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Metal–Nonmetal Transition in Metal–Ammonia Solutions*

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A review is given of the properties of metal–ammonia solutions together with a summary of the evidence for the existence of a metal–nonmetal transition.

I. INTRODUCTION

Alkali metals, among others, may be reversibly dissolved in liquid ammonia and form true solutions.[1] The metal may be recovered by simply boiling off the ammonia. When free from water, and other agents which catalyze the reaction of metal and solvent, the solutions are stable and may be studied by most techniques applicable to liquid conductors. The convenient temperature range is approximately 200°–300°K, though in special cases data have been taken outside this range. These solutions show a variety of conduction mechanisms, as well as a metal–nonmetal transition. I propose first to review the extremes of concentration wherein the conduction processes appear relatively simple and are hopefully well understood, so that I may introduce the constructs used to interpret the available data. As this system has been more widely studied than any other exhibiting a metal–nonmetal transition, there are a wealth of data which might be applied to the characterization of the transition. I am obliged to be selective in my discussion.

I express concentrations throughout in terms of mole percent metal (MPM), i.e., 100 times the mole fraction x of metal. As few, if any, of the properties are observed to depend upon solute ion whatever the concentration,[1] I ignore that parameter in presenting data. Saturation occurs near 20 MPM, except for cesium solutions.

II. DILUTE SOLUTIONS

Those properties which lead to the assertion that the solutions containing less than 0.1 MPM, which I term dilute, are analogous to electrolyte solutions, are as follows: (1) The electrical conductivity is low, increases with T, and correlates moderately well with the viscosity.[2] The mobilities of the positive and negative carriers differ by only a factor of seven.[3] (2) The Knight shift at the metal nucleus is small, below 20 ppm at 240°K, indicating low s-electron density at the metal.[4] (3) The static susceptibility is very close to the value expected for a nondegenerate set of noninteracting spins. The spin susceptibility is close to the static, and the ESR line, the narrowest known, is without structure.[5] The vapor pressure decreases upon the addition of metal, as upon the addition of salt.[6]

The properties of the dilute solutions may be understood by application of the conventional theory of weak electrolytes upon the assumption[1] that the following entities exist: solvated ion M^+; solvated electron e^-; ion pair M^+e^-; ion triple $e^-M^+e^-$; etc. The solvated ion M^+ is an ion surrounded by several solvent molecules. The solvent molecules are bound by the attraction of their dipole moments for the ion. The solvated electron e^-, defined in analogy to a solvated ion, may be crudely described as an electron bound into a cavity in the solvent by the polarization energy of the oriented solvent molecules surrounding the cavity. Jortner[7] has shown that such an electron will have at least two bound states ($1s$ and $2p$) if a cavity radius of 3 Å is chosen, consistent with the very low density of the solutions. Time does not permit a complete discussion of the consequences of the model, but I shall observe that the 0.9-eV separation of the two states fits the characteristic, solute-independent optical absorption of the dilute solutions. The same absorption is observed in experiments where liquid ammonia is irradiated with electrons and no positive ions are present.[8] The separation of ion and electron in the model provides an explanation of the small Knight shift at the metal nucleus as well as the narrow ESR line.

The associated species, M^+e^-, etc., are not atoms but ion pairs, triples, etc., wherein the solvation shells are retained.[9] Association into neutral and spin-paired species is required to explain, respectively, the decrease in the equivalent conductance above 10^{-2} MPM and the observation that the susceptibility above 10^{-2} MPM lies below that expected for noninteracting spins. The susceptibility shows an exponential increase with

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[1] T. P. Das, Advan. Chem. Phys. **4**, 303 (1961); Colloque Weyl, at Lille, France, proceedings published as *Metal-Ammonia Solutions*, G. Lepoutre and M. J. Sienko, Eds. (W. A. Benjamin, Inc., New York, 1964).

[2] E. C. Evers and P. W. Frank, J. Chem. Phys. **30**, 61 (1959).

[3] J. L. Dye, R. F. Sankuer, and G. E. Smith, J. Am. Chem. Soc. **82**, 4797 (1960).

[4] D. E. O'Reilly, J. Chem. Phys. **41**, 3729 (1964).

[5] D. A. Hutchison and R. C. Pastor, J. Chem. Phys. **21**, 1959 (1953).

[6] P. R. Marshall, J. Chem. Eng. Data **7**, 399 (1962).

[7] J. Jortner, J. Chem. Phys. **30**, 829 (1959).

[8] D. M. J. Compton, J. A. Brant, R. A. Cesena, and B. L. Gehman, in *Pulse Radiolysis*, M. Ebert *et al.* Eds. (Academic Press Inc., New York, 1965), p. 43.

