ELECTRONS IN LIQUID AMMONIA

BY

J. C. THOMPSON

CLARENDON PRESS · OXFORD
1976

Oxford University Press, Walton Street, Oxford OX2 6DP

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ISBN 0 19 851343 7

FILMSET IN N. IRELAND AT THE UNIVERSITIES PRESS, BELFAST
PRINTED IN GREAT BRITAIN
BY J. W. ARROWSMITH LTD., BRISTOL

PREFACE

SOLUTIONS of metals in liquid ammonia have been known for over a century and studies of their properties have resulted in hundreds of papers. This enduring interest is sustained by the extraordinarily rich variety of properties which is observed as the concentration of metal is changed. Electrical conductivities range from 10^{-8} to $10^4\Omega^{-1}$ cm^{-1}; spin resonance lines are the narrowest known; densities are lower only for the cryogenic fluids; and the blue color characteristic of the dilute solutions has become the hallmark of the lightest anion—the solvated electron. Whether one's interests are chemical or physical, whether one studies kinetics, reactions, electrolytes, critical phenomena, metals, insulators, or the metal–insulator transition, there are even now experiments to be done, models to be constructed and understanding to be gained. Indeed, developments at the 4th Colloque Weyl have added to our knowledge of the metal–nonmetal transition and the solid hexammines.

I have not attempted to cover all the available studies of M–NH_3 solutions, rather limiting myself to those topics which come under the headings of chemical physics and physical chemistry.† In the chapters which follow I have tried to bridge the gap between readers with chemical and those with physical background, making the arguments intelligible to both (at the risk of explaining the obvious to some). I hope to find an audience in both camps. Section 1.4 contains a more detailed outline of the contents.

There are disadvantages to this wealth as well, for a single individual cannot adequately review all of the available information and my prejudices and ignorance have doubtless led me to slight work deserving of high praise. For this I apologize.

I must not, however, slight those who have provided me with guidance and support during the years I have studied M–NH_3 solutions. The latter has come from the U.S. Office of Naval Research, monitored by Jack Soules, from the U.S. National Science Foundation, monitored by Langdon Crane and Rolf

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† One can find an introduction to more chemical topics in the series *Chemistry of non-aqueous solvents*, edited by J. J. Lagowski.

Sinclair, and from the R. A. Welch Foundation of Texas, directed by W. O. Milligan. These agencies and individuals have sustained me not only by their funds but also by their trust and encouragement, which I deeply appreciate.

Guidance has come from many students, friends, and colleagues, but two individuals have contributed more than the rest: Morrel Cohen and Nevill Mott. Morrel and I came together one weekend in 1967. I was possessed by a mountain of data while he, as always, had the experience and insight to help me organize and begin to understand what it was that I was about. Sir Nevill I met at 'his' conference in 1968. Since then in conversation and correspondence he has shared his extraordinary intuition with me. In their separate ways and with repeated kindness they have helped me along the way. They have my eternal gratitude.

Most authors acknowledge the sustenance, encouragement, and patience of their wives, and this debt I certainly owe to my wife, Carol May. But I owe her infinitely more, for it was she who introduced me to the existence and excitement of metal–ammonia solutions and who, with skill and tact, taught me the chemistry I needed to read and to understand the vast literature behind this book. And, finally, it was she who strove to reduce my bad English and bad science. For all this, and more, I owe her everything. That this book exists at all is a tribute to her.

