QUARTERLY REVIEWS

NATURE OF METAL SOLUTIONS

By M. C. R. SYMONS, PH.D.
(THE UNIVERSITY, SOUTHAMPTON)

THIS Review is concerned with the physical nature of blue solutions which result when alkali or alkaline-earth metals dissolve, with no net reaction, in solvents such as ammonia, amines, and ethers. Concentrated solutions of these metals in ammonia are metallic in appearance and general properties, and will only be considered when appropriate to the main discussion. The reactivity of these solutions will be mentioned when it bears upon the problem, but this topic has been discussed in detail by Birch and Herchel Smith,[1] and there have been several other reviews.[2,3,4] Kraus, whose pioneering work is still the most extensive and reliable in many of the fields of study, has stressed[2] that these unique solutions have attracted relatively little experimental attention and their importance to fundamental theory warrants much more careful study. One object of this Review is to examine recent results and theories and hence to suggest avenues of investigation which might prove fruitful.

In section 1 some relevant facts are recorded, stress being laid on recent work. In section 2 mention is made of the various theories that have been forthcoming concerning the nature of these solutions, and in section 3 these theories are compared and discussed in the light of the facts. Section 4 concludes the Review with brief reference to possible future developments and certain related phenomena.

There are many properties of these solutions which resemble those of "solutions" of alkali metals in solid alkali halide crystals. Because the latter phenomenon is far better understood, some reference will be made to such additively coloured crystals which will be considered in detail in a forthcoming Review.[5]

1. Facts

All alkali and alkaline-earth metals, other than beryllium, dissolve to some extent in ammonia. Other solvents include primary and secondary amines and diamines, certain ethers, in particular diethers such as ethylene

---

[1] Birch and Herchel Smith, *Quart. Rev.*, 1958, **12**, 17.
[2] Kraus, *J. Chem. Educ.*, 1953, **30**, 86.
[3] Becker, Linquist, and Alder, *J. Chem. Phys.*, 1956, **25**, 971.
[4] Bingel, *Ann. Physik*, 1953, **12**, 57.
[5] Doyle and Symons, *Quart. Rev.*, 1959, in the press.

glycol dimethyl ether, $MeO{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$,[6] alcohols, and even oxygen-free water.[7] Solutions in alcohols and water are extremely unstable, and little can yet be said about them. Blue solutions also result when alkali metals are added to molten salts such as halides, hydroxides, and amides:[8,9] these solutions present an interesting meeting point between the solutions under discussion and additively coloured crystals, but unfortunately little is yet known of the relevant physical properties.

When ammonium and tetra-alkylammonium salts in ammonia are electrolysed, blue colours are detected, but the solutions are stable only in the latter case.[8] These solutions deserve attention since they might well provide a means for choosing between the two models for dilute solutions outlined in section (2).

Electrical Properties.—Little recent work has been reported, and this subject is fully reviewed elsewhere.[2,8] Conductivities show a marked minimum at about 0·05M for ammonia and 0·1M for methylamine,[10] which can be viewed as the merging point between concentrated solutions mentioned earlier, and dilute solutions, which have electrical properties that are often described as "salt-like". The reader is referred to these earlier reviews for details; suffice it to say here that in the region between 0·01M and infinite dilution, solutions of metals are truly "salt-like" in their electrical properties, the negative ion, whatever its nature, being responsible for the conduction of about six-sevenths of the total current. It can be argued from the results of conductivity studies that ion-pairing is extensive:[2] however, since considerable ambiguity still clouds the physical significance of this statement when simple salts are considered, it is probably unsafe to infer much from this conclusion. In solvents of low dielectric constant, such as ethers, direct contact between ions is to be expected, and has been beautifully demonstrated by Adam and Weissman.[11] Such a phenomenon is of great importance here, and will be discussed in detail later.