[9] M. Gold, W. L. Jolly, and K. S. Pitzer, J. Am. Chem. Soc. **84**, 2264 (1962).

temperature as if spins were being unpaired by thermal agitation, as is expected for clusters of ions.

III. METALLIC SOLUTIONS

The properties which lead us to describe the solutions more concentrated than 8 MPM as metallic are those by which a metal is usually characterized: conductivity σ; Hall coefficient R_H; thermopower; optical constants; susceptibility; and compressibility. Each is in qualitative agreement with free electron theory and quantitatively similar to liquid metals.[10] There are no indications of effective masses appreciably different from m_0. The electron densities are in the range of 1.0 to 4.0×10^{21} cm^{-3} and thus Fermi energies and plasma frequencies are lower than for common metals. Two features which *may* be considered at variance with the simple theory of conduction are $d\sigma/dx$ and $d\sigma/dT$, where σ is the conductivity and x the concentration.[11] The first quantity is much larger than one would expect from looking at the data for simple metals and the second has a positive sign, in contrast with monovalent liquid metals.[12] One of my students, Schroeder,[13] will report next week in Berkeley a computation using the Ashcroft–Lekner–Langreth[14] theory of binary, metallic alloys which is able to account phenomenologically for σ, $d\sigma/dx$, the compressibility, and the thermopower as well as indicating the probable source of $d\sigma/dT>0$. The primary constituent in this model is the solvated *ion* already introduced in treating the dilute solutions. The entities presumed to exist in the concentrated solutions are: solvated ions, free electrons, and ammonia molecules.

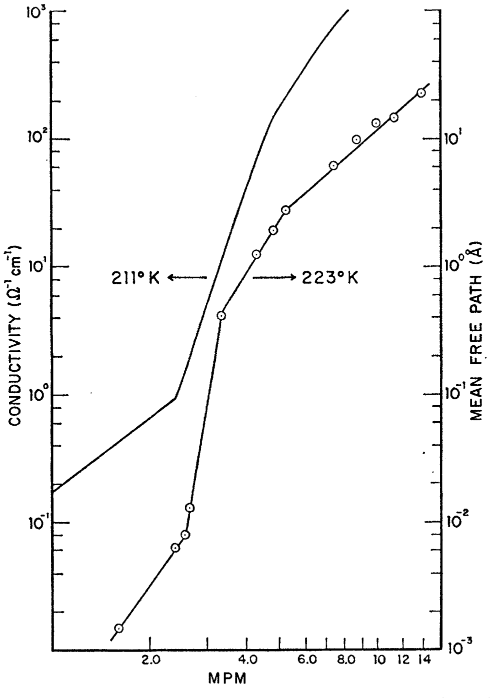

Fig. 1. The electrical conductivity (left-hand scale) and mean free path (right-hand scale) of Li–NH_3 solutions. The mean free path is calculated from the conductivity by using measured Hall coefficients (see Refs. 11 and 15) similar to those in Fig. 2.

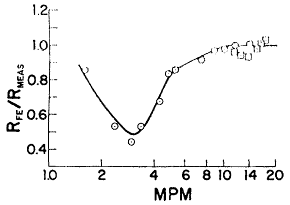

Fig. 2. The ratio of the Hall coefficient calculated from the valence electron density to that measured by Nasby (Ref. 15) and Kyser (see Ref. 10 for other references).

IV. METAL–NONMETAL TRANSITION

Our present interest lies in the range between 0.1 and about 10.0 MPM. We presume isolated ammonia molecules and solvated ions to exist throughout this range as they exist on either side. The fate of the solvated electron is not so clear. Let us look first at some of the properties in this range.

Figure 1 shows the conductivity; most of the data are due to R. D. Nasby in my laboratory and will also be reported in detail in Berkeley next week.[15] Note the sharp change in slope near 2.5 and 5 MPM and that $\sigma=100\ \Omega^{-1}\ \text{cm}^{-1}$ at 4.5 MPM. There is only a slight shift with T though the break points move slightly. The curves are smooth below 2 MPM and are not shown for that reason. The trends of mean free path are somewhat similar. Mott's condition for the metal–nonmetal transition, $k_F\Lambda=1.0$, is satisfied at 6 MPM.[16] The Hall coefficient, also to be reported more fully by Nasby next week and shown in Fig. 2, departs only slightly from free-electron theory in the range of interest and remains temperature independent. Similarly the thermopower[17] has values appropriate to a liquid metal down to about 3 MPM then rises rapidly to 800 μV/deg. The dielectric constants at optical frequencies progress from Drude behavior at 8 MPM to insulating behavior at 1 MPM. Figure 3 shows data in part from my laboratory. [18] The three lower curves show the real part of the dielectric constant to vary with energy in a Drude manner; the shift is due to the decrease of electron

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[10] J. C. Thompson, Advan. Chem. **50,** 96 (1965).