Austin, Texas J.C.T.
April, 1976

ACKNOWLEDGEMENTS

The publishers of the following journals and books and the authors are due acknowledgement for their permission for reproduction of the figures specified: Academic Press, from *Chemistry of non-aqueous solvents*, Vol. 2 (Fig. 5.10); *Adv. Phys.* (Fig. 2.24, 2.25, 3.33); International Union of Pure and Applied Chemistry, from *Metal-ammonia solutions* (Fig. 3.3, 3.36, 4.3, 7.2); *J. Chim. phys.* (Fig. 3.32); *J. chem. Engng. Data* (Copyright Am. Chem. Soc.) (Fig. 3.22, 4.4); *J. chem. Phys.* (Fig. 2.6, 2.7, 2.10, 2.11, 2.12, 2.13, 2.14, 2.15, 2.20, 2.28, 3.10, 3.14, 3.20, 3.21, 3.26, 3.34, 3.37, 3.38, 4.1, 4.6, 5.1, 5.6, 7.3, 7.9); *J. phys. Chem.* (Copyright Am. Chem. Soc.) (Fig. 3.1, 3.17, 3.19, 5.7, 6.6, 8.2); *J. Solid State Chem.* (Fig. 7.7, 7.8, 7.10, 7.13, 7.14); *J. Am. chem. Soc.* (Copyright Am. Chem. Soc.) (Fig. 3.31); *Phys. Rev.* (Fig. 2.10, 2.22); *Rev. mod. Phys.* (Fig. 4.2, 4.9); Springer-Verlag from *Electrons in fluids* (Fig. 2.8, 2.14, 2.19, 7.1, 7.9, 7.12, 8.1, 8.8, 8.9); Université Catholique de Lille, from *Metal-ammonia solutions* (Fig. 3.25, 3.30).

CONTENTS

1

INTRODUCTION

1.1. Ammonia as a solvent

MANY solids combine with liquids to form homogeneous mixtures of only one phase; these mixtures are usually called solutions. Familiar examples include salt in water and sugar in tea. The solvent is generally taken to be the majority component and the solute or solutes the minority component. This monograph concerns a class of solutions in which the solute is an element: a metal. The most common solvent is liquid ammonia. Solutions of metals in ammonia differ from more common solutions in the extraordinarily wide range of values observed for many properties.

These materials have been studied for over a century, yet their nature is not resolved and controversy persists, even over such apparently simple properties as the density. This book does not attempt to resolve many of the discrepancies.

The archetypal solution for man is salt in water and the major thrust of most solution research has been the elucidation of the properties of similar solutions. When dealing with non-aqueous solutions, however, one must consider the differences between water and the solvent of interest. Several differences immediately appear when water and ammonia are compared. Water has the higher low-frequency relative permittivity (80 versus 22 at 20 °C) and the lower polarizability ($1{\cdot}45$ Å^3 versus $2{\cdot}26$ Å^3). Hydrogen bonding is more important in solvent–solvent interactions in H_2O than NH_3. Finally, the ammonia molecule is more stable against dissociation in the liquid than the water. In water the equilibrium concentrations of H^+ and OH^- ions are near $0{\cdot}1$ p.p.m. as compared to H^+ and NH_2^- concentrations of 10^{-10} p.p.m. in ammonia. On the other hand, the H_2O molecule is more stable in the vapour phase. There are, of course, major differences between metal–ammonia solutions and salt water due to the fact that the solutes discussed here are elements. The anion is thus an electron instead of a halide ion, charge transfer can occur without transfer of matter, and quantum effects can be important.

Perhaps most important to the understanding of these solutions, though certainly *not* well known, is the nature of the short-range electron–molecule interaction. Cohen, Jortner, and their co-workers have characterized the repulsive pseudopotential in liquids such as He, Ar etc. by the energy of an electron in the conduction band relative to the vacuum state. They find that for helium the band lies higher than the vacuum and for argon the band lies lower. Thus in the former case the electron can lower its energy by repelling the solvent and 'blowing itself a bubble' in the liquid, whereas in the latter the electron may move directly into the solvent. Both H_2O and NH_3 are isoelectronic with Ne, for which the band and vacuum states are very close. In the absence of a detailed calculation we can only guess that these polar solvents will have a weak repulsive interaction with electrons somewhat like that of Ne. Minor differences in energy may well produce significant changes in behaviour, as shall be seen when solvated electron spectra are discussed.

In the present chapter we briefly survey the early history of metal solutions in various solvents, then outline precisely the materials which are known to form metal solutions, and finally describe the preparation and preservation of metal solutions.

Recent application of M–NH_3 solutions has included the production of superconductors by the intercalation of e.g. Na into transition metal dichalcogenides (Acrivos, Liang, Wilson, and Yoffe 1971; Somoano and Rembaum 1971). They have been used in organic reactions for many years (Smith 1963) and in conventional inorganic chemistry (Watt 1957). These and other, more esoteric (Jäger and Lochte-Holtgreven 1967), uses of these materials are beyond the scope of this book.