Ionic Volumes.—When alkali metals dissolve in ammonia there is a remarkable increase in volume, amounting, in the case of concentrated solutions, to about 43 $cm.^3$ per "mole" of electrons. Unfortunately nearly all the work which has been done relates only to concentrated solutions (down to about 1M). Kraus *et al.*[12] suggested that their results could be extrapolated to about 40 $cm.^3$ in the dilute range but this very long extrapolation is certainly unjustified as it stands. One recent experiment does appear to support this view, however: Stosick and Hunt have obtained a value between 20 and 70 $cm.^3$ for a solution containing about 10^{-3}M-

---

[6] Down, Lewis, Moore, and Wilkinson, *Proc. Chem. Soc.*, 1957, 209.
[7] Jortner and Stein, *Nature*, 1955, **175**, 893.
[8] Fernelius and Watt, *Chem. Rev.*, 1937, **20**, 195.
[9] Johnson and Bredig, *J. Phys. Chem.*, 1958, **62**, 604.
[10] Evers, Young and Panson, *J. Amer. Chem. Soc.*, 1957, **79**, 5118.
[11] Adam and Weissman, *ibid.*, 1958, **80**, 1518.
[12] Kraus, Carney, and Johnson, *ibid.*, 1927, **49**, 2206.

sodium.[13] Considerable weight has to be put on this result to justify the extensive calculations which have been made;[14,3] the datum is of very great significance, however, and it would be far more satisfactory if more results were available for a range of different dilute solutions.

Concentrated solutions of potassium[15] and lithium[16] in ammonia behave similarly. The net volume change for potassium is somewhat smaller than that for sodium, but if suitable adjustment is made for the volume changes which occur when atoms are converted into ions, and for electrostriction effects,[14] then the final volume changes are comparable for all three metals.

The very high compressibilities[17] and low viscosities[18] of concentrated solutions parallel the large volume expansions, but again results for dilute solutions have not been obtained.

Magnetic Properties.—Freed and Sugarman's[19] very careful work on the static magnetic susceptibilities of potassium solutions down to about 0·003M, together with somewhat less extensive work by Huster[20] on sodium solutions, has recently been supplemented by a study of the electron-spin resonance spectra of these solutions down to about 0·004M.[21] These alternative methods give, broadly, the same results, except that the diamagnetism due to the electron centres is included in the former but not in the latter measurements. The small difference in susceptibility obtained by these two methods is therefore a measure of residual diamagnetism and has been used by Hutchinson and Pastor[21] to give information concerning the solute species.

The major result of these studies is that extensive electron-pairing occurs, such that for solutions above about 0·1M pairing is nearly complete, whilst below about 0·001M the concentration of paired electrons is negligible. For a given concentration, pairing decreases with increasing temperature, and, at least at room temperature, sodium solutions show less tendency to form electron-pairs than potassium solutions of equal molarity. Once again, concentrated solutions resemble liquid metals in their magnetic properties.

One of the most striking features of the electron-spin resonance spectra is the extreme narrowness of the line. For dilute solutions of sodium or potassium in ammonia at —33° the width between points of maximum slope ($\triangle H_{\mathrm{MS}}$) is about 0·05 gauss.[21] This width decreases with an increase in temperature and increases when methylamine is used as solvent, and also when ammonia is replaced by ND_3. When ammonia solutions are frozen the metal is precipitated as very small clusters and the resonance is then a

---

[13] Stosick and Hunt, *ibid.*, 1948, **70,** 2826.
[14] Lipscomb, *J. Chem. Phys.*, 1953, **21,** 52.
[15] Johnson and Meyer, *J. Amer. Chem. Soc.*, 1932, **54,** 3621.
[16] Johnson, Mayer, and Martens, *ibid.*, 1950, **72,** 1842.
[17] Maybury and Coulter, *J. Chem. Phys.*, 1951, **19,** 1326.
[18] Kikuti, *J. Soc. Chem. Ind. Japan.* 1944, **47,** 488.
[19] Freed and Sugarman, *J. Chem. Phys.*, 1943, **11,** 354.
[20] Huster, *Ann. Physik*, 1938, **33,** 477.
[21] Hutchison and Pastor, *J. Chem. Phys.*, 1953, **21,** 1959.

function of the metal itself.[22] If, however, the solutions are saturated with sodium iodide, they solidify to clear blue glasses on cooling and the electron resonance signal changes to a single line having $\triangle H_{\mathrm{MS}} = 3{\cdot}5$ gauss.[23]

Only certain metals in amine solvents give paramagnetic solutions. Thus, lithium in methylamine gives an intense electron resonance absorption, potassium a weak one, whilst sodium in ethylenediamine is diamagnetic.[24] No paramagnetism can be detected for solutions in ethers.[25]