[11] J. A. Morgan, R. L. Schroeder, and J. C. Thompson, J. Chem. Phys. **43,** 4494 (1965).

[12] J. M. Ziman, Phil. Mag. **16,** 551 (1967).

[13] R. L. Schroeder and J. C. Thompson, Bull. Am. Phys. Soc. **13,** 397 (1968).

[14] N. W. Ashcroft and J. Lekner, Phys. Rev. **145,** 83 (1966); N. W. Ashcroft, Phys. Letters **23,** 48 (1966); N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156,** 685 (1967); **159,** 500 (1967); **166,** 934 (1968).

[15] R. D. Nasby and J. C. Thompson, Bull. Am. Phys. Soc. **13,** 397 (1968).

[16] N. F. Mott and R. S. Allgaier, Phys. Status Solidi **21,** 343 (1967).

[17] J. F. Dewald and G. Lepoutre, J. Am. Chem. Soc. **76,** 3369 (1954); **78,** 2956 (1956).

[18] W. T. Cronenwett and J. C. Thompson, Advan. Phys. **16,** 439 (1967).

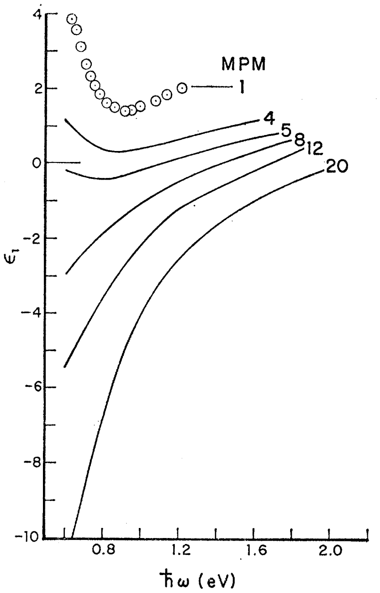

FIG. 3. Measured values of the real part of the dielectric constant in metal–ammonia solutions at 210°K. The solid lines represent data taken by Cronenwett (Ref. 18) on lithium–ammonia solutions of the concentrations shown while the points represent as yet unpublished data of W. H. Koehler on potassium solutions.

density and relaxation time as x decreases. The points at the top of the graph were taken recently by Koehler of the U.T. Chemistry Department[19] and are just those expected from the dilute-solution optical absorption at 0.9 eV mentioned earlier. At 4 and 5 MPM we see the absorption line superposed onto the Drude curve. We shall hear about the microwave dielectric constants later in this conference.[20]

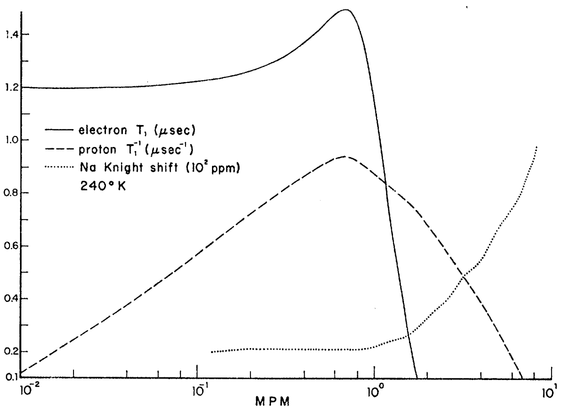

FIG. 4. These curves represent several parameters determined by magnetic resonance techniques. The solid line shows T_1 as measured by Pollak (Ref. 21) in an ESR experiment. The dashed line is the inverse of the proton spin–lattice relaxation time recently reported by Waugh (Ref. 22). The dotted line is the Knight shift at the sodium nucleus reported by O'Reilly (Ref. 4). In each, the trend is toward metallic behavior at higher concentrations.

Figure 4 shows data derived from magnetic resonance experiments and somewhat different trends. The data shown are the electron spin–lattice relaxation time,[21] the inverse of the proton spin–lattice relaxation time,[22] and the Knight shift at the metal nucleus.[4] Each shows a change in slope near 1 MPM. The most striking point is that the changes in slope appear to occur at concentrations measurably lower than those of the transport coefficients. There is also an apparent minimum in the atomic susceptibility at about the same concentration. No significant shift in the trends with concentration of Knight shift data is observed at either of the nuclei in the NH_3 molecule.[23]

