-to-solvent spectra of this species in other solvents⁵. That is, the iodide ion occupies a solvent cavity and the excited state corresponds to an electron in an orbital defined by the solvent molecules which form the cavity. Under a given set of experimental conditions, solutions of most of the alkali and alkaline earth iodides are indistinguishable (*Table 4*) on the basis of their spectral characteristics. This behaviour, together with the association phenomena inferred from conductivity data suggests that the ion-pairs formed probably consist of associated solvated ions rather than solvent-shared or contact ion pairs. Indeed, even in the presence of a large concentration of inert salt, the position of the charge-transfer-to-solvent band is virtually unchanged. However, in the presence of cations with a high charge density, the usual charge-transfer-to-solvent band is perturbed suggesting that the cation may either be sharing a solvent molecule with the iodide ion or be within the solvent sphere. Solutions of calcium iodide exhibit no free iodide ion absorption band suggesting that a molecular species is present; it is very likely that these solutions contain the species $\text{CaI}_2(\text{NH}_3)_4$.

Charge-transfer-to-solvent spectra have been observed for solutions containing these anions and cations with a relatively low charge density are virtually superimposable. Changes in the spectrum occur if more polarizing cations are present. These results can be interpreted in terms of the existence of solvent separated ion pairs for large cations; the more polarizing cations either enter the solvation sphere or form solvent shared ion pairs.

Table 4. Positions and temperature coefficient for band maxima in iodide solutions in liquid ammonia^a

Solute	λ max, Å ^b	$\frac{d\lambda}{dt}$ max, Å-deg ⁻¹	$\frac{dE}{dt}$ max, cal-deg ⁻¹
LiI	2500	1.28 ± 0.05	-59.0
LiI + LiClO ₄ ^c	2493	1.42 ± 0.07	-72.6
NaI	2500	1.36 ± 0.04	-62.8
KI	2500	1.34 ± 0.06	-61.5
RbI	2499	1.24 ± 0.05	-56.0
RbI + KClO ₄ ^c	2491	1.31 ± 0.03	-66.8
RbI + LiClO ₄ ^c	2493	1.33 ± 0.10	-67.8
CcI	2499	1.39 ± 0.02	-64.0
CsI + LiClO ₄ ^c	2491	1.32 ± 0.03	-67.4
SrI ₂	2485	0.74 ± 0.03	-32.0
BaI ₂	2504	1.06 ± 0.08	-30.3
CaI ₂ ^d	—	—	—

^a J. T. Nelson, R. E. Cuthrell and J. J. Lagowski. *J. Phys. Chem.* **70**, 1492 (1966).^b Measured at -50°.^c 100-fold excess of inert salt.^d Featureless.

Table 5. Positions and temperature coefficients of the absorption band for some sulphides and amides in liquid ammonia

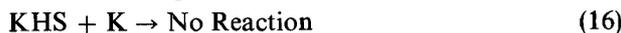
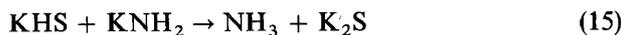
Solute	λ max, m μ	t, °C	$\frac{dE}{dt}$ max, cal-deg ⁻¹
K ₂ S ^a	270	-77	77
H ₂ S ^a	270	-77	68
LiNH ₂ ^c	340	-50	—
NaNH ₂ ^c	319	-50	—
KNH ₂ ^c	332	-50	-47.7
RbNH ₂ ^c	332	-50	—
CsNH ₂	332	-50	—

^a J. T. Nelson and J. J. Lagowski. *Inorg. Chem.* **6**, 862 (1967).^b J. A. Caruso, J. H. Takemoto and J. J. Lagowski. *Spectroscopy Letters* **1**, 311 (1968).^c R. E. Cuthrell and J. J. Lagowski. *J. Phys. Chem.* **71**, 1298 (1967).

An interesting example of ion association occurs in solutions containing ammonium ions and sulphide ions. The charge-transfer-to-solvent spectrum of such solutions do not exhibit the same characteristics as those of alkali metal sulphides (Table 5). This behaviour has expression in the chemical characteristics of a liquid ammonia solution of H₂S. One proton in such solutions reacts readily with either potassium amide or potassium metal,



however the second proton will only react with potassium amide, insoluble K₂S being formed in the process.



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If a half-neutralized solution of H_2S is saturated with a very soluble potassium salt, there is no precipitation of K_2S . These observations suggest that the second proton is still strongly associated with sulphur, probably as a hydrogen bonded species such as $\text{H}_3\text{N} \cdots \text{HS}^-$.

Solutions of elemental substances

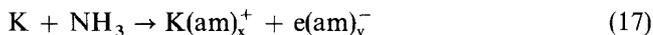
Perhaps one of the most interesting characteristics of liquid ammonia is its ability to dissolve elemental substances such as sulphur⁹, selenium¹⁰, tellurium¹¹, the alkali metals and the alkaline earth metals¹². Not only is the nature of the species existing in solution of interest, but the solutions themselves are useful from a physico-chemical or synthetic standpoint.

The more active metals dissolved readily in pure ammonia to form stable blue solutions (*Table 6*); at higher concentrations of metals, the solutions are

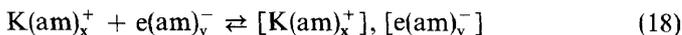
Table 6. Ionization potentials, heat of sublimation, and charge density of some metals

Metal/ion	$(Z^2/r), \text{\AA}^{-1}$	I.P., ev	$\Delta H_s, \text{ev}$
Soluble metals			
Cs/Cs ⁺	0.59	3.89	0.82
Rb/Rb ⁺	0.68	4.17	—
K/K ⁺	0.75	4.24	0.93
Na/Na ⁺	1.05	5.14	1.13
Li/Li ⁺	1.66	5.39	1.68
Bu/Bu ²⁺	2.96	15.16	2.00
Sr/Sr ²⁺	3.54	16.67	1.84
Eu/Eu ²⁺	3.67	17.04	1.82
Ca/Ca ²⁺	4.04	18.98	2.00
Yb/Yb ²⁺	4.30	18.50	1.65
Mg/Mg ²⁺	6.15	22.67	1.55
Insoluble metals			
Sm/Sm ²⁺	3.60	7.71	2.00
Pb/Pb ²⁺	3.31	22.4	2.04
Al/Al ³⁺	18.0	53.24	3.37
Tl/Tl ⁺	0.69	6.11	1.87
Sc/Sc ³⁺	11.1	44.11	3.90
Yb/Yb ³⁺	9.68	39.2	4.41

bronze coloured. The electrical, optical, and magnetic properties of these solutions¹² indicate that the solutions contain solvated electrons. Although there is still a great deal of controversy concerning the detailed structure of the solvated electron in liquid ammonia and the species which may be formed at higher metal concentrations, it is generally agreed that the dilute blue solutions contain electrons trapped in solvent cavities (equation 17).



These charged species appear to be electrostatically associated with solvated cations in much the same way as are the ordinary ion-paired species (equation 18).



The energy changes associated with the dissolution of a metal in liquid

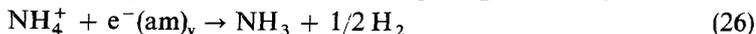
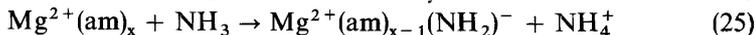
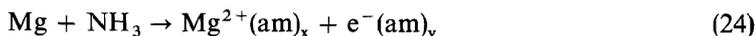
ammonia may be simply represented by equations 19 through 22.