Nuclear Magnetic Resonance.—McConnell and Holm have studied the nuclear resonance spectra from ^{23}Na, ^{14}N, and ^{1}H in solutions of sodium in ammonia and found very large shifts to low fields for ^{23}Na and ^{14}N, but the proton resonance was not detectably different from the standard.[26] These measurements were made on a low-resolution instrument so that relatively small "chemical shifts" would not have been detected. These shifts were described as Knight shifts, because they closely resemble the shifts found for metals: however, it is a general phenomenon for nuclear resonance spectra to be both broadened and shifted when there is the chance of close proximity between species containing unpaired electrons and the magnetic nuclei concerned. The shift may, in a general sense, be thought of as a modification of the magnetic field experienced by the nucleus under observation by the extra field due to the magnetic electrons. This shift is often much greater than the more familiar "chemical shifts" which occur in the absence of paramagnetic material.

The shifts observed for ^{23}Na and ^{14}N decrease on dilution and could not be detected when the concentration of sodium was less than about 0·1M. At this concentration the sodium valency electrons are almost entirely paired and the results unfortunately cannot be extrapolated to the dilute region. McConnell and Holm consider that the shifts are due to contact hyperfine interactions which give a finite density for the unpaired electrons at the magnetic nuclei, and they express their results in terms of a parameter P_i, the contact density of an electron on the atom in these solutions. This is compared with estimated values for P_i°, the contact density for an electron permanently in a given orbital on atom i. They conclude that the unpaired electrons are about 5×10^{-3} times as effective in shifting the sodium line as $3s$ electrons on sodium, and 0·1 times as effective as unpaired electrons in a $2s$ state on nitrogen. There is a significant decrease with dilution in the value of P_{Na}, but P_{N} remains nearly constant in the concentration range 1·0—0·1M.[26] These very important results will be discussed in detail later.

Electronic Spectra.—Generally there are only two intense absorption

---

[22] Levy, *Phys. Rev.*, 1956, **102,** 31.
[23] Clark and Symons, *J.*, 1959,
[24] Fowles, McGregor, and Symons, *J.*, 1957, 3329.
[25] Wilkinson, Cotton, Fischer, Down, and Moore, *Abs.* 133*rd A.C.S. Meeting*, 1958, 12L.
[26] McConnell and Holm, *J. Chem. Phys.*, 1957, **26,** 1517.

bands in dilute metal solutions, one or both of which are invariably detected.[24,27] These bands, which are found in the 7000 and 15,000 cm.$^{-1}$ regions will be referred to as the infrared and visible bands respectively. These bands are so intense ($\epsilon_{\text{max.}} \fallingdotseq 4 \times 10^4$) that even when 0·1 mm. cells are used the solutions still have to be very dilute (*ca.* 10^{-3}M) for measurements near the band maxima. This point is of great importance since nearly all other physical measurements are made with more concentrated solutions. The solutions appear blue irrespective of which band is present.

Very dilute solutions of all alkali and alkaline-earth metals in ammonia have identical spectra consisting only of the infrared band.[27,28] The position of maximum absorption and the band width depend on temperature and concentration but not on the nature of the metal. Addition of a strong electrolyte results in a very small shift to higher energy but does not alter the band width. High concentrations of added salts give rise to a new band of low intensity with a peak at about 12,500 cm.$^{-1}$.[23] The infrared band is very broad, and is asymmetrically broadened on the high-energy side. When the high-energy edge is examined in more concentrated solutions (*ca.* 10^{-3}M) it is found to extend into the near ultraviolet region, and there is a pronounced shoulder in the 15,000 cm.$^{-1}$ region.[23] Thin films of more concentrated solutions in ammonia show the visible and ultraviolet bands at 20°K, though these are both at higher energies than usual because of the very low temperature.[29]

In methylamine, and mixtures of ammonia and methylamine, either or both bands appear depending upon the choice of metal, temperature, and solvent composition. Both bands in methylamine are shifted to somewhat higher energies compared with those in ammonia, and the positions and widths are again found to be a function of temperature and concentration though they are not sensitive to the nature of the metal ion.[27] In ethylamine[27] and certain diamines[24] the visible band predominates, and this is the only band found for solutions in ethers.[6] It has been reported that the spectra of the very unstable blue solutions in water have a band maximum at 11,000 cm.$^{-1}$.[7]

There is a close link between the spectra and magnetic properties of these solutions. Paramagnetism is only detected in those solutions which have a band in the infrared region, and it has accordingly been postulated that this band is characteristic of the units containing unpaired electrons whilst the visible band is due to units containing electron-pairs.[24] Thus, very dilute solutions in ammonia, in which all the solute electrons are unpaired, show only the infrared band. More concentrated solutions in which electron-pairing is significant, show both bands. Again, solutions of lithium in methylamine are paramagnetic and show both bands, but other

---

[27] Blades and Hodgins, *Canad. J. Chem.*, 1955, **33**, 411.