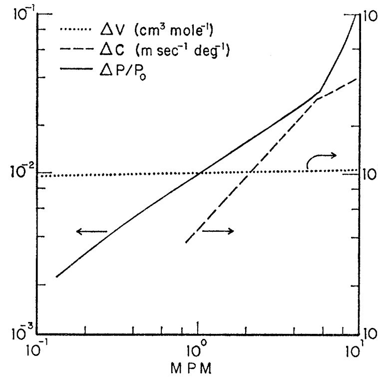

FIG. 5. Three mechanical properties of metal–ammonia solutions. The dotted line shows the excess volume per mole of added metal. The quantity ΔV is obtained from the density after correcting for the volumes of the ammonia and of the metal and for the electrostriction at the cation (see Ref. 24). The dashed line shows the difference between the temperature coefficient of sound speed in the solutions and in pure ammonia (see Ref. 26). The solid line shows the quantity $(P_0-P)/P_0$, where P and P_0 are the vapor pressure in the solution and in pure ammonia, respectively (see Ref. 6). The last two quantities show discontinuities in their concentration derivatives near 6 MPM.

It is interesting to compare these specifically electronic data with data on the mechanical or thermodynamic properties of the solutions. Figure 5 shows three such quantities. The excess volume[24] measures the difference between the volume of the solution and that of the constituents, per mole of added metal. It increases by only 10% over the entire range and shows but a slight maximum near 10 MPM. It and the vis-

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[19] W. H. Koehler and J. J. Lagowski (private communication).

[20] D. W. Mahaffey and D. A. Jerde, Bull. Am. Phys. Soc. **12**, 193 (1967); Rev. Mod. Phys. **40**, 710 (1968), this issue.

[21] V. L. Pollak, J. Chem. Phys. **34**, 864 (1961); D. E. O'Reilly, Phys. Rev. Letters **11**, 545 (1963).

[22] R. A. Newmark, J. C. Stephanson, and J. S. Waugh, J. Chem. Phys. **46**, 3514 (1967).

[23] J. V. Acrivos and K. S. Pitzer, J. Phys. Chem. **66**, 1693 (1962); T. R. Hughes, J. Chem. Phys. **38**, 202 (1963).

[24] S. R. Gunn and L. R. Green, J. Chem. Phys. **36**, 363 (1962); **36**, 368 (1962).

cosity,[25] alone among thermodynamic properties, show only a slight shift in trend with concentration over the 0.1 to 10 MPM range. Note that ΔV is large and consistent with the 3 Å cavity radius chosen by Jortner.

Contrastingly, the vapor pressure[6] drops markedly in the metallic range. Finally, the temperature coefficient of sound speed[26] in the solutions (measured relative to that of pure NH_3) shows a discontinuity in its concentration derivative at concentrations comparable to those at which the transport coefficients change.

One of the most striking phenomena found in these solutions is the liquid–liquid phase separation. The metallic solution floats out on top of the nonmetallic as oil floats above vinegar. The interface is sharp and easily observed because of the metallic bronze luster of the high concentration phase and the ink-blue color of the nonmetallic phase. The phase diagram for Li–, Na–, and Ca–NH_3 solutions[1,27] is shown in Fig. 6. Regions IV and V are heterogeneous mixtures of excess solvent and solute, respectively, with the solution. Region II is a homogeneous metallic solution. Region I separates solutions of metallic (to the right) and nonmetallic behavior (region III). Those who have kept score of the numbers in the previous figures will observe a strong correlation between the changes in the transport coefficients and the phase separation.

Having introduced the temperature as a variable, I must say something about the effect of temperature on the transition above the mixed phase region. There are presently inadequate data on the conductivity itself to indicate the nature of the shift, if any. However, Catterall[28] has studied the effect of temperature upon the asymmetry of the ESR line. Dyson[29] has shown that asymmetry results when the conductivity becomes large, so that we may take the locus of the onset of asymmetry as indicative of the locus of the transition. These data are shown in Fig. 7. Figure 7 also shows the phase separation, and a few points of significant change from the conductivity. Though the asymmetry onset obviously occurs at concentrations well below those we have been discussing, we may conclude that the solutions become metallic at lower concentrations when the temperature is raised.

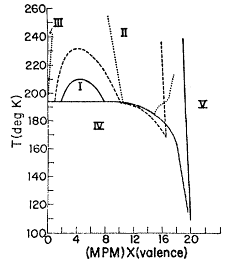

FIG. 6. The phase diagram for several metal–ammonia solutions. The abscissa is the concentration of valence electrons (twice the atomic concentration for Ca–NH_3 solutions). Region I is the miscibility gap; solutions cannot be made with concentrations and temperatures in that range. The "critical" point for the gap for Ca–NH_3 solutions is not known. Regions II and III are homogeneous; metallic solutions are formed in region II, nonmetallic in region III. In region IV there is excess, solid ammonia and in region V there is excess, solid metal. See Ref. 1 for details and references.