The symbols ΔH_s , IP , $\Delta H_{\text{M}^+(\text{am})}$, and $\Delta H_{\text{e}^-(\text{am})}$ represent the heat of sublimation and ionization potential of the metal, the heat of solvation of the metal ion and the heat of solvation of the electron, respectively. Thus, sufficient energy must be released in the solvation of the charged species to overcome the lattice forces of the metal plus the energy to ionize metal atoms to form a stable solution.

$$\Delta H_s + IP < \Delta H_{\text{m}^+(\text{am})} + \Delta H_{\text{e}^-(\text{am})} \quad (23)$$

Although sufficient data are not yet available to complete this analysis, it is possible to understand the factors underlying the formation of metal-ammonia solutions in a qualitative way. The solvation energy for the electron (equation 22) is constant for all metals, the value of $\Delta H_{\text{e}^-(\text{am})}$ being estimated as -39 Kcal/mole¹³ from a thermo-chemical cycle. The energy of solvation is, in general, dependent upon the charge of the ion and its radius (equation 4). The alkali metals have relatively low ionization potentials and heats of sublimation so that the solvation energy of the electron and ion [measured by (Z^2/r)] need not be large to compensate for the former factors. In the case of the alkaline earth metals, both the ionization potentials and the sublimation energy are larger than the corresponding quantities for the alkali metals, but apparently the solvation energy increases accordingly. It is interesting to note in this respect that the alkaline earth metals form stable ammoniates with the formula $\text{M}(\text{NH}_3)_6$ ¹⁴. The compensation of energies apparently is finely balanced in the case of magnesium since this metal will not dissolve in pure ammonia to form a blue solution. Prolonged contact with ammonia or with solutions containing inert salts¹⁵ gives hydrogen. These observations suggest that if magnesium dissolves the magnesium ions formed undergo solvolysis to form ammonium ions which then react with solvated electrons (equations 24–26).



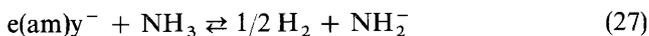
A magnesium ion possesses the highest charge density of all the ions in the alkaline earth series and it would be expected to be the most solvolyzed of these ions. The basic incompatibility of solvated electrons and solvated magnesium ions has also been illustrated by electrolyzing an ammonia solution of MgCl_2 ¹⁶. Rather than forming the stable blue solution which occurs during the electrolysis of a solution of sodium chloride, hydrogen was liberated at the cathode.

These observations suggest that stable magnesium ammonia solutions can be formed if the solvolysis of Mg^{2+} (equation 25) could be suppressed.

It has been observed that magnesium dissolves readily in ammonia solutions containing KNH_2 , KOCH_3 or $\text{KOC}(\text{CH}_3)_3$; the solutions are blue and have optical characteristics indistinguishable from those of the other alkaline earth metals¹⁷.

The rare earths europium and ytterbium dissolve to form blue metal–ammonia solutions^{18, 19}. These elements possess characteristics very similar to those of the alkaline earth metals (*Table 6*). *Table 6* also contains data on several other metals which might be candidates for forming solutions containing solvated electrons. In these cases, the ionization potentials and heat of sublimation are too large to be overcome by the solvation effects. Attempts to dissolve these metals in basic solutions did not yield solutions containing solvated electrons. The properties of samarium and thallium strongly suggest that these metals should be soluble, however stable solutions could not be obtained in either pure ammonia or in basic solution¹⁷.

The metal–ammonia solutions are perfectly stable in the absence of catalysis such as finely divided metals or metal oxides. When these solutions decompose, hydrogen is liberated (equation 27)

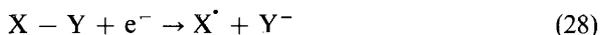


Metal amides also appear to be good catalysts for this reaction; in a practical sense, this observation means that the reaction of metals with ammonia is autocatalytic. The reaction of solvated electrons with ammonia to form hydrogen (equation 27) is reversible, i.e. it is possible to prepare the characteristic blue solutions by introducing hydrogen under pressure into a solution containing NH_2^- . The value of the equilibrium constant for equation 27 has been estimated from electron spin resonance data and from optical data; at 25°C the equilibrium constant for reaction 27 is 5×10^4 ²⁰.

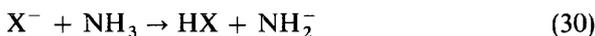
OXIDATION-REDUCTION PROCESSES

The utility of ammonia as a medium in which to study oxidation–reduction reactions using conventional electro-chemical techniques has not yet been widely recognized. Metal–ammonia solutions have found extensive use as chemical reducing agents in the synthesis of a variety of organic compounds²¹. As has been discussed previously, ammonia is a very good solvent for organic substances; a wider variety of compounds can be dissolved if a co-solvent is present. Thus, it is possible to obtain experimental conditions suitable for the homogeneous reduction of covalent molecules. Numerous kinetic studies involving reduction by metal–ammonia solutions have been made in an attempt to formulate the mechanisms by which such processes occur²⁰.

In general, electron addition to saturated compounds leads to bond cleavage with the formation of either radicals and/or ionic species (equations 28 and 29).



The ions formed in such reactions are usually conjugate bases of very weak acids and abstract protons from either the solvent or from other stronger proton donors in the system (equations 30 and 31).



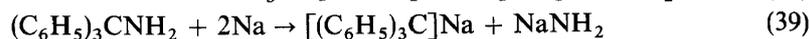
The radicals formed in the original process can take up another electron (equation 32), undergo dimerization with other radicals (equation 33), or they can abstract radicals from molecular species (equation 34).



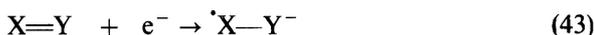
The dimerized species can, of course, arise from the reaction of an anion with the molecular species (equation 35).



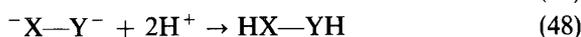
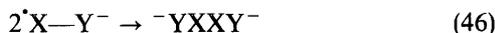
Although there are numerous examples of each of these pathways available for discussion only a representative number appear in equations 36 to 42.



The reaction of solvated electrons with unsaturated bonds generally follows similar pathways, except that bond fission need not occur. Either one or two electrons can be added to unsaturated bonds to form a radical anion or a dianion, respectively (equations 43 to 45).

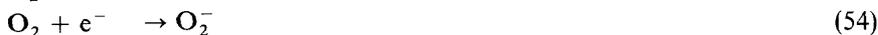
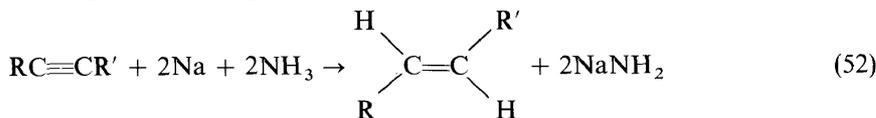
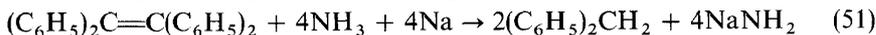


Radicals can dimerize (equation 46) and anions which are conjugate bases of weak acids can abstract protons (equations 47 through 49).

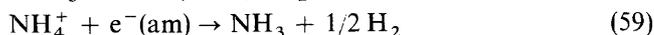


Again there are numerous examples of those possible pathways, but only a few representative reactions are given in equations 50 through 56.

SOLUTION PHENOMENA IN LIQUID AMMONIA



Little has been done with electrolytically generated solvated electrons from either a synthetic or an electro-chemical point. The electrolysis of solutions possessing non-reducible functions such as simple salts gives blue solutions at the cathode (equation 57) and an acidic solution arising from the decomposition of the solvent at the anode (equation 58).



If these solutions mix, there will, of course, be a reaction of the solvated electron (equation 59).