[28] Jolly, U.S. Atomic Energy Comm. Nat. Sci. Foundation, Washington, D.C., 1952, U.C.R.L. 2008, 3.

[29] Bosch, *Z. Physik*, 1954, **137**, 89.

metals in amines and ethers which show only the visible band are diamagnetic.

In all these solutions no other band appears before the onset of intense absorption by the solvent. The similarity to alkali halide crystals containing *F* or *F′* centres is striking. (An *F* centre is a single electron and an *F′* centre an electron-pair, in a halide ion vacancy.) Both these centres give rise to intense absorption bands in the visible region, but, in contrast with metal solutions, the *F′* or electron-pair band is always found on the low-energy side of the *F* band. Extinction coefficients and oscillator strengths are comparable, and the long-wavelength sides of the crystal bands are again asymmetrically broadened.[23] As with the solutions, no other bands attributable to these centres are detected before the onset of the fundamental absorption bands of the crystals.

Photolysis.—There is no net decomposition when solutions of sodium in ammonia are photolysed either within the absorption bands, or down to the onset of absorption by the solvent (about 40,000 cm.$^{-1}$). However, the solutions are readily bleached when irradiated with light of wavelength less than 250 mμ to give sodamide and hydrogen, although ammonia itself is not affected under these conditions.[30]

Rigid solutions of sodium in ammonia containing sodium iodide are apparently unaffected by visible light,[23] but rigid solutions of lithium in a glass containing methylamine, whose spectra are dominated by the visible band (600 mμ), are readily bleached by light of wavelength less than 500 mμ. When the glass is softened and recooled the 600 mμ band reappears, showing that no net decomposition has occurred.[31] As the 600 mμ band is bleached, so a broad band with a maximum in the near infrared region appears, which must be caused either by the ejected electron[31] or possibly by the electron left behind.[24]

***X*-Ray Scattering.**—The small-angle scattering of *X*-rays from concentrated solutions of lithium, sodium, and potassium in ammonia has been investigated by Schmidt.[32] Unfortunately, reliable results could only be obtained in the 1·0M region, but Schmidt draws some very interesting conclusions. He finds scatttering units with dimensions of the order of 15 Å (but somewhat different for different metals) and states that only a few types of centre can be present. There does not seem to be any scattering which can be associated with large cavities (radius *ca.* 3 Å) independently of the metal. The scattering shows a maximum intensity at a scattering angle well removed from zero. Schmidt concludes that the centre must therefore have regions of both excesses and deficiencies of charge.

Energies.—Jolly has discussed some thermodynamic functions for metal–ammonia solutions. He estimates $\triangle H_f$ ($\frac{1}{2}e_2$) = 40·5 kcal./mole,

---

[30] Ogg, Leighton, and Bergstrom, *J. Amer. Chem. Soc.*, 1933, **55**, 1754.
[31] Linschitz, Berry, and Schweitzer, *ibid.*, 1954, **76**, 5833.
[32] Schmidt, *J. Chem. Phys.*, 1957, **27**, 23.

ΔH_f (e_1) = 43·5 kcal./mole, ΔF_f = 44·4 kcal./mole and ΔH = 6 kcal./mole for the process

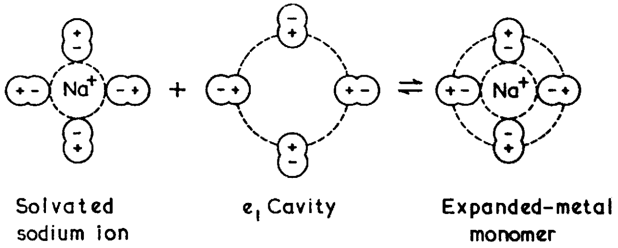
$$e_2 \rightarrow 2e_1 \quad \ldots\ldots\ldots \quad (1)$$

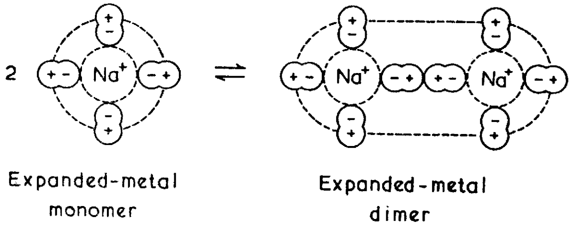
where e_1 and e_2 symbolise the units containing the unpaired and paired valence electrons of the solute.[33] Hutchinson and Pastor[21] calculate ΔH = 2·3—3·9 kcal./mole for reaction (1). For the same process in mixed ammonia–methylamine solvents, Blades and Hodgins[27] estimate ΔH = 4·6 kcal./mole.