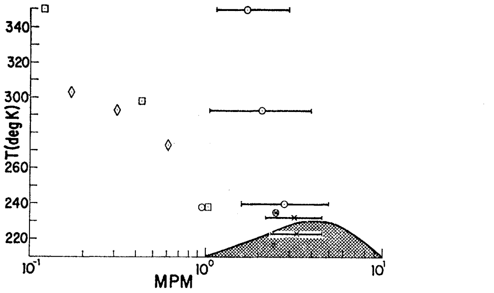

FIG. 7. The locus of the metal–nonmetal transition in the temperature-concentration plane. The ⊙, ⊡, and ◈ denote the onset of ESR asymmetry (see text) for Na–, K–, and Cs–NH_3 solutions, respectively (see Ref. 28). Regions of steep slope in a conductivity-concentration plot such as Fig. 1 are denoted by –×– or –○– for Li– and Na–NH_3 solutions (see S. Naiditch in the proceedings of the Colloque Weyl, Ref. 1). The peak in $\sigma^{-1}d\sigma/dT$ (Ref. 15) is shown as a circled asterisk. The crosshatch denotes region I of Fig. 6 for Na–NH_3 solutions. The correlation of phase separation and metal–nonmetal transition is believed significant.

It is, of course, my assertion that the changes displayed are caused by or cause a metal–nonmetal transition.[30] The existence of a transition is clear; the low mean free path at 1 MPM and the rapid rise with metal concentration in the 2–5 MPM range indicate that the transition is from a nonmetallic to a metallic state. The magnetic properties of the solutions foretell at 1 MPM a change in the electronic state, yet the absorption characteristic of the solvated electron persists to 5 MPM. Changes in the thermodynamic properties correlate well with those of the transport coefficients and with the phase separation. Finally, increasing temperature produces a metallic state at lower metal concentrations. With this summary in mind, let us now discuss these phenomena.

V. DISCUSSION

Because the metal atoms are imbedded in a molecular medium, rather than a vacuum, ionization is obtained at 200°K instead of 2000+°K. But the dipolar medium exerts other influences. It provides well-defined traps for the electrons in the dilute solutions.[1,7] Hence bound

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[25] S. Kikuchi, J. Soc. Chem. Ind. **47**, 488 (1944); D. E. O'Reilly Ph.D. thesis, University of Chicago 1955, quoted by R. Catterall in *Metal-Ammonia Solutions*, G. Lepoutre and M. J. Sienko, Eds. (W. A. Benjamin, Inc., New York, 1964), p. 41.

[26] D. E. Bowen and J. C. Thompson, Phys. Rev. **168**, 114 (1968).

[27] P. D. Schlettler and A. Patterson, J. Phys. Chem. **68**, 2865 (1964); C. W. Tobias and Wa-She Wong, Chem. Abstr. **64**, 1405*e* (1966); (private communication).

[28] R. Catterall, J. Chem. Phys. **43**, 2262 (1965); (private communication).

[29] F. J. Dyson, Phys. Rev. **98**, 349 (1955).

[30] N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949); Can. J. Phys. **34**, 1356 (1956); Phil. Mag. **6**, 287 (1961); J. A. Krumhansl, in *Physics of Solids at High Pressures*, C. T. Tomizuka and R. M. Emrick, Eds. (Academic Press Inc., New York, 1965), p. 425.

valence electron states can exist in charged systems other than negative metal ions. As the concentration is increased the interaction of solvated ions and solvated electrons leads to their association[2] in clusters containing four charged particles already at 10^{-2} MPM. The extent of the clusters and the electron wave function overlap must both be great enough by 1 MPM to move spin states within kT of each other, if the magnetic data are to be understood. Yet the optical absorption characteristic of the solvated electron persists for at least a fraction of the electrons above 1 MPM. The transport coefficients at 1 MPM also indicate that the electron wave function must be still localized upon the cavities. In particular, the absence of a temperature coefficient for R_H appears to confirm that the electrons are in deep traps (though the meaning of R_H is unclear in such a low mobility material). The conductivity rises rapidly near 4 MPM. I repeat the observation that there is no sign of a high effective mass in the susceptibility, optical data, or other transport properties in the 4–10 MPM range. Those electrons which are partaking in conduction must therefore do so from a broad band. The changes in the magnetic resonance data are consistent with the delocalization of the electron wave functions above 4 MPM. What is not clear is the mechanism limiting the number of bound states or of free electrons in this same range. It is possible that the number of ammonia molecules is too low to complete the solvation layers for every metal valence electron, leaving some free. That is, interactions between ions, solvent, and electrons may lead to a number of deep electron traps (with the properties of the electron cavity) smaller than the number of electrons to be solvated because of the low solvent fraction. While double occupancy of a cavity is plausible in a dynamic sense during hopping, the static existence of a doubly occupied cavity seems to have been ruled out by a recent calculation of O'Reilly.[31] As a consequence some of the electrons must be put in the conduction band.

Let us turn to the thermodynamic data in the transitional range. We note little change in ΔV, yet a primary reason for introducing the solvated electron was its large effect upon ΔV.[1] Both the drop in the vapor pressure and an increase in the surface tension indicate that the interactions among the ammonia molecules and the constituents of the solution are being strengthened as metal is added. The absence of a discernible anomaly in the viscosity, in contrast to ΔP and the surface tension,[32] is therefore quite surprising. Perhaps one can tie this all together with arguments of the following sort. The basic idea is the gradual removal of electrons and their layers of oriented solvating NH_3 molecules from the matrix of solvated ions and solvated electrons and the introduction of screening by the released free electrons.

It seems reasonable to assume that by 1 MPM the clusters of associated charges extend over several interionic distances and contain many charges. Conditions of charge neutrality must force the clusters into a local order much like that of a molten salt. Indeed the activity or chemical potential derived from the vapor pressure[1,6] shows below 3 MPM the $x^{1/3}$ dependence expected of a molten salt.[33] Further increase in concentration increases the numbers of ions and electrons in a cluster, probably increases the numbers of solvated electrons near a given solvated electron (as the cavity is much larger than the ion) and leads to greater hopping from cavity-to-cavity. Eventually, near 4 MPM the decrease in kinetic energy accompanying the hopping outweighs the Coulomb repulsion and many of the electrons become delocalized.

Should the clusters continue to grow without limit, we should eventually obtain, I believe, a metallic state within the molten salt structure. The cavity is much larger than the ion and the overlap must eventually become large enough to delocalize the electrons as the density and the number of close neighbors also increases. The molten salt structure must fill the solution by the time the rapid rise in conductivity occurs. From that point—say 4 MPM—there will be a gradual diminution of the fraction of the electrons in cavities and finally a gradual washing out of the cavity itself near 8 MPM. Above 8 MPM, we have the metallic structure dictated by the binary alloy theory.

On this model, the phase separation is the analog of a liquid–vapor separation in a molten salt. That is, going from 4 to 10^{-1} MPM is equivalent to boiling the molten salt and dispersing the vapor to the point that only small droplets or ion multiples occur. Also on this model, the limiting factor in electron transport is the transfer of charge from cluster-to-cluster. The composition of a given cluster must shift as individual solvated ions or electrons or even the solvating ammonia molecules move. Hence the calculation of any transport coefficient is impossible. We can nevertheless understand that the conductivity will vary rapidly as the cluster size changes and that thermal excitation will be required to move an electron from one cluster to another, yielding the exponential relation between σ and T observed below 6 MPM. At the same time the carrier density will be temperature-independent, also as is observed.

An essential part of this argument is that the "boiling" of the molten salt, the metal–nonmetal transition, and the phase separation are all thermodynamically interrelated. Of course, we cannot determine whether the Mott transition triggers the phase separation, or

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[31] R. H. Land and D. E. O'Reilly, J. Chem. Phys. **46**, 4496 (1967).

[32] M. J. Sienko, in *Metal-Ammonia Solutions*, G. Lepoutre and M. J. Sienko, Eds. (W. A. Benjamin, Inc., New York, 1964), p. 22.

[33] H. S. Frank, in *Chemical Physics of Ionic Solutions*, B. E. Conway and R. G. Barradas, Eds. (John Wiley & Sons, Inc., New York, 1966), p. 53.

vice versa. It is also possible that there is no transition in the Mott sense and that the effects observed are the consequence of the disjointness of the clusters, in which case we have a percolation problem. A third possibility is that we are seeing the consequence of an Anderson-type delocalization.[34] That is, below 1 MPM the electron sees a more or less random potential of sufficient strength to produce localization. The increase of the metal content, on the one hand, increases the order of the system and, on the other hand, decreases the strength of the potential through overlap and electron—and solvent—screening effects. Thus at the transition one has too weak and too ordered a potential to capture the electrons and delocalization follows. In this case, the phase separation may remain a consequence of the molten-saltlike properties of the solution, but the correlation of the phase separation and the metal–nonmetal transition becomes a happenstance.

My own opinion, developed in many discussions[35] with Morrel Cohen (which I most gratefully acknowledge), is that we are observing a Mott transition within a molten-saltlike structure. The over-all picture of the solutions then is as follows. In the most dilute solutions the metal atoms are ionized and the ion and valence electron trapped (solvated) separately in the solvent. As more metal is added to the solution the solvated ions and electrons are drawn together by Coulomb forces into progressively larger clusters, yet retain their layers of "solvating" ammonia molecules. In those clusters containing two or more solvated electrons there is sufficient overlap to produce spin pairing. When the concentration is near 1 MPM the cluster size has reached a point such that a spin may be flipped within a cluster by expending only thermal energies. The magnetic properties thus are those of a set of not quite degenerate electrons. By 4 MPM the molten-salt structure extends throughout the solution, some of the electrons are in the conduction band, and a Mott transition has begun. Finally, above 8 MPM, the properties of the system become those of a liquid metal or metal alloy.

Happenstance, Mott transition, or the "boiling" of a molten salt, we have a rich system upon which to sharpen our experimental or theoretical tools.

Discussion of Thompson's Paper

M. CUTLER (Oregon State University): The relationship observed by Dr. Thompson between the metal–insulator transition and phase stability is very interesting because a very similar relationship occurs in the case of liquid semiconductors. Liquid semiconductor behavior is frequently found in certain types of molten binary alloy systems which may perhaps be typified by the intensively studied thallium–tellurium system [M. Cutler and C. E. Mallon, J. Appl. Phys. **36**, 201 (1965); Phys. Rev. **144**, 642 (1966); M. Cutler and M. B. Field, Phys. Rev. **169**, 632 (1968)]. Tl–Te has semiconductor behavior in the composition range 0–70 at. % Tl. The phase diagram has a miscibility gap between a nearly pure Tl composition which is undoubtedly metallic and a composition containing ~70 at. % Tl. In the course of an exploratory study of liquid semiconductors whose results are in a not readily accessible report [M. Cutler, Report No. GA4420, General Atomic Div. of General Dynamics, 23 Oct. 1963], this type of phase diagram was observed to occur in a very large number of chemically analogous binary systems. Two liquid regions between a nearly pure metal and a liquid containing ~30 at. % chalcogenide are found in the following systems: Cu–O, Cu–S, Cu–Se, Cu–Te, Ag–O, Ag–S, Ag–Se, Ag–Te, Al–S, In–S, In–Te, Ga–Te, Tl–S, Tl–Se, Tl–Te, and As–S. In most cases, the chalcogenide-rich liquid is known to be a liquid semiconductor, and it may reasonably be expected to be one in the others. We are currently studying in detail the metal–semiconductor transition in Tl–Te at temperatures above the liquidus. The implication of the over-all situation seems to me to be that "dilute metals," in which the electron concentration is a factor ~10 smaller than in normal metals, are relatively unstable and tend to separate into a metallic phase plus one that is an insulator or a semiconductor As far as the thermodynamic properties relating to phase stability are concerned, a small concentration of electrons which may occur in a semiconductor does not lead to a significantly different behavior from an insulator.

J. C. THOMPSON: This is, of course, consistent with what Professor Mott was saying this morning: that there might be an effect in the transition which would cause a distortion in a lattice, but, of course, in a liquid system it can cause a phase separation. It is also interesting to me that the correlation of Mott transition and phase separation is also found in the mercury system.

B. PHIPPS (IBM): Two questions. Do you have data from the Knight shift of the sodium which would show the evidence of clusters in the concentrated liquid? Second, do you have x-ray diffraction of the liquid which would show any ordering at the higher concentrations in the order of 6 MPM?

J. C. THOMPSON: As noted in Fig. 4, the Knight shift increases markedly when one enters the metallic state and this I would take to be a consequence of the delocalization. There is no measurable Knight shift at the metal nucleus at concentrations below those where ion pairing is assumed. However, on the nonmetallic side, if one takes the model I proposed, the electron is still separated from the metal nucleus by the solvating ammonia molecules and therefore, the Knight shift in the nonmetallic state, in spite of the clustering, remains small. There have been two experiments on the x-ray properties of these solutions. Neither, unfortunately, is adequate to answer your second question. I wish someone would do an accurate x-ray diffraction experiment.

L. ONSAGER (Yale): I could perhaps explain a little why I think we do have this simple unit containing just a pair of electrons. It is not so much on theoretical grounds as on experimental, and it is not even new experiments. The data I looked at were first the transport data: conductivity and transference number. That is, you can determine separately the speeds of the electrons and of the sodium ions. On the other hand, there were the magnetic data, primarily in dilute solutions. Now the conductivity per atom decreases with increasing concentration, but decreases less, relatively, than for any other known electrolyte. The different alkali metals hardly differ. The minimum of this function is about half the limiting conductivity and that is a remarkably high minimum. I admit I am not sure how it is at temperatures other than near the boiling point. On the other hand, the paramagnetic susceptibility doesn't differ much whether you take it