Since solvated electrons exhibit a characteristic spectrum (Figure 3), the

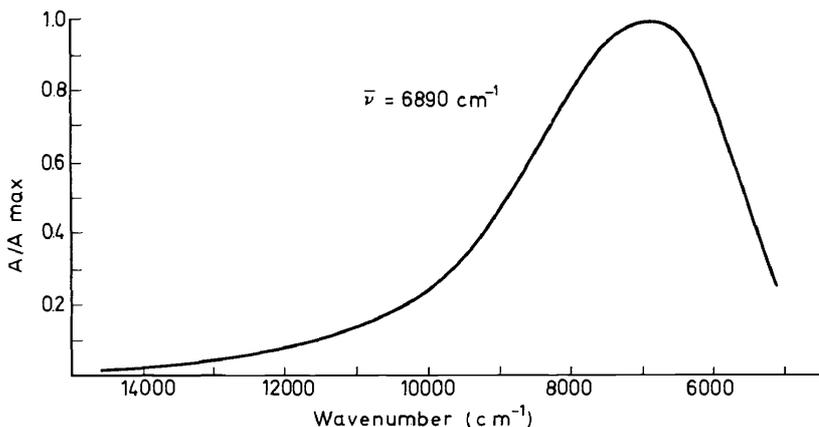


Figure 3. A typical spectrum of a metal-ammonia solution ($\text{Na}-\text{NH}_3 \sim 10^{-4}\text{M}$)

interesting possibility exists of following the course of oxidation-reduction reactions using spectroscopic methods. The unusually high extinction coefficient at the wavelength of the maximum suggests that at reasonably low concentrations of solvated electrons, the reduction product can be detected. Indeed, optical absorption spectroscopy was one of the methods used to determine the value of the equilibrium constant for the reaction between solvated electrons and ammonia²⁰.

ELECTROCHEMICAL PHENOMENA

In addition to the redox processes which have been described for the reactions of metal-ammonia solutions, a number of electrochemical investigations incorporating the usual experiment techniques have appeared. Standard electrode potentials have been established for a variety of systems in liquid ammonia solutions (Table 7). A more direct comparison of the

Table 7. Experimental electrode potentials in liquid ammonia

Electrode	E, volts	<i>t</i>	Reference electrode	Ref.
Li/Li ⁺	2.597	-50	Pb/PbNO ₃	a
Cs/Cs ⁺	2.317	-50	Pb/PbNO ₃	b
K/K ⁺	2.316	-50	Pb/PbNO ₃	c
Rb/Rb ⁺	2.286	-50	Pb/PbNO ₃	a
Na/Na ⁺	2.174	-50	Pb/PbNO ₃	c
Ca/Ca ²⁺	1.968	-50	Pb/PbNO ₃	a
Zn/Zn ²⁺	0.866	25	H ₂ /H ⁺	d
Zn/Zn ²⁺	1.27	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
H ₂ /H ⁺	0.75	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
Cd/Cd ²⁺	0.506	25	H ₂ /H ⁺	d
Cd/Cd ²⁺	0.93	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
Pb/Pb ²⁺	0.42	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
Cu/Cu ²⁺	0.32	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
Tl/TlCl	0.037	25	H ₂ /H ⁺	d
Hg/Hg ²⁺	0.00	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
Cu/Cu ²⁺	-0.05	-50	Pb/Pb(NO ₃) ₂	g
Ag/Ag ⁺	-0.08	-50	H ₂ /H ⁺ (H ₂ O, 20°)	e
I ₂ /I ⁻	-0.70	0	H ₂ /H ⁺ (H ₂ O, 20°)	f
Br ₂ /Br ⁻	-1.08	0	H ₂ /H ⁺ (H ₂ O, 20°)	f
Cl ₂ /Cl ⁻	-1.28	0	H ₂ /H ⁺ (H ₂ O, 20°)	f

^a V. A. Pleskov. *Zh. Fiz. Khim.* **9**, 12 (1937); *Acta Physicochim. URSS*, **6**, 1 (1937).

^b V. A. Pleskov. *Zh. Fiz. Khim.* **20**, 163 (1946); *Acta Physicochim URSS*, **21**, 253 (1946).

^c V. A. Pleskov and A. M. Monossohn. *Acta Physicochim URSS*, **2**, 615 (1935).

^d H. W. Ritchy and H. Hunt. *J. Phys. Chem.* **43**, 407 (1935).

^e V. A. Pleskov and A. M. Monossohn. *Acta Physicochim URSS*, **2**, 621 (1935).

^f V. A. Pleskov. *Acta Physicochim URSS*, **2**, 679 (1935).

^g V. A. Pleskov. *Acta Physicochim URSS*, **13**, 659 (1940).

standard potentials in aqueous and liquid ammonia solutions has been made²² using Pleskov's method²³ of obtaining a common reference ion. The ideal reference ion would exhibit the same free energy of solvation in all solvents so that it would have zero free energy of transfer from one solvent to another. The reference ion chosen should exhibit no specific mode of interaction with a solvent; these conditions are approximated for large cations with a small charge. Originally, the rubidium ion was used as a reference; subsequently organometallic cations (i.e., ferricinium and cobalticinium ions) have been employed for this purpose. Using extra-thermodynamic arguments, the free energy of solvation of Rb⁺ in water and ammonia have been estimated as 72.5 kcal/mole and 71.0 kcal/mole, respectively²⁴. Thus, the Pleskov approximation appears to be reasonably good. If the potentials measured in liquid ammonia and in water are corrected for the same conditions a direct comparison of these potentials can be obtained on a common scale using the Rb/Rb⁺ system as reference (Figure 4). The results

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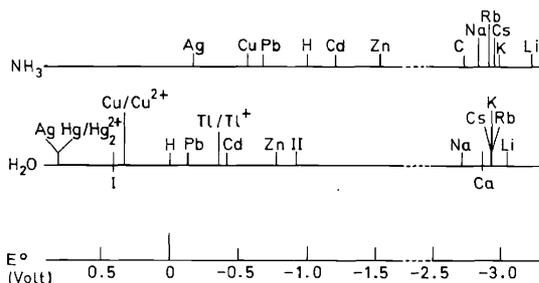


Figure 4. A comparison of the voltage series in ammonia and in water at 25° normalized by the Pleskov method

suggest that, in general, cations with a high charge density are more highly solvated in liquid ammonia than in water. There are, however, some notable exceptions, i.e. in the case of Ca^{2+} ions.

On the basis of the experimental difficulties in handling liquid ammonia solutions, it is not surprising that the results of polarographic techniques have not been employed extensively in understanding the nature of solution species in this solvent. Polarographic measurements at a dropping mercury electrode²⁵ and at platinum microelectrodes²⁶ have been made. Unfortunately, the dropping mercury electrode finds rather limited use in liquid ammonia because of the temperature range available between the freezing point of mercury (-38.9°) and the normal boiling point of ammonia (-33.4°). The reduction of several metallic ions have been studied in liquid ammonia (Table 8). The alkali metal ions and the ammonium ion are reduced at a

Table 8. Half wave potentials of some cations in liquid NH_3 (-36°) at a dropping mercury electrode vs. $\text{Pb}/\text{Pb}(\text{NO}_3)_2$

Ion	$E_{1/2}$, volts	Slope ^a	Ref.
Li^+	-1.67	0.058	b
Na^+	-1.31	0.057	b
K^+	-1.24	0.056	b
Rb^+	-1.21	0.061	b
Cs^+	-1.15	0.065	b
Ca^{2+}	-1.64	0.046	c
Sr^{2+}	-1.37	0.069	c
Ba^{2+}	-1.22	0.037	c
Tl^+	+0.15	0.057	d
$\text{Cu}^{2+}/\text{Cu}^+$	+0.16	0.049	d
Cu^+	-0.21	0.066	d
NH_4^+	-1.37	0.050	d

^a Reciprocal slope of $\log(i_r - i) vs. E$ plot. Under the conditions of these experiments, this value should be 0.047 for a reversible process.