Photoelectron emission from dilute solutions of sodium in ammonia gives a threshold of about 34 kcal./mole.[34] It has been suggested that this figure gives a rough measure of the solvation energy for electrons in these solutions.[3]

2. Theories

It is convenient to consider these solutions in three groups depending upon concentration. These will be described as concentrated solutions (above about 1·0M), medium solutions (between 1·0M and 0·05M) and dilute solutions (less than 0·05M). The metallic properties of concentrated solutions set them apart from the others, and most of this discussion will be concerned with medium and dilute solutions. In many solvents these are the only solutions formed.





There are two models for medium and dilute solutions, which are fundamentally different but have an equal claim for serious consideration. These will be referred to as the "expanded-metal" theory and the cavity

---

[33] Jolly, *Chem. Rev.*, 1952, **50**, 351; U.C.R.L. 2201, 1953.
[34] Häsing, *Ann. Physik*, 1940, **37**, 509.

theory. The former presents a solution containing solvated positive ions, with the valence electrons of the metal moving in "expanded orbitals" around these solvated ions. This theory is not new, but has recently been given prominence by Becker, Lindquist, and Alder[3] who explain the formation of electron-pairs by postulating an "expanded-metal" dimer in which two solvated cations are weakly bound together by two electrons of opposed spins.

The cavity theory, favoured by Kraus, presents a solution containing solvated metal ions and solvated electrons. The solution is thought to resemble that of any strong electrolyte except that, in place of negative ions in cavities of oriented solvent molecules, there are electrons in similar cavities. Under certain conditions two electrons, with opposed spins, are thought to occupy the same cavity.

These are overall pictures: there is a lot to commend both models and they will be considered in turn in section 3. Many authors have attempted to make one or other of these theories more precise, and some of these detailed descriptions will first be considered. An attempt will be made to keep these two aspects separated, since there has been a tendency to assume that when experiment has shown that a *particular* description of one of the theories is in error, then the whole model is proved false. Before presenting these mathematical descriptions, some alternative models should also be mentioned.

The Colloidal-metal Theory.—From time to time it has been suggested that the metal is present as a colloid, probably with a net negative charge. The case was put quite strongly by Krüger,[35] who pointed out that small colloidal metal particles should be coloured, but his evidence was strongly criticised by Freed and Thode.[36] Hunt and his co-workers favour this theory,[37] but there seems to be little evidence for it at present. Carefully prepared solutions in liquid ammonia or amines do not show a Tyndall cone. Colloids showing a band maximum in the 15,000 cm.$^{-1}$ region probably would be too small to scatter light, but colloids absorbing at 7000 cm.$^{-1}$ should certainly show such a cone. The colloid theory offers no explanation for the appearance of two distinct bands in certain solutions, but one could argue that only one of these is a colloid band. Since the infrared band has been associated with the unpaired-electron species, it cannot be a colloid band, since the number of unpaired electrons in a colloid particle would be small. Let us, therefore, consider the postulate that the visible band is due to colloidal metal. It is a general property of the colloid band, due to excess alkali metal in alkali halide crystals, that the position of maximum absorption is strongly dependent upon the nature of the metal and host crystal, but both the peak and width are independent of temperature, and the band is unaffected when the crystal is irradiated

---

[35] Krüger, *ibid.*, 1938, **33**, 265.
[36] Freed and Thode, *J. Chem. Phys.*, 1939, **7**, 85.
[37] See Meranda, *Diss. Abs.*, 1957, **17**, 249.

with visible light.[38] The visible band in metal solutions has properties which are opposite to these in each case (section 2).