1.2. Early history

The earliest known experiments in which a metal was observed to dissolve in ammonia were those reported by Weyl (1864). He studied sodium and potassium in ammonia and concluded that 'ammoniums' (NH_4) were being formed. (See also Joannis 1889.) Only seven years later Seely (1871) was able to recover Na dissolved in NH_3 by evaporating the solvent. He concluded that the metal did not react with the solvent and that the solution was similar to salt in water. No work was reported between 1873 and 1889. NH_3 became commercially available in 1898 and research was accelerated.

Further confirmation of these observations came from the 'Kansas group' of H. P. Cady, E. C. Franklin, and C. A. Kraus (Taft 1933). A series of experiments, beginning in 1895, was continued into the 1930s and provided the world with much of the available information on metal–ammonia solutions. Kraus was author or co-author of over fifty major papers on the solutions, and his students, or their students, are still major contributors. Phase diagrams, vapour pressures, and conductivities were among the properties studied by Kraus and his co-workers (Kraus 1931). His aim was to study the expected gradual change from electrolytic to metallic properties. He was able to conclude in 1908 (Kraus 1908) that the valence electron from the metal was associated with the solvent in dilute solutions yet free in concentrated solutions. He proposed that the electron in dilute solutions was surrounded by 'an envelope of solvent molecules'—a construct still in use (see Chapter 3). He realized at a very early date that the 'metallic electron' was involved and that the mobilities were very high (Kraus 1921), even by metallic standards. These deductions are remarkable in light of the poor understanding of metals at the time he worked. (The Drude model was only proposed in 1900.) Kruger (1938) was a proponent of the view that colloids existed rather than solutions. As we shall see this view does not fit the observations. Herzfeld (1927) pointed out that a rapid metal–nonmetal (M–NM) transition might exist (Cohen and Thompson 1968; Thompson 1968; Mott 1974) and that these solutions would be a good system in which to search for such a transition, as Kraus had foreseen. Mott's classic paper (1961) on the M–NM (or Mott) transition again drew attention to the metal–ammonia solutions as a system in which such a transition might exist.

1.3. Other sources of information

An extensive (perhaps exhaustive) bibliography of work on metal–ammonia solutions has been prepared by Professor G.

Lepoutre.[†] Further references to research can be found in the reports of conferences devoted to the subject.[‡] Many important papers have been collected by Jolly (1972) and there have been several reviews (Kraus 1931; Jolly 1959; Symons 1959; Das 1962; Dye 1967; Cohen and Thompson 1968). We turn now to a survey of the materials involved, their preparation, and stability.

1.4. Accessible concentrations and temperatures

Though ammonia (NH_3) is the primary solvent used, other amines have also been reported to dissolve metals to some extent. Henceforth, except in the final chapter, we shall limit ourselves to a discussion of solutions of metals in liquid ammonia. In the last chapter (chapter 8) we shall take up solutions of metals in solvents such as methylamine, some ethers, etc. The emphasis will be on solutions of alkali metals as more information is available on them.

Liquid ammonia is known to dissolve the following metals: Li, Na, K, Rb, Cs, Ca, Sr, Ba, Yb, and Eu (Jolly 1959). One may also prepare solutions containing radical cations such as tetraalkylammonium (Quinn and Lagowski 1968) by electrolysis. Finally, one may introduce electrons from an accelerator and study the anion without cationic effects (Dye 1968; Hart 1969). The alkali metals have been more extensively studied than the others and will be the major subject of all chapters except Chapter 6.

The present author has speculated (Thompson 1970) that the alkali metals and liquid ammonia will be miscible in all proportions at temperatures near the melting point of the metal. This speculation is based on the reported complete miscibility of Cs and NH_3 (Schroeder, Thompson, and Oertel 1969) and upon Kraus's observation that NH_3 is soluble in an alloy of Na with K (NaK) (Kraus 1907). Most experiments, however, are carried out

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[†] G. Lepoutre, Laboratoire de Chimie-Physique, Faculté Catholique de Lille, Lille, Nord, France.