^b H. A. Laitinen and C. J. Nyman. *J. Am. Chem. Soc.* **70**, 2241 (1948).

^c C. J. Nyman. *J. Am. Chem. Soc.* **71**, 3914 (1949).

^d H. A. Laitinen and C. E. Shoemaker. *J. Am. Chem. Soc.* **72**, 4975 (1950).

mercury electrode; these processes are nearly polarographically reversible. As indicated in a previous section, if there are no reducible species present in solution, it is possible to prepare a solution of electrons by electrolytic

methods. The potential for the dissolution of electrons at a mercury electrode has been estimated from polarographic data to be -2.27 to -2.23 volts versus a $\text{Pb}/\text{Pb}(\text{NO}_3)_2$ reference^{25, b}.

The polarographic data for the reduction of NH_4^+ at a dropping mercury electrode^{25, d} and at a platinum microelectrode²⁶ indicate that two different processes are occurring. The reduction product at a mercury electrode appears to be free ammonium stabilized by amalgam formation. On the other hand, the reduction of ammonium ions at a platinum microelectrode appears to involve the formation of an intermediate platinum-hydrogen (or ammonium) compound of unspecified structure which strongly interacts with the electrode surface. At relatively high concentrations of ammonium salts, the current-voltage curves were not reproducible after one or two determinations with a given microelectrode; the platinum microelectrode becomes coated with a layer of platinum black.

Extensive data collected on solutions of different ammonium salts and different supporting electrolytes indicate that the reduction process at the solid microelectrode is diffusion controlled and that the limiting current arises from the reduction of other ammonium ions and ion aggregates containing the ammonium ion or ion aggregates alone. In agreement with previous arguments, the polarographic data for the reduction of the alkali metals and NH_4^+ indicate that the reduction of the latter is directly comparable to the former. The magnitude of the diffusion currents indicate that the solvated ammonium ion diffuses as an entity through the solvent. The transfer of protons from one solvent molecule to the next is relatively slow in liquid ammonia.

ACID-BASE BEHAVIOUR

As in the case of aqueous systems, acid-base reactions occur in liquid ammonia by participation of the solvent. Acid-base processes which involve proton transfer or the ability of ammonia to act as a Lewis base are well documented.

Proton transfer reactions

The low conductivity of liquid ammonia, i.e. 10^{-11} ohm⁻¹cm⁻¹ at -33.40 ²⁷, has been interpreted as a measure of the low degree of autoprotolysis of this substance.



Neither the solvated proton in liquid ammonia, nor the amide ion exhibits unusual conductance characteristics when compared with other ionic species in that solvent (*Table 9*). This is in marked contrast to the behaviour of the solvated proton and the hydroxide ion in water. The unusually high conductivity of the parent acid and base species in water has been attributed to a Grotthuss type mechanism where proton or hydroxide ion are transferred because hydrogen bonds are made and broken in a concerted manner (*Figure 5*). In this view, it is incorrect to speak of the movement of a given proton or hydroxide ion through the solution in the same sense as we think of a sodium ion moving under the influence of an electric field. Since liquid ammonia is an associated liquid it might be expected superficially that the

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Table 9. Equivalent ionic conductivities in water and in ammonia

Ion	H ₂ O ^a	NH ₃ ^b
Na ⁺	50.00	130
K ⁺	73.52	168
NH ₄ ⁺	72.4	131
H ⁺	349.82	—
OH ⁻	198.0	—
NH ₂ ⁻	—	133

^a At 25° and infinite dilution.

^b At -33.5°. C. A. Kraus and W. C. Brey. *J. Am. Chem. Soc.* **25**, 1315 (1913).

 Table 10. Hydrogen bond energy and proton affinity for NH₃ and H₂O

	H bond energy kcal/mole ^a	Proton affinity kcal/mole
H ₂ O	5.0	182 ^b
NH ₃	4.4	209 ^c

^a J. D. Lambert. *Disc. Faraday Soc.* **11**, 226 (1953).

^b J. Sherman. *Chem. Rev.* **11**, 93 (1932).

^c T. C. Waddington. *Adv. Inorg. Chem. Radiochem.* **1**, 205 (1959).

solvated proton in this solvent might also have an abnormally high conductivity, an expectation that is not fulfilled (*Table 9*). The Grotthuss-type mechanism could be suppressed in ammonia if weaker hydrogen bonds are formed, if the interaction of a proton with ammonia is stronger than with water, or if a combination of these factors were operative. A comparison of the hydrogen bond energy and the proton affinity for ammonia and water show that both of these effects are present (*Table 10*). The hydrogen bond energy between solvent molecules for ammonia is about 88 per cent that for water, but the proton affinity of a water molecule is 88 per cent of an ammonia molecule. As an incidental point, these arguments suggest that the solvates of strong acids should be more stable for ammonia than for water, a conclusion verified by the relative ease of isolating crystalline ammonia salts compared with the corresponding hydronium salts.

The autoprotolysis constant of ammonia has been estimated from electrochemical experiments as well as from thermodynamic data. As is apparent from the summary in *Table 11*, there is relatively little agreement on the value

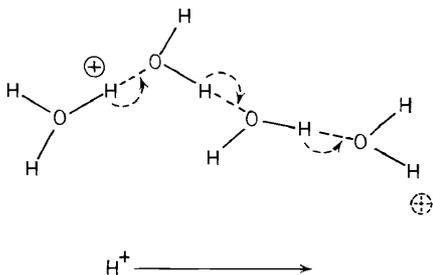


Figure 5. Proton movement in water under the influence of an electric field

of this constant. The data do indicate, however, the fact that the autoprotolysis constant for ammonia is considerably smaller than that of water. This observation is consistent with the more marked basic character of liquid ammonia compared to that of water.

Order of protonic acid strengths

Numerous observations indicate that the acidic nature of covalently bound hydrogen atoms is enhanced in liquid ammonia solutions compared to their behaviour in aqueous solutions. Substances such as acetic acid that are weak acids in water are completely ionized (but not necessarily completely

Table 11. Ion product of liquid ammonia

Value	Temp.	Method	Ref.
1.9×10^{-33}	-50°	Electrochemical cell, H, H ₂ /NH ₄ NO ₃ /KNO ₃ /KNH ₂ /H, H ₂	a, b
10^{-32}	-60°	Electrochemical	c, d
10^{-29}	-50°	—	e
5.1×10^{-28}	25°	Thermochemical	f
2.2×10^{-28}	25°	Thermochemical	g

^a V. A. Pleskov and A. M. Monossohn. *Acta Physicochim. URSS*, 1, 713 (1935).

^b V. A. Pleskov and A. M. Monossohn. *Acta Physicochim. URSS*, 2, 615 (1935).

^c M. Herlem. *Bull. Soc. Chim. France* 1687 (1967).

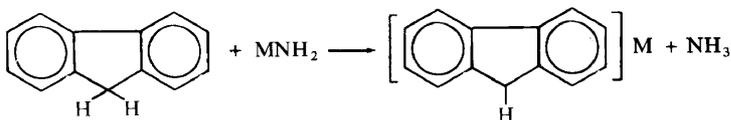
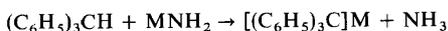
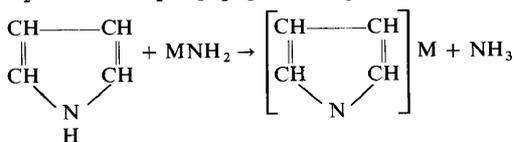
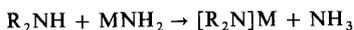
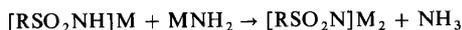
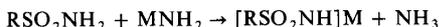
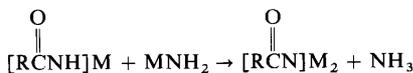
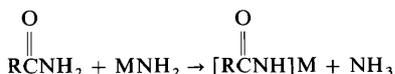
^d J. Badoz-Lambling, M. Herlem and A. Thiebault. *Anal. Letters* 2, 35 (1969).

^e J. Cuellieron and M. Herlem. *Bull. Soc. Chim. France* 800 (1956).

^f W. L. Jolly and C. J. Hollada. *Non-Aqueous Solvent Systems* T. C. Waddington (ed.), p 30. Academic Press, New York (1965).

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

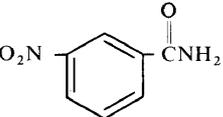
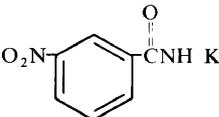
Table 12. Some acidic species in liquid ammonia



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dissociated) in ammonia. Other substances that exhibit little or no acidity in water undergo acid-base type reactions readily in liquid ammonia (*Table 12*). Thus, a wide variety of substance types such as acid amides²⁸, sulphonamides²⁹, amines³⁰, and hydrocarbons³¹ react with metal amides in liquid ammonia to give the corresponding metal derivatives that can be thought of as the salts of very weak acids. In many instances, it is possible to obtain similar metal salts of weak acids by reacting the acids with metal ammonia solutions in which instance hydrogen gas is liberated. Although there is no evidence in every case that the molecular species shown in *Table 12* ionize in liquid ammonia, there are some instances where conductivity data indicate the presence of ions (*Table 13*). For example, solutions of aliphatic acid amides have a small but measurable conductivity; the mono-potassium salts behave as strong electrolytes (*Table 13*). Amides which would be expected to be inherently stronger acids on the basis of their structures give

Table 13. Molecular conductivity of some acid amides and their salts at -33°

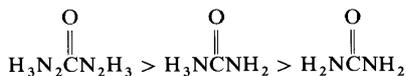
Acid	Λ $\text{ohm}^{-1}\text{cm}^{-2}$	Salt	Λ $\text{ohm}^{-1}\text{cm}^{-2}$
$\text{CH}_3\overset{\text{O}}{\parallel}\text{CNH}_2$	0.9	$[\text{CH}_3\overset{\text{O}}{\parallel}\text{CNH}]\text{K}$	155
$\text{CH}_3(\text{CH}_2)_3\overset{\text{O}}{\parallel}\text{CNH}_2$	0.5	$[\text{CH}_3(\text{CH}_2)_3\overset{\text{O}}{\parallel}\text{CNH}]\text{K}$	123
$(\text{CH}_3)_2\text{CH}\overset{\text{O}}{\parallel}\text{CNH}_2$	0.02	$[(\text{CH}_3)_2\text{CH}\overset{\text{O}}{\parallel}\text{CNH}]\text{K}$	126
	162		201
$(\text{CH}_3\overset{\text{O}}{\parallel}\text{C})_2\text{NH}$	138	$[(\text{CH}_3\overset{\text{O}}{\parallel}\text{C})_2\text{N}]\text{K}$	135

solutions that are markedly more conducting. Thus, both succinimide and *m*-nitroacetanilide are more markedly ionized than the aliphatic acid amides. The molecular conductivity of succinimide is virtually the same as that of the corresponding potassium salt. Since the ionic conductivities of NH_4^+ and K^+ are essentially the same, these data strongly suggest that succinimide is virtually completely ionized in liquid ammonia.

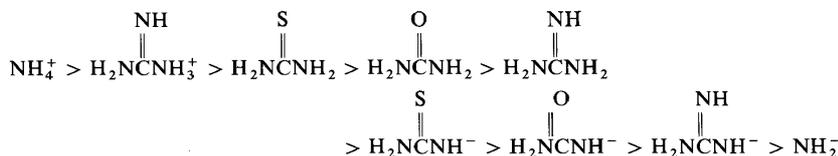
The relative order of acid strengths of several series of compounds have been determined using displacement reactions³², potentiometric titration data³³, and NMR data³⁴. Unfortunately the groups of compounds investigated did not possess common members so that the series could be interrelated (*Table 14*).

Table 14. Relative acidities of some substances in liquid ammonia

1. Displacement Reactions:



2. Potentiometric Titrations:



The displacement reactions were based upon the decolourization of solutions containing the sodium salts of indene (yellow), fluorine (yellow) and triphenylmethane (red). The potentiometric titrations of mixtures of acids were followed with a platinum differential indicator electrode and a Hg/Hg²⁺ reference electrode^{33a}. Since the indicator electrode reaction could not be defined explicitly, only a relative order of acid strengths was obtained from these experiments.

The NMR method depends upon the fact that the spectrum resulting from two species involved in rapid exchange is dependent upon fundamental characteristic magnetic parameters of the species and their relative concentrations. Thus, the NMR spectrum of a mixture containing two acids and their conjugate bases (i.e. 4 species) should exhibit peaks (or groups of peaks



if spin-spin interaction is present) characteristic of each species. The concentration ratio of the acid form of a substance and its conjugate base can be obtained from the intensity ratio of the corresponding peaks. The difference in pK between the two acids in question is then simply calculated from the expression:

$$\Delta\text{pK} = \log \frac{[\text{HB}]}{[\text{B}^-]} - \log \frac{[\text{HA}]}{[\text{A}^-]} \quad (62)$$

The positions of the characteristic NMR peaks for each of the species can be obtained unambiguously from independent experiments on the individual species. It was observed that certain substituted anilines (Table 15) were particularly amenable to this type of analysis since the ring protons for the unionized molecules were at lower field than those of the conjugate anions. The method can be used only to determine pK differences of pairs of acids and the results were reported with reference to the strongest acid of the series, 2,5 dichloroaniline. As might be expected, the relative pK values are linearly related to the Hammett sigma constant of the substituents. The NMR method was also used to obtain the relative acidities of a series of metal hydrides in liquid ammonia (Table 16). Unfortunately, quantitative data could be obtained for only four pairs of compounds with this technique.

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Table 15. Relative acidities of some substituted anilines in liquid ammonia

Substituent(s)	pK
2,5-dichloro	0
3,5-bis(trifluoromethyl)	0.06
4-cyano	0.34
2,4-dichloro	1.16
3,4-dichloro	2.45
3-trifluoromethyl	3.22
4-chloro	4.34
—	5.65
4-fluoro	5.88
3,5-dimethyl	6.22
2,5-dimethyl	6.26
4-ethyl	6.43
4-methyl	6.58

 T. Birchall and W. L. Jolly. *J. Am. Chem. Soc.* **88**, 5439 (1966).

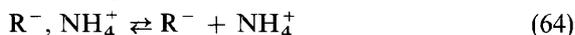
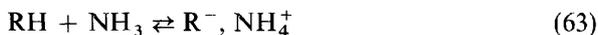
Table 16. The relative acidities of some metal hydrides in liquid ammonia

AsH ₃ > GeH ₄ > CH ₃ AsH ₄ > PH ₃ > (C ₆ H ₅) ₃ GeH >
—ΔpK = 0.7— —ΔpK = 0.3—
C ₂ H ₅ GeH ₃ > CH ₃ GeH ₃ > (C ₂ H ₅) ₂ GeH ₂ >
—ΔpK = 0.7— ΔpK = 0.45—
(CH ₃) ₂ GeH ₂ > CH ₃ PH ₂

 T. Birchall and W. L. Jolly. *Inorg. Chem.* **5**, 2177 (1966).

The data indicate that arsines are more acidic than the corresponding phosphines and that replacement of a hydrogen atom by a proton reduces the acidity. It is interesting to note that substitution of a phenyl group in the germane series also makes the compounds more acidic. A possible explanation of this unexpected behaviour involves the interaction of the Π cloud on the benzene moiety with empty d orbitals on the germanium atom which would increase the charge density on the latter making it more difficult to remove a proton.