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[34] P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

[35] M. H. Cohen and J. C. Thompson (to be published).

statically or by magnetic resonance. This indicates that the total of paramagnetic species, that is, a sum of both free electrons (single electrons) and sodium atoms if you have any, drops way below 50%. You may simply conclude that it is a *fast* diamagnetic species. Now the question is, does the said diamagnetic species contain sodium? Well, the transport number for sodium answers that. Sodium, regardless of concentration, moves to the cathode. If the very fast diamagnetic species contained sodium in sufficient quantity to explain the conductivity, then sodium would go to the anode. As to the explanation, it may be enough just to list that the contact repulsion between the electron and ammonia molecule is significant. This gives rise in the case of electrons in liquid helium to quite sizable effects and the electron in helium takes cavities of 18-Å size; it can give a bigger cavity in a high-pressure vapor. So the exchange repulsion is clearly there and those who have computed these things as best they could from first principles have come to the conclusion they can get repulsive interactions up to about neon in otherwise saturated electron systems. So NH_3 would qualify. I think in this respect the alkali metal–ammonia solutions would be in a class by themselves, because I don't know any other systems on which on this basis you would expect a repulsive interaction between the electron and the solvent. For the rest, some of the transition then would be explained in terms of a hopping mechanism but then the hopping mechanism is from singly to doubly occupied cavities. A hopping mechanism in the solvent alone would give you an increase in the limiting mobility in the first place. In the concentrated solutions you might very well have to consider cavities predominantly occupied by pairs but occasionally by singles and you get a somewhat oblique approach to the metal–nonmetal transitions which would be in some respects unique and in other respects not too unlike the ordinary.

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Microwave Dielectric Constants of Sodium–Ammonia Solutions

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Measurements have been made of the complex dielectric constant $\epsilon'-i\epsilon''$ of sodium–ammonia solutions at 10 GHz. The real part of the dielectric constant ϵ' was a very dramatic function of solution concentration. At very low concentrations ϵ' was close to the pure ammonia value, then increased slowly with concentration in the range $\chi=2\times10^{-3}$ to $\chi=2\times10^{-2}$. This increase has been attributed to the presence of permanent dipoles, and a dipole moment of approximately 10^{-16} esu at room temperature was determined. At $\chi=2\times10^{-2}$ the value of ϵ' decreased very abruptly to large negative values. This decrease is interpreted as the nonmetal to metal transition, indicating a very rapid decrease in the mass of the negatively charged carriers as the concentration is increased. In this same concentration range ϵ'', the imaginary part of the dielectric constant, increased rapidly as would be expected from the increasing dc conductivity. Temperature-variation studies of the dielectric constant have also been made and are consistent with the known temperature behavior of the solution's conductivity, i.e., the lower the temperature the higher the concentration required to reach the metallic concentration region and hence produce a negative real part to the dielectric constant.

The nonmetal to metal transition may be readily observed in solutions of alkali metals in liquid ammonia.[1] The transition is observed from the electrical conductivity of the solutions as a function of concentration. Figure 1 shows the dc conductivity as a function of the mole fraction of sodium in ammonia. This is a composite curve extracted from the literature and interpolated to temperatures which were used in our experiments. The curves are for 25°, 0°, and −45°C. For mole fraction $\chi<2.5\times10^{-3}$ the solutions are electrolytic and exhibit a large temperature coefficient of resistance. For $\chi>2.5\times10^{-2}$ the conductivity is comparable with that of metals and the temperature coefficient of resistivity is correspondingly small. The conductivity of mercury at room temperature is approximately 10^4 mhos/cm and that of a saturated solution of sodium in ammonia is 5×10^3 mhos/cm. For $2.5\times10^{-3}\leq\chi\leq2.5\times10^{-2}$ the nature of the conducting species is a subject of much controversy. The region of steepest slope in Fig. 1 is generally regarded as the nonmetal to metal transition. The transition region occurs at higher concentrations as the temperature is decreased.

In very dilute solutions the conducting species are thought to be positive metal ions and solvated electrons. A solvated electron is one which has bound to it several ammonia molecules, forming heavy negative ions. Such dilute solutions conduct electricity by an electrolytic process which involves thermally activated "hopping" of the electrons, as indicated by the large temperature coefficient of resistance. In the concentrated range the conduction mechanism is almost exclusively metallic, and the current-carrying species are well established as degenerate free electrons.[2] In the

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[1] J. C. Thompson, *Chemistry of Non-Aqueous Solvents*, J. J. Lagowski, Ed. (Academic Press Inc., New York, 1967), Vol. 2.

[2] D. S. Kyser and J. C. Thompson, J. Chem. Phys. **42,** 3910 (1965).