Ammonium-metal Theory.—The term is misleading for dilute solutions. Certainly if a solution contained ammonium ions and sodium ions there might be a competition between these positive centres for the electrons, provided that one postulated the "expanded-metal" model mentioned above. However, if ammonium salts are added to metal–ammonia solutions, hydrogen is rapidly evolved and the solutions are decolourised. In other words, conditions which favour the formation of NH_4 radicals also favour hydrogen evolution, probably because these neutral radicals provide a low-energy pathway for decomposition which does not require the transient formation of hydrogen atoms:[23]

$$e + NH_4^+ \rightleftharpoons NH_4; \quad 2NH_4 \rightarrow 2NH_3 + H_2 \quad \ldots\ldots\ldots (2)$$

If NH_4 formation were important in solutions containing no added ammonium salt[26] there would have to be an equal concentration of amide ion in the solutions. The absence of any absorption in the 340 mμ region in these solutions means that, in fact, the concentration of amide ion is negligibly small, since the amide ion has an intense absorption band in this region.[30]

Pitzer,[39] in an attempt to explain the results of nuclear resonance studies,[26] has postulated the formation of the ion NH_3^-, in which the unpaired-electron orbitals are "3*s*-like for nitrogen with the outer node at the N–H bond radius". He goes on to show that this would explain both the large shift for nitrogen and the small shift for hydrogen. Since this is not a bonding orbital for ammonia molecules in the gas phase the only way in which it can become one in solution is by polarisation of the surrounding medium. If this is complete, then the NH_3^- ion will presumably be solvated by an oriented shell of solvent molecules, and the model becomes very similar to the cavity model, with an extra ammonia molecule at the centre of the cavity. It is not clear from the text whether or not this is the intended model.[39] The alternative would be a model in which the electron moves amongst solvent molecules so rapidly that orientational polarisation cannot occur. Such a state of affairs is probably similar to the ionized state envisaged by Becker *et al.*[3] This "conduction electron" model is probably incompatible with spectroscopic results since the very well-defined infrared band must be associated with these electrons and it is hard to see how such a precise transition could be associated with a mobile electron of this sort. Also one might have expected high conductivity in frozen solutions, but dilute solid solutions seem to be non-conducting.[37]

Detailed Descriptions of the Expanded-metal and the Cavity Model.—Becker *et al.*[3] made two suggestions about the expanded-metal postulate.

---

[38] Compton, *Phys. Rev.*, 1957, **107,** 1271.
[39] Pitzer, *J. Chem. Phys.*, 1958, **29,** 453.

When discussing spectra, they used a model in which the electron is constrained to move on the surface of a sphere defined by the hydrogen atoms of the first layer of oriented ammonia molecules surrounding the cation. They suggested that the transition is one which involves a change in angular momentum and showed that the infrared band is predicted satisfactorily on such a model. However, when discussing energies, they made use of a different model, in which a hydrogen-like 1*s* function is used such that it has a maximum at 3·5 Å. McConnell and Holm[26] postulated a very diffuse orbital and compared the system with that of silicon containing traces of phosphorus. By loss of one electron to form P^+, the phosphorus is able to replace silicon and the unpaired electron is then held in an orbital centred on the positive charge, but extending a considerable distance from the phosphorus atom.

The simplest description of the cavity model is that of an electron (or an electron-pair) in a spherical box.[40,14] The lowest energy level in such a box is $h^2/8mr_0^2$. In addition to this there are terms due to the polarisation of the dielectric medium by the electron, including orientation of permanent dipoles around the cavity, and for the surface-tension energy. Lipscomb[14] developed this model in order to account for the volume expansion mentioned in section 1. He estimated from the experimental data that cavities of radius 3·2 Å were required, and his detailed calculations gave a value of about 4·8 Å for the radius of the spherical box.

Stairs[41] modified this theory by assuming a finite depth for the box: he assumed a value of 3·2 Å for the radius and calculated values for the energy of the system. A somewhat different approach was made by Platzman[42] who used Platzman and Frank's model[43] which was developed to explain the absorption spectra of halide ions in solution. In this model the electron moves in a discrete, centrosymmetric orbital defined by the potential field of the polarised solvent molecules around the electron. The medium is treated as a continuous dielectric and the wave function is a 1*s* function similar to that suggested by Becker *et al.* for the "expanded-metal" model.[3] He suggested[42] that the different bands observed in various solutions are all part of a series of transitions of the electron in this potential well, but the considerations given in section 1 show that this theory is untenable. A very similar discussion has recently been presented by Jortner[44] who estimated a value of 3·6 Å for the cavity radius, assuming four solvent molecