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Conduction in Concentrated Solutions of Several Metals in Liquid Ammonia*

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Measurements are reported of the electrical conductivity of solutions of Cs, Ca, Sr, Ba, and Yb in liquid ammonia. Cs-NH_3 solutions were studied at concentrations above 6 mole % metal (MPM) and at temperatures from 200 to 300 K. Cesium and ammonia can apparently be mixed in any proportion near room temperature. In the case of the other metals, the concentration range is from 2 to 7 MPM at temperatures between 190 and 250 K. The observed conductivities ranged from 200 to 16 000 $\Omega^{-1}\mathrm{cm}^{-1}$. The conductivity was observed to increase with temperature, except for Cs-NH_3 solutions above 30 MPM. The present results are compared with those available on other metal-ammonia solutions, and with the behavior of simple liquid metals. In addition, the phase diagrams of the solutions are reported.

I. INTRODUCTION

The common alkali and alkaline earth metals are known to dissolve in liquid ammonia in sufficient concentration to produce bronze colored solutions with metal-like properties.[1] Much of the conductivity data on sodium and potassium solutions was reported over 50 years ago by Kraus.[2] More recently, conductivity measurements have been made on lithium-ammonia solutions by Morgan *et al.*[3] and by Evers and Longo.[4] Each of these investigations reveals a conductivity in the metallic range ($\sim 10^3\ \Omega^{-1}\mathrm{cm}^{-1}$) and strongly dependent upon metal concentration.[5] In addition, the conductivity is found to increase with increasing temperature, even though other transport properties (e.g., the Hall effect[6]) indicate the carrier density to be temperature independent. Pressure decreases the conductivity.[7]

A survey of the properties of the solutions reveals a general insensitivity to the particular solute. For example, the optical absorption in dilute metal-ammonia solutions is solute independent.[8,9] The present investigation was undertaken to see if a similar solute-independent effect would exist in the electrical conductivity. The conductivity was measured in solutions of Cs, Ca, Sr, Ba, and Yb in ammonia over the concentration range 1.5 MPM to saturation and over the temperature range 180 to 300 K. Little data are to be found in the literature.[1,9] With the exception of Cs, each of the metals goes into solution as a divalent ion.[10] The next section contains a description of the procedure and a compilation of the results. A determination of a portion of the phase diagram, obtained incidentally, is also given. The final section contains a discussion of the results and a comparison with other properties.

II. EXPERIMENT

The conductivity data reported herein were obtained by one of two[11,12] electrodeless techniques. In one[11] the sample is the cylindrical core of a coil which it loads. The change in the apparent resistance of the coil, measured at audio frequencies with a simple bridge,[3,13] is related by a Bessel function[14] to the conductivity of the material. The useful conductivity range is from 400 $\Omega^{-1}\mathrm{cm}^{-1}$, up. The other technique[12] involves measuring the attenuation of an rf signal by a thin slab sample. In the present case,[14] there is a linear relation between the attenuation, the conductivity, and the frequency. Each apparatus was calibrated against liquid Hg and Li-NH_3 solutions.[3]

With either technique, the liquid sample was contained in a glass ampoule of the appropriate geometry. Cesium could be doubly distilled into the makeup bulb for the cylindrical sample, and dissolved by adding a known amount of ammonia. The amount of Cs was determined after the experiment by reacting the Cs with water, driving off the ammonia, and titrating for the total Cs. By measuring the H_2 evolved when the Cs reacted with the water, the amount of Cs which had decomposed to $CsNH_2$ during the run was determined. The other metals were cleaned and weighed in a He-filled glove box, then dropped into the makeup tube for the slab cell, then dissolved by the addition of a known amount of liquid NH_3. In each system the vapor pressure was monitored for signs of decomposition. Typically, the measurements were discontinued after decomposition reached 3–5% of the original metal. The Cs samples, stored at 200 K, were studied intermittently for periods of more than two weeks. The other solutions seldom could be kept more than ten hours.

Temperature regulation was provided by baths of dry ice-alcohol and thermister-controlled circuits.[3,6] In a few cases, the samples were kept in Freon-12 baths cooled by liquid N_2.

Typical conductivity data for Cs, Ca, and Yb solutions are shown in Fig. 1. The scatter of the data provides a fair representation of the precision. At concentrations below about 18 MPM the conductivity σ *increases* linearly with increasing temperature T. In the high-concentration Cs-NH_3 solutions, σ begins to decrease with increasing T, as also has been observed in Li-NH_3 solutions at comparable concentrations.[3] The temperature coefficient $\gamma = \sigma^{-1}d\sigma/dT$ is shown in Fig. 2. It is clear that the divalent solutions exhibit values of γ similar to those of the solutions of alkali metals.

Figure 3 displays the available σ data for concentrated solutions of both alkali and alkaline earth metals (and Yb). Values reported by several earlier workers have been included.[2–4,15–17] As has been observed previously,[1] the conductivity

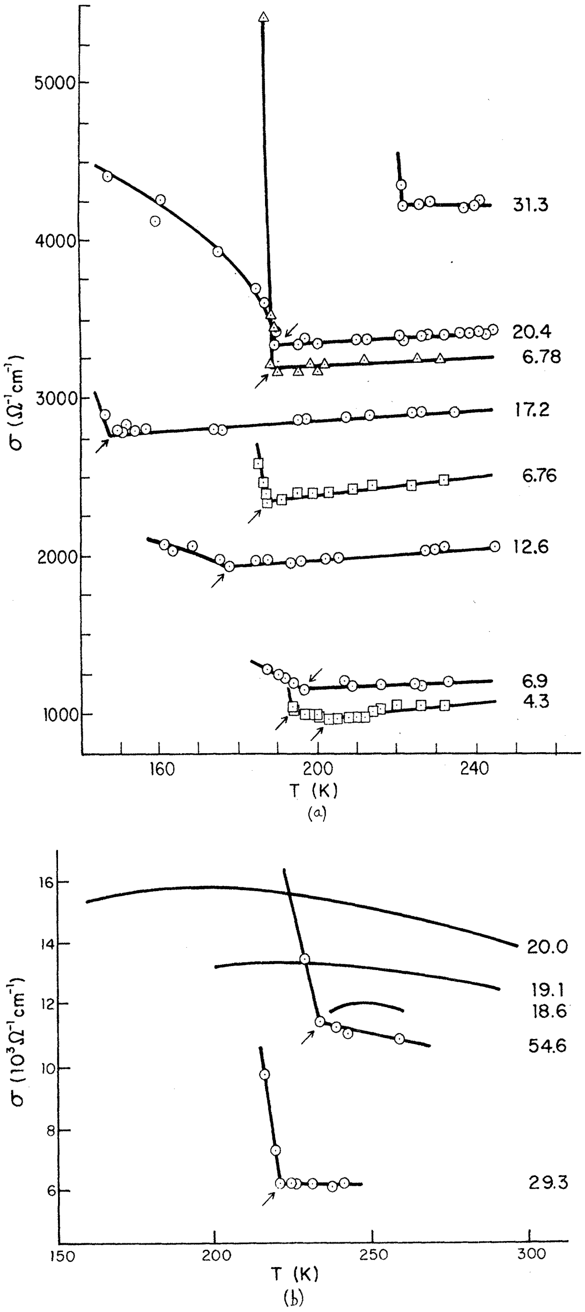

FIG. 1. (a) The electrical conductivity of several metal-ammonia solutions: -⊙-, Cs; -⊡-, Ca; and -△-, Yb. The arrows denote phase changes, and the numbers give concentrations in MPM. The 4.3 MPM $Ca-NH_3$ solution intersects the liquid-liquid phase boundary (see Fig. 5) at 203 K and the liquid-solid boundary at 194 K. (b) The solid lines show $Li-NH_3$ data (see Ref. 3) and the other notation is unchanged.

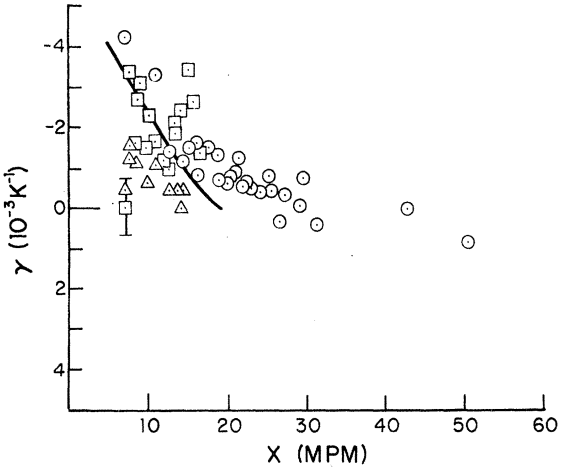

FIG. 2. The temperature coefficient of conductivity $\gamma = \sigma^{-1} d\sigma/dT$ for several metal-ammonia solutions. The solid line denotes data for $Li-NH_3$ solutions and the other symbols are as in Fig. 1. The error bar shown is typical for divalent solutions; the $Cs-NH_3$ data are much better. The $Cs-NH_3$ data extrapolate smoothly to pure Cs ($\gamma = -3.3 \times 10^{-3}$ K^{-1}). The divalent data are expressed in terms of electron concentration.

is a strong function of the concentration of metal, though less strong in divalent than in monovalent solutions. Note that there is a knee in the curve for $Cs-NH_3$ in the concentration range above the saturation point for the other metals. There is a smooth extrapolation from the most concentrated $Cs-NH_3$ solutions to "pure Cs." (Because pure Cs freezes at 301 K, the data were extrapolated to 240 K by use of the known temperature coefficient.[18])

Curves such as those in Fig. 1(a) provide information on the phase diagrams of the solutions. The abrupt change in conductivity occurs when the phase separation occurs, leaving a higher concentration phase in the measuring coil.[16] In some cases the inhomogeneity of the sample was revealed by the change in resistance which resulted when the coil was moved. Figure 4 shows the available data on the $Cs-NH_3$ system, while Fig. 5 shows typical data for the solutions of divalent metals. As with previous observers,[19] we do not find evidence for a miscibility gap in $Cs-NH_3$. However, previous evidence that Cs and NH_3 are miscible in all proportions has been discounted by previous experimenters.[20] With Cs (and possibly[19,21] Rb) aside, there is a strong resemblance among all the other phase diagrams both as to the consulate concentrations (insofar as they are known) and the eutectic points. The available data on eutectics are collected in Table I. It should be noted that both Na and K precipitate from NH_3 on freezing[3,22–24] whereas all other frozen metal-ammonia solutions are bronze metallic solids.

III. DISCUSSION

We now have conductivity data available over most of the temperature-composition plane, wherein solutions of eight metals in liquid ammonia exhibit properties that are essentially those of liquid

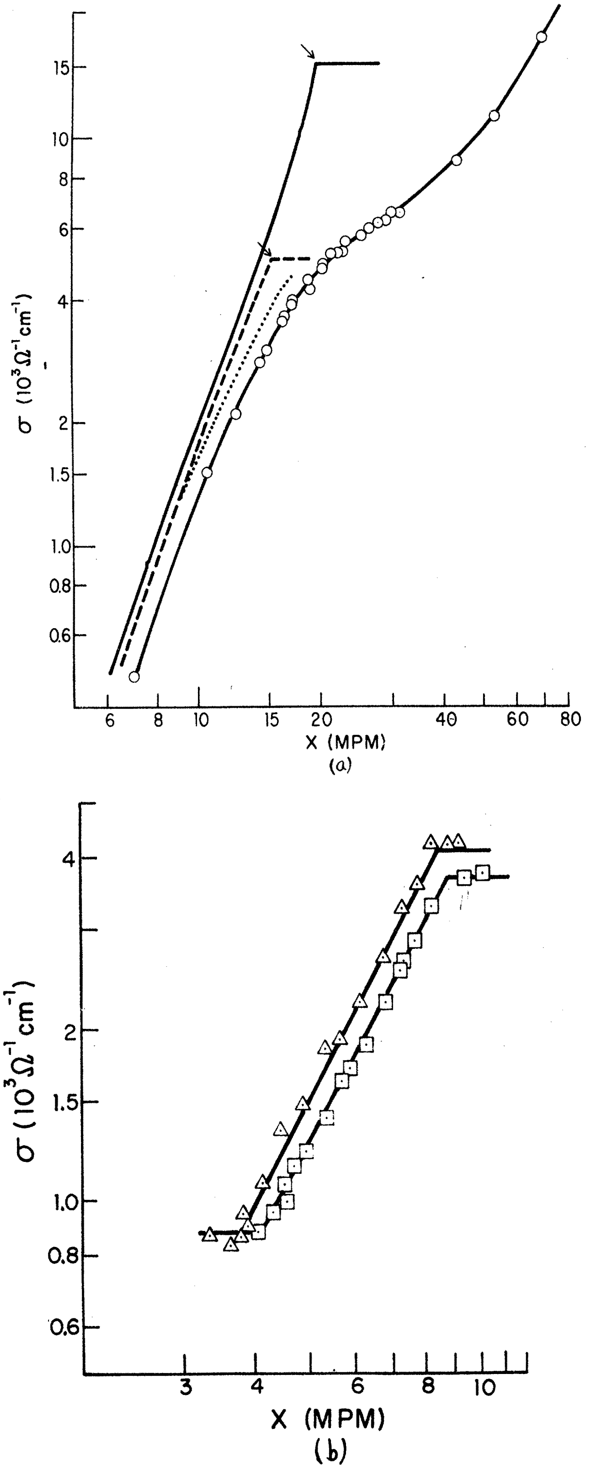

FIG. 3. (a) Electrical conductivity of several alkali metal-ammonia solutions at 240 K: ———, Li-NH_3; ----, Na-NH_3; ····, K-NH_3; and –○–, Cs-NH_3. The conductivity of liquid cesium is ~35 × 10^3 Ω^{-1} cm^{-1}, when extrapolated to 240 K. (b) Electrical conductivity of some divalent metal-ammonia solutions at 240 K: –□–, Ca-NH_3; and –△–, Yb-NH_3. Data for Sr-NH_3 and Ba-NH_3 solutions lie between the two lines shown.

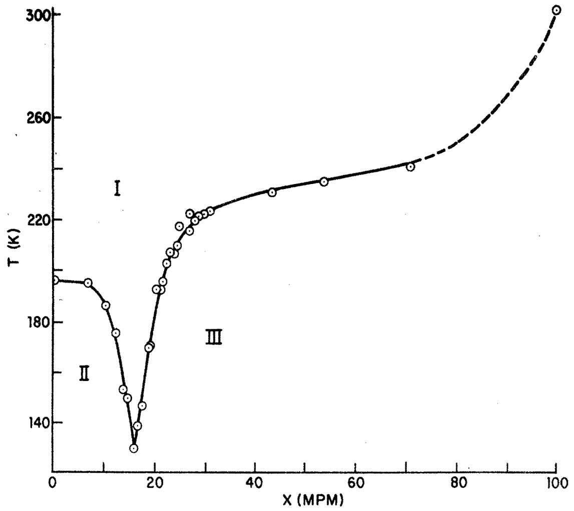

FIG. 4. The phase diagram of Cs-NH_3 solutions as determined by conductivity measurements [see Fig. 1 (a)]. Error bars do not exceed 10 K. Region I denotes a homogeneous liquid, region II a liquid plus excess, solid ammonia, and region III a liquid plus a bronze solid. The solid in region III does *not* have the appearance of solid Cs, rather that of the solid formed on freezing a Li-NH_3 solution (see Ref. 13, 22–24).

metals. In this section the qualitative and quantitative trends are summarized and compared with other available data. A composite picture of a metal-ammona solution is deduced, and an outline given of the salient points to be explained by any theory. The close similarity in behavior of Yb and alkaline earth solutions together with the optical data of Ostertag and of Catterall[10] lead us to treat Yb along with the alkaline earths as divalent in these solutions.

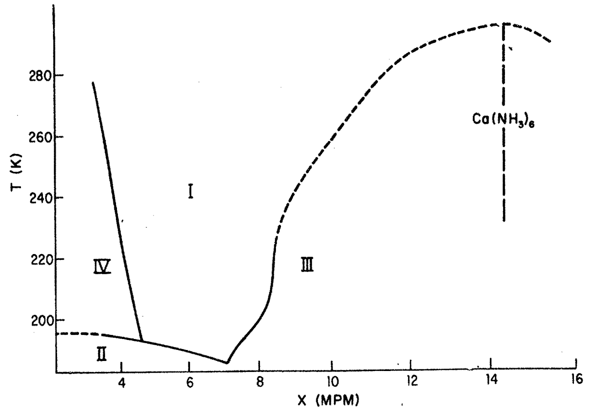

FIG. 5. The phase diagram of Ca-NH_3 solutions as determined by conductivity measurements. Data are from Ref. 1 and 17 as well as the present work. Regions I–III are as in Fig. 4 while region IV is the miscibility gap. Solid Ca(NH_3)$_6$ has been observed (see Ref. 1, 16) but the melting point is not known, nor is the consolute point for region IV.

TABLE I. Known eutectic points for metal-ammonia solutions. The concentration quoted for the solutions of divalent metals is twice the metal ion content so as to reflect the dependence upon valence electron density.

Solute	Composition (MPM)	Temperature (K)	References
Li	20	88.8	3, 22
Na	17	163	16
K	15	116	16
Cs	16	130	Present work
Ca	13.3	185	Present work
Sr	13.3	185	Present work
Ba	13.5	186	Present work
Yb	14.3	183	Present work

When the conductivity σ and available density data are combined, one finds that near 240 K the conductivity may be approximately represented by a power law n^a in the electron density n with $a = 3$ for the alkali metal solutions and $a = 2$ for the solutions of divalent ions. There is thus a clear dependence on the charge or number density of the positive ion. Nevertheless the magnitudes of the conductivities in the solutions are much closer than for the pure liquid metals,[18] so that there seems to be little sensitivity to the details of the ionic pseudopotential. In each instance the strength a of the dependence of conductivity on electron density is somewhat greater than one would anticipate from an examination of the available data on simple liquid metals.[18,25] Another aspect of this point is revealed by the dependence of electrical conductivity on temperature T.

It is very surprising to find $\gamma = \sigma^{-1} d\sigma/dT > 0$ in a material where σ is numerically large, and in spite of the somewhat similar behavior of liquid Zn near its melting point,[25] several authors have concluded that these solutions are liquid semiconductors.[1,26] This conclusion has been shown to be untenable by Hall effect data[1,6] and is furthermore, not consistent with the known properties of other liquid conductors.[27] We note again no difference between the behavior of the monovalent and of the divalent ion solutions.

The standard kinetic theory formula for the conductivity is

$$\sigma = (e^2/12\pi^3\hbar)\Lambda S , \qquad (1)$$

where Λ is the mean free path and S is the area of the Fermi surface.[28] Both Λ and S are functions of the Fermi wavenumber k_F, and it is instructive to plot the conductivity as a function of k_F. Since k_F is temperature dependent (through the density) as well as concentration dependent, we have the choice of varying T or x.[5] As is shown in Fig. 6, the results are not at all the same. If we increase k_F by adding metal, then σ increases with k_F; yet if we increase k_F by lowering the temperature (so as to increase the density), then σ decreases as k_F increases. Similarly, an increase in k_F produced by increasing the pressure leads to a decrease in σ.[7] The difference in behavior imposes severe limits on any proposed theory.

The available data on the Hall effect,[6] thermopower,[29] magnetic susceptibility,[30] and optical constants[1,31] do not cover so wide a variety of solutes, temperatures, or compositions as do the conductivity data. Data on the solutions of divalent ions are particularly lacking.[16,17] Insofar as these data are available, they seem to follow free electron theory rather well,[1] though the electron densities are well below those typical of common metals. The Hall data[6] indicate the presence of localized electrons at concentrations below 8 MPM (in alkali solutions) and thus limit our considerations of metallic properties to higher concentrations.[1]

It appears, in summary, that the properties of concentrated metal-ammonia solutions are much like those of many liquid metals with two significant exceptions: $d\sigma/dT \geq 0$ and $d\sigma/dn$ is large. In view of the successes of the theory of liquid metals developed by Ziman[25] and others,[32] it is to be hoped that these properties can be reproduced by a calculation based on that theory. This computation will be the subject of a subsequent paper.[33]

There is presently no theory of the phase separation which is a characteristic feature of metal-ammonia solutions. The data presented in Fig. 4 and 5 serve to reinforce the assertion that the properties of the solutions depend little on solute ion insofar as the valence electron concentration of the phase separation is concerned. There is clearly a strong solute effect on the temperature of the phase separation and also on the saturation curve. The observed saturation curves for the divalent metal solutions are consistent with pre-

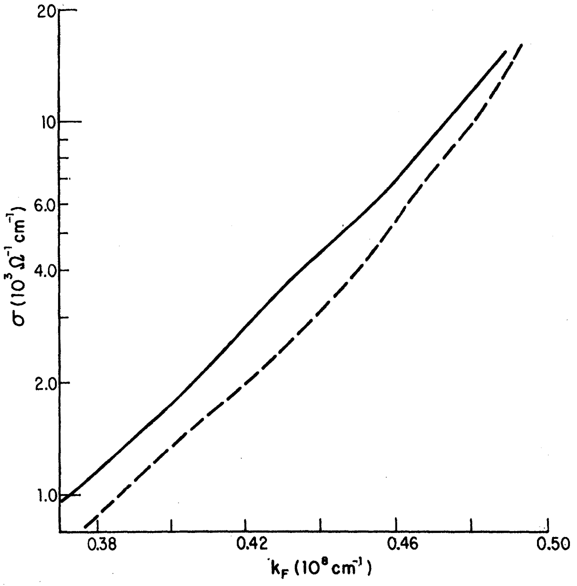

FIG. 6. The electrical conductivity as a function of Fermi wave number as determined at two temperatures: solid line 240 K; dashed line 200 K. Changes of temperature and concentration are seen *not* to produce the same effect upon the conduction process.

vious data,[1,15,16] including the existence of stable compounds such as $Ca(NH_3)_6$. The apparent total miscibility of Cs and NH_3 make that system particularly attractive for experimentation as the pure liquid metal is fairly well understood.[25] The probable correlation of the phase separation and the metal-nonmetal transition[1] has been discussed by Cohen and Thompson.[34]

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