Spectrophotometric methods have been developed to estimate the equilibrium constants for the equilibria which exist when a weak acid ionizes in liquid ammonia³⁵.



The constant for the ionization, defined as equation 63, is given by equation 65 while that for the dissociation process (equation 64) is given by equation 66.

$$K_i = \frac{[\text{NH}_4^+ \text{R}^-]}{[\text{RH}]} \quad (65)$$

$$K_d = \frac{[\text{NH}_4^+] f_+ [\text{X}^-] f_-}{[\text{NH}_4^+, \text{X}^-]} \quad (66)$$

Assuming the concentration of the anion in all its forms (i.e. $[R^-]$ and $[R^-, NH_4^+R]$) can be obtained from the intensity of a characteristic absorption band, a simple relationship can be derived between the experimentally determined concentrations of the species at equilibrium.

$$\frac{[R^-] + [NH_4^+R]}{[RH]} = \frac{(K_i K_d)^{\frac{1}{2}}}{f + [HX]^{\frac{1}{2}}} + K_i \quad (67)$$

o- or *p*-nitroacetanilide ionize in pure liquid ammonia; the spectra of these solutions exhibit well defined bands for both the acid and its conjugate base. The spectra of solutions containing various concentrations of *o*, or *p*-nitroacetanilide and a constant concentration of potassium iodide were determined and the data treated according to equation 67; mean activity coefficients (f_{\pm}) were estimated from the extended form of the Debye-Hückel equation. Figure 6 shows a plot of the data for *p*-nitroacetanilide, from which K_i and K_d can be estimated as $9.3 \pm 0.6 \times 10^{-2}$ and $8.9 \pm 0.6 \times 10^{-3}$ respectively. A similar analysis has been used to estimate the first ionization

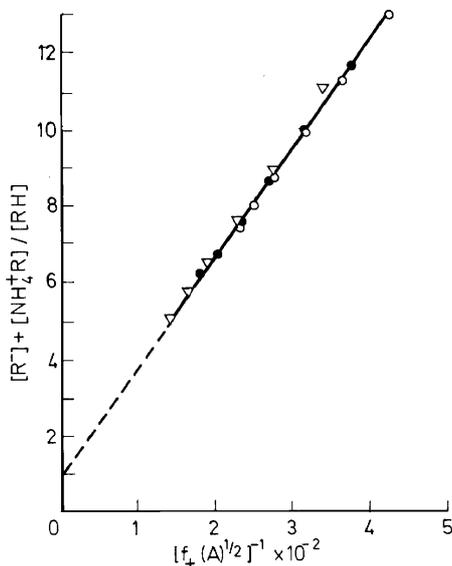


Figure 6. Absorbance data for *p*-nitroacetanilide, corrected for activity, plotted according to Eq. 67.

constant of H_2S^6 in pure liquid ammonia and a variation of the method suitable for use with very weak acids which can only form their conjugate bases in the presence of a strong base such as KNH_2 was used to determine the acidities of several hydrocarbon acids in liquid ammonia³⁶. All of the spectroscopically estimated equilibrium constants are listed in Table 17. Unfortunately, the spectroscopic methods are most applicable for compounds that are either weaker or stronger acids than the extensive series of anilines for which relative pK values had been estimated using NMR methods.

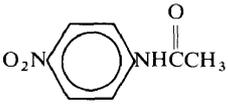
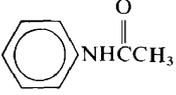
A link between the relative acidities established by the NMR method (Table 15) and the spectroscopically determined constants was established by

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estimating ΔpK between *N,N*-dimethyl-*p*-phenylenediamine and *p*-ditolylmethane using the NMR technique (Figure 7); the ΔpK between *N,N*-dimethyl-*p*-phenylenediamine and 4-methylaniline, was then estimated from a Hammett $\sigma\rho$ plot of the relative acidities of substituted anilines and the σ value for the $(\text{CH}_3)_3\text{N}$ — moiety. Since the ionization constant for *p*-ditolylmethane is known, the absolute value of the ionization constants of the substituted anilines can be established (Table 18).

An independent estimate of the ΔpK values of several weak acids were determined using a potentiometric method employing a platinum indicator

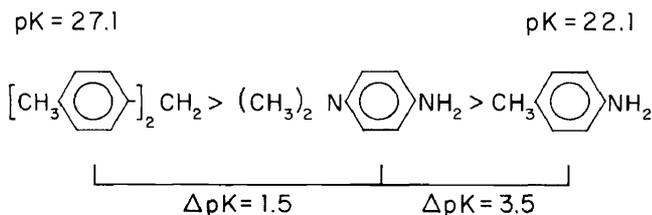
Table 17. Ionization constants of some acids in liquid ammonia

Acid	K_1	T, °C	Ref.
	$9.3 \pm 0.6 \times 10^{-2}$	-55.6	a
	$2.2 \pm 1.4 \times 10^{-2}$	-55.6	a
H_2S	$1.04 \pm 0.19 \times 10^{-2}$	-77	b
	7.33×10^{-28}	-34.5	c
	2.53×10^{-29}	-34.5	c

^a R. E. Cuthrell, E. C. Fohn and J. J. Lagowski. *Inorg. Chem.* **5**, 111 (1966).

^b J. T. Nelson and J. J. Lagowski. *Inorg. Chem.* **6**, 862 (1967).

^c J. H. Takemoto and J. J. Lagowski. *J. Am. Chem. Soc.* **91**, 3785 (1969).


 Figure 7. The pK differences between several aromatic compounds

electrode and a Ag/Ag^+ reference electrode³⁷. The results of the potentiometric measurements suggest that aniline and 4-chloroaniline are 7–8 orders of magnitude weaker acids than are indicated by the spectroscopic data. The data for both methods were collected at different temperatures but it

Table 18. Acidities of carbon and nitrogen acids in liquid ammonia

Compound	pK ^a	pK ^b
Di-(4-methoxyphenyl)methane	28.6	
Di-(<i>p</i> -tolyl)methane	27.1	
N,N-dimethyl- <i>p</i> -phenylenediamine	25.6	
4-Methylaniline	22.1	
4-Ethylaniline	22.0	
2,5-Dimethylaniline	21.8	
3,5-Dimethylaniline	21.7	
4-Fluoroaniline	21.4	
Aniline	21.2	28.8
4-Chloroaniline	19.9	27.4
3-Trifluoromethylaniline	18.7	
3,4-Dichloroaniline	18.0	
2,4-Dichloroaniline	16.7	
4-Cyanoaniline	15.9	
3,5-Bistrifluoromethylaniline	15.6	
2,5-Dichloroaniline	15.5	

^a Based on spectrophotometric and NMR data. J. H. Takemoto and J. J. Lagowski. *Inorg. and Nuclear Chem. Letters* in the press.

^b J. Badoz-Lambling, M. Herlem and A. Thiebault. *Anal. Letters* **2**, 35 (1969).

would appear unlikely that so great a difference could arise because of this factor. At this point it is difficult to understand the source of the apparent discrepancy and it would be prudent not to speculate until more extensive data are available. It is interesting however, that ΔpK for these two substances is the same for both methods. The potentiometric technique was also used to determine the pK values of a variety of other compounds (Table 19). Certain of these data are consistent with the earlier results³³ obtained from

Table 19. pK Values for some weak acids in liquid ammonia

Compound	pK
Aniline	28.8
4-chloroaniline	27.4
Acetone	22.5
Water	18.9
Diphenylguanidine	10.7
Diphenylcarbazon	9.5–11
Diphenylsemicarbazone	7.6
Diphenylurea	7.0
Thiosemamine	6.6
Thiosemicarbazide	4.7 (pK ₂ = 8.5)
Thioacetamide	4.6
Phenylthiourea	3.8
Phenol	3.5
Thiophenol	} <2
Diphenylurea	
Thiocarbohydrazide	

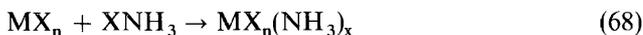
J. Badoz-Lambling, M. Herlem and A. Thiebault. *Anal. Letters* **2**, 35 (1969).

potentiometric titration methods. That is, the order of acidities of pairs of compounds such as semicarbazones and urea, and guanidine and urea are the same for both experiments.