[‡] *J. phys. Chem.* **57,** 547 *et seq.* (1953). Colloque Weyl I at Lille, France, 1963; published as *Metal–ammonia solutions*, ed. G. Lepoutre and M. J. Sienko, W. A. Benjamin, New York, 1964. 150th Meeting Am. chem. Soc., Atlantic City, New Jersey, 15–16 September 1965; published as *Solvated Electron, Adv. Chem Ser.* 1965, **50**. Colloque Weyl II at Ithaca, New York, June 1969, published as *Metal–ammonia solutions*, ed. J. J. Lagowski and M. J. Sienko, Butterworths, London, 1970. *Ber. Bunsenges. physik. Chem.* 1971, No. 7, **75**. Colloque Weyl III at Hanita, Israel, June 1972; published as *Electrons in Fluids*, ed. J. Jortner and N. R. Kestner, Springer-Verlag, Heidelberg, 1973. Colloque Weyl IV at East Lansing, Michigan, June 1975; published as *J. Phys. Chem.* **79,** No. 26 (1975).

TABLE 1.1

Solubilities (in m.p.m.[†]*) at the n.b.p.* (239·8 K) *of ammonia*

Metal	Li	Na	K	Rb	Cs	Ca	Sr	Ba	Eu	Yb
Solubility	20	16	15	—	65	16	16	16	—	16
Reference	(Jolly 1959; Lo 1966; Bridges, Ingle, and Bowen 1970)	(Jolly 1959)			(Schroeder *et al.* 1969)					

[†] For this paper, the concentration will be expressed either in mole fractions x, where $x = (\text{moles metal})/(\text{moles metal} + \text{moles solvent})$, or as mole percent metal (m.p.m.) $= 100\,x$. In the case of divalent metals, the number of moles of metal may be multiplied by 2 to reflect the electron concentration. Such concentrations will be denoted 'electron concentration'. Other units include molarity and molality (Eggers, Gregory, Halsey, and Rabinovitch 1964).

near the normal boiling point (n.b.p.) of ammonia and solubilities for several metals at that temperature are given in Table 1.1. The addition of metal to liquid depressed the freezing point from its usual value of 195·4 K to temperatures as low as 89 K (Mammano and Coulter 1967). Table 1.2 collects the known eutectics.

TABLE 1.2

Eutectics of metal–ammonia solutions (Thompson 1967)

Metal	Li	Na	K	Rb	Cs	Ca	Sr	Ba	Eu	Yb
Eutectic concentration (m.p.m.)	20	17	15	—	15·7	13·3	13·3	13·5	—	14·3
Eutectic temperature (K)	88·6	163	116	—	98	185	185	186	—	183
Reference	(Mammano and Coulter 1969)				(Lelieur and Rigny 1973*b*)	(Schroeder *et al.* 1969)				

Experiments may thus be carried out over a wide range of composition and over a wide range of temperature, extending, perhaps, above the critical point (406 K) of ammonia (Naiditch 1964; Schindewolf 1968; Hart 1970; McNutt, Kinnison, and Ray 1974). The available range for lithium in ammonia is summarized in Fig. 1.1. Region I is the miscibility gap—solutions cannot be made at the temperatures and concentrations within that region

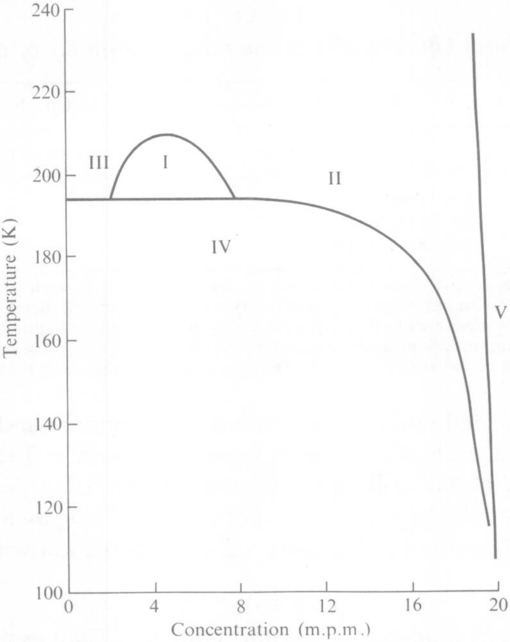

FIG. 1.1. Phase diagram for Li–NH_3 solutions. *Note* here and throughout the text m.p.m. = moles per cent metal (see p. 5).