Although the usual pH sensitive glass electrodes show no detectable response toward ammonium ions in liquid ammonia³⁸, several investigators have reported the use of glass cation sensitive electrodes to follow the activity of the ammonium ion in liquid ammonia³⁹. However, little has been done thus far with such devices to establish an acidity scale in this solvent, although theoretically such techniques should be practical.

Coordination chemistry

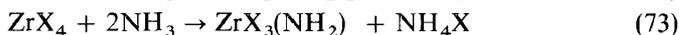
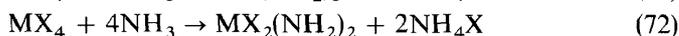
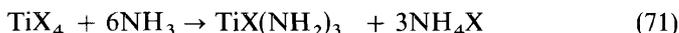
Since ammonia molecules possess unshared electron pairs, strong interactions would be expected with substances that act as Lewis acids, i.e. substances that have vacant orbitals which could accept electron pairs in the formation of a coordinate covalent bond. Many compounds containing a metal atom in a formal positive oxidation state interact with ammonia to form ammoniates by simple addition (equation 68) or displacement of the anions present (equation 69).



Thus, for example, $TiCl_2$ forms a tetra-ammoniate ($TiCl_2, 4NH_3$) but $TiCl_3$ forms a hexammoniate ($TiCl_3, 6NH_3$)⁴⁰. Very often, transition metal ammoniates undergo further reaction in liquid ammonia to give solvolysis products (equation 70).



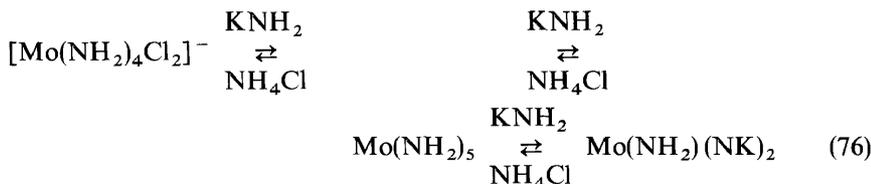
Thus, depending on conditions, titanium (IV) and zirconium (IV) halides yield mixed halogeno amides when dissolved in liquid ammonia (equations 71, 72 and 73)⁴¹.



In some instances complex amines do not undergo ammonolysis in pure liquid ammonia, but the addition of a strong base leads to the formation of solvolysis products, (equation 74)⁴², which are often amphoteric (equation 75)⁴² as is the case in aqueous solutions.



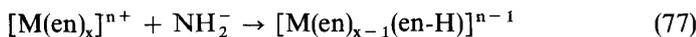
The nature of the solvolysis products can be governed by the relative acidity or basicity of the solution, and intermediate amphoteric species can be inter-converted one into the other reversibly. The ammonolytic products formed from $MoCl_5$ serve as a good example of these processes (equation 76)⁴³.



Addition of KNH_2 leads to successively more ammonolyzed species, whereas solutions of NH_4Cl bring about the reverse reaction.

In general, ammonolysis products are formed when compounds containing small highly charged cations are dissolved in ammonia. As the cation charge-density decreases, ammoniation products are favoured over solvolysis products. Thus, for a given metal, we would expect ammonolysis reactions to occur for the species with the highest oxidation state, whereas stable complex compounds would result when lower valent compounds were dissolved in ammonia.

The effect of coordination of the acidity of amine protons has been observed for amines other than ammonia. The N-H protons in the bidentate ligand ethylenediamine become markedly more acidic when this substance coordinates to transition metal ions. Indeed, this ligand complexed to Gold III $[\text{Au}(\text{en})_3\text{Br}_3]$ is sufficiently acidic to be detectable in aqueous solutions⁴⁴. A wide variety of ethylene-diamine complexes of transition metals have been deprotonated in liquid ammonia using potassium amide (equation 77);



in some instances the course of these deprotonation reactions has been followed potentiometrically³³. In many cases the deprotonated species have been isolated and characterized (Table 20). An inspection of the compounds in

Table 20. Formulations for some deprotonated ethylenediamine complexes

$[\text{Os}(\text{en})_2(\text{en-H})]_2^a$	$[\text{M}(\text{en})_2(\text{en-H})]_2$	$[\text{M}(\text{en})(\text{en-H})]_1$
$[\text{Os}(\text{en})(\text{en-H})_2]_1^a$	$[\text{M}(\text{en})(\text{en-H})_2]_1$	$\text{M}(\text{en-H})_2$
	$\text{M}(\text{en-H})_3$	$\text{K}[\text{M}(\text{en-H})(\text{en-2H})]$
	$\text{K}[\text{M}(\text{en-H})_2(\text{en-2H})]$	$m = \text{Pt}, \text{Pd}^c$
	$\text{K}_2[\text{M}(\text{en-H})(\text{en-2H})_2]$	
	$\text{M} = \text{Ir}, \text{Rh}, \text{CO}^b$	

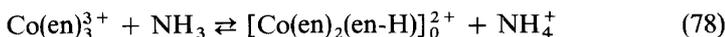
^a G. W. Watt, J. T. Summers, E. Potrafke and E. Birnbaum. *Inorg. Chem.* **5**, 857 (1966).

^b G. W. Watt, L. Sharif and E. Helvenston. *Inorg. Chem.* **1**, 6 (1962); G. W. Watt and J. K. Crum. *J. Am. Chem. Soc.* **87**, 5366 (1965); G. W. Watt, J. K. Crum and J. T. Summers. *J. Am. Chem. Soc.* **87**, 4651 (1965); G. W. Watt, P. W. Alexander and B. S. Manhas. *J. Am. Chem. Soc.* **89**, 1483 (1967).

^c G. W. Watt and J. Dawes. *J. Am. Chem. Soc.* **81**, 8 (1959); G. W. Watt, R. M. McCarley and J. Dawes. *J. Am. Chem. Soc.* **79**, 5163 (1957); G. W. Watt and R. Layton. *J. Am. Chem. Soc.* **82**, 4465 (1960).

Table 20 indicates that it is possible to deprotonate each of the ligands in some compounds, as well as to remove two protons per ligand.

The spectra of $\text{Co}(\text{en})_3^{3+}$ ion in pure liquid ammonia and in mixtures containing NH_2^- suggest that even in pure ammonia, this species undergoes deprotonation (equation 78) to an appreciable extent¹⁷.



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An analysis of the deviation of the data obtained in pure ammonia from Beer's law gives a value of $2.3 \pm 0.3 \times 10^{-1}$ for the equilibrium constant for equation 78.

References

- ¹ J. Nessler. *The Chemistry of Non-Aqueous Solvents* Vol. 1, (J. J. Lagowski, ed.), Academic Press, New York (1966).
- ² J. J. Lagowski and G. A. Moczygemba. *The Chemistry of Non-Aqueous Solvents* Vol. 2, (J. J. Lagowski, ed.), Academic Press, New York (1967).
- ³ F. London. *Trans. Faraday Soc.* **33**, 8 (1937).
- ⁴ J. T. Nelson, R. E. Cuthrell and J. J. Lagowski. *J. Phys. Chem.* **70**, 1492 (1966).
- ⁵ (a) M. Smith and M. C. R. Symons. *Discussions Faraday Soc.* **24**, 206 (1957); (b) *Trans. Faraday Soc.* **54**, 338 (1958); (c) *Ibid.* **54**, 346 (1958); (d) G. Stein and A. Treinen. *Ibid.* **55**, 1086 (1959).
- ⁶ J. T. Nelson and J. J. Lagowski. *Inorg. Chem.* **6**, 862 (1967).
- ⁷ R. E. Cuthrell and J. J. Lagowski. *J. Phys. Chem.* **71**, 1298 (1967).
- ⁸ J. A. Caruso, J. H. Takemoto and J. J. Lagowski. *Spectroscopy Letters* **1**, 311 (1968).
- ⁹ O. Ruff and L. Hecht. *Z. Anorg. Allgem. Chem.* **70**, 49 (1911).
- ¹⁰ F. W. Bergstrom. *J. Am. Chem. Soc.* **48**, 2319 (1926).
- ¹¹ E. C. Franklin and C. A. Kraus. *Am. Chem. J.* **20**, 820 (1898)
- ¹² J. C. Thompson. *The Chemistry of Non-Aqueous Solvents* Vol. 2, (J. J. Lagowski, ed.), Academic Press, New York (1967).
- ¹³ W. L. Jolly. *Progress in Inorganic Chemistry* Vol. II, (F. A. Cotton, ed.), p 235. Interscience, New York (1959).
- ¹⁴ (a) W. Biltz and G. F. Huttig. *Z. Anorg. Allgem. Chem.* **114**, 241 (1920); (b) C. A. Kraus. *J. Am. Chem. Soc.* **30**, 653 (1908); (c) R. C. Mentrel. *Compt. rend.* **135**, 740 (1902); (d) Roederer. *Compt. rend.* **140**, 1252 (1905); (e) P. Marshall and H. Hunt. *J. Phys. Chem.* **60**, 732 (1956).
- ¹⁵ F. W. Bergstrom. *J. Am. Chem. Soc.* **48**, 2848 (1926).
- ¹⁶ R. K. Quinn and J. J. Lagowski. *Inorg. Chem.* **9**, 414 (1970).
- ¹⁷ G. A. Moczygemba, Ph.D. Dissertation, The University of Texas at Austin, 1968.
- ¹⁸ J. W. Warf and W. L. Korst. *J. Phys. Chem.* **60**, 1590 (1956).
- ¹⁹ D. S. Thompson, D. W. Schaefer and J. S. Waugh. *Inorg. Chem.* **5**, 324 (1966).
- ²⁰ E. J. Kerschke and W. L. Jolly. *Inorg. Chem.* **6**, 855 (1967).
- ²¹ For a comprehensive discussion, see H. Smith, *Organic Reactions in Liquid Ammonia* Interscience, New York (1963).
- ²² H. Strehlow. *The Chemistry of Non-Aqueous Solvents* Vol. 1, (J. J. Lagowski, ed.), p 129, Academic Press, New York. (1966).
- ²³ V. A. Pleskov. *Usp. Khim.* **16**, 254 (1947).
- ²⁴ N. A. Ismailov. *Dobd. Akad. Nauk. SSR*, **149**, 288, 320, 348 (1963).
- ²⁵ (a) H. A. Lartnen and C. J. Nyman. *J. Am. Chem. Soc.* **70**, 2241 (1948); (b) H. A. Lartnen and C. J. Nyman. *J. Am. Chem. Soc.* **70**, 3002 (1948); (c) H. A. Lartnen and C. E. Shoemaker. *J. Am. Chem. Soc.* **72**, 4975 (1950); (e) C. J. Nyman. *J. Am. Chem. Soc.* **71**, 3914 (1949).
- ²⁶ R. N. Hammer and J. J. Lagowski. *Anal. Chem.* **34**, 597 (1962).
- ²⁷ (a) J. Carvallo. *Ann. Phys.* **2**, 208, 224 (1914); (b) V. F. Hnizda and C. A. Kraus. *J. Am. Chem. Soc.* **71**, 1565 (1949).
- ²⁸ (a) E. C. Franklin. *J. Am. Chem. Soc.* **37**, 2279 (1915); (b) E. C. Franklin. *J. Am. Chem. Soc.* **55**, 4915 (1933).
- ²⁹ E. C. Franklin and O. F. Stafford. *Am. Chem. J.* **28**, 83 (1902).
- ³⁰ (a) G. F. White and K. H. Knight. *J. Am. Chem. Soc.* **45**, 1781 (1923); (b) G. F. White, A. B. Morrison and E. G. E. Anderson. *J. Am. Chem. Soc.* **46**, 961 (1924); (c) E. C. Franklin. *J. Phys. Chem.* **24**, 81 (1920).
- ³¹ (a) J. B. Conant and G. W. Wheland. *J. Am. Chem. Soc.* **54**, 1212 (1932); (b) C. A. Kraus and W. H. Kahler. *J. Am. Chem. Soc.* **55**, 3537 (1933).
- ³² A. H. Corwen and J. D. Reinheirner. *J. Am. Chem. Soc.* **73**, 1184 (1951).
- ³³ (a) G. W. Watt and D. M. Sowards. *J. Electrochem. Soc.* **102**, 46 (1955); (b) G. W. Watt, D. M. Sowards and W. R. McBride. *J. Am. Chem. Soc.* **77**, 5835 (1955).
- ³⁴ T. Birchall and W. L. Jolly. *J. Am. Chem. Soc.* **87**, 3007 (1965).
- ³⁵ R. E. Cuthrell, E. C. Fohn and J. J. Lagowski. *Inorg. Chem.* **5**, 111 (1966).

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- ³⁶ J. H. Takemoto and J. J. Lagowski. *J. Am. Chem. Soc.* **91**, 3785 (1969).
- ³⁷ M. Herlem. *Bull. Soc. Chim. France* 1687 (1967); J. Badoz-Lambling, M. Herlem and A. Thiebault. *Anal. Letters* **2**, 35 (1969).
- ³⁸ A. H. A. Heyn and M. J. Bergin. *J. Am. Chem. Soc.* **75**, 5120 (1953).
- ³⁹ (a) R. A. Shurba and W. L. Jolly. *J. Am. Chem. Soc.* **90**, 5289 (1968).
- ⁴⁰ W. C. Schumb and R. F. Sundström. *J. Am. Chem. Soc.* **55**, 596 (1933).
- ⁴¹ (a) G. W. A. Fowles and F. H. Pollard. *J. Chem. Soc.* 2588 (1953); (b) G. W. A. Fowles and D. Nicholls. *J. Chem. Soc.* 95 (1961); (c) G. W. H. Fowles and D. Nicholls. *J. Chem. Soc.* 990 (1959); (d) G. W. A. Fowles and F. H. Pollard. *J. Chem. Soc.* 4128 (1953); (e) A. Stahler and B. Denk. *Ber.* **38**, 2611 (1905).
- ⁴² (a) O. Schnitz-Dumont. *Angw. Chem.* **62**, 560 (1950); (b) O. Schnitz-Dumont. *Z. Elektrochem.* **47**, 221 (1941); (c) O. Schnitz-Dumont, J. Pilzecker and H. E. Prepenbank. *Z. Anorg. Allgem. Chem.* **248**, 175 (1941).
- ⁴³ (a) F. W. Bergstrom. *J. Am. Chem. Soc.* **47**, 2317 (1925); (b) D. A. Edwards and G. W. A. Fowles. *J. Less-Common Metals* **3**, 181 (1961).
- ⁴⁴ B. P. Block and J. C. Burlar. *J. Am. Chem. Soc.* **79**, 5163 (1957).