(see Chapter 5); region II is a homogeneous, metallic liquid (Chapter 2); region III a homogeneous, nonmetallic liquid (Chapter 3); in region IV there is excess solid ammonia; and in region V there is excess solid metal or metal amine (Chapter 7). The phase diagrams are all quite similar, as may be seen in Figs 1.2 and 1.3 though Cs–NH_3 solutions lack region I (Schroeder *et al.* 1969).

1.5. Preparation of solutions

As noted earlier one is able to dissolve a variety of metals in liquid ammonia. In this section and in the next the preparation of the solutions and the measures required to keep the solutions for times sufficient to perform an experiment will be described.

Problems are derived from the combination of low temperatures required to maintain the NH_3 in the liquid state (though gaseous NH_3 will cause Li to deliquesce) and the inert atmospheres and extreme purities required to keep the solutions from decomposing. We will first describe the preparation of pure NH_3

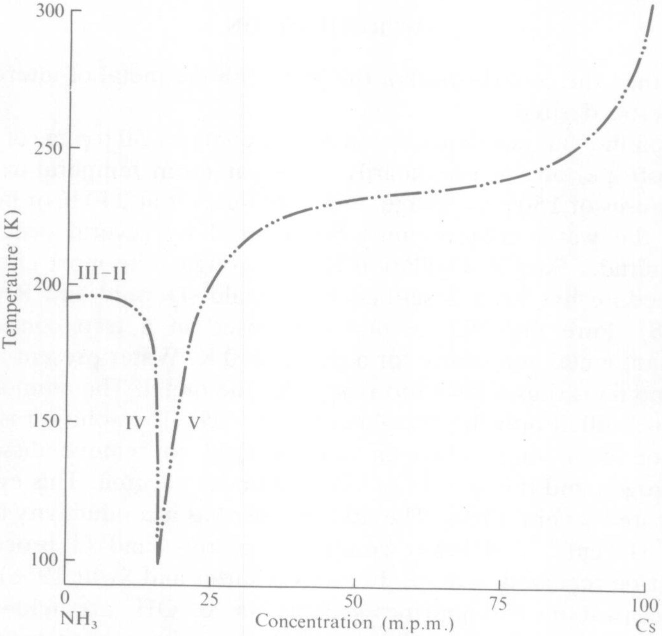

FIG. 1.2. Phase diagram for Cs–NH$_3$ solutions.

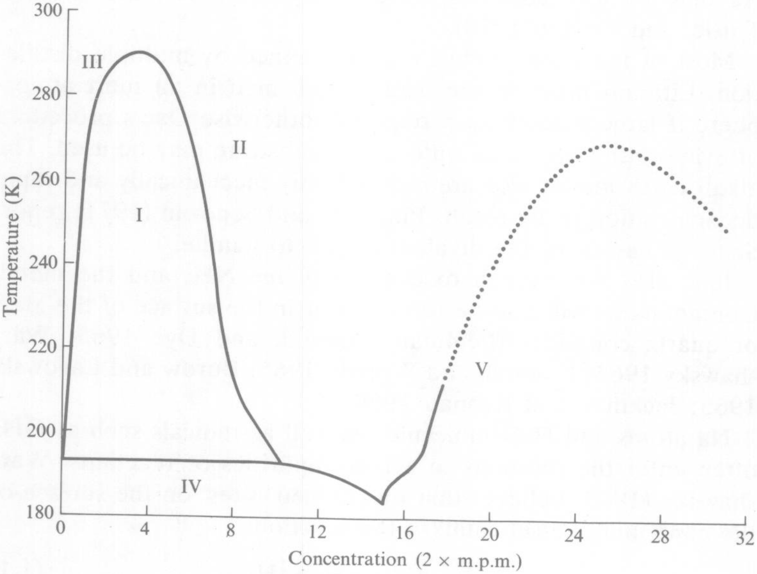

FIG. 1.3. Phase diagram for Ca–NH$_3$ solutions. The dotted portion is speculative (see Chapter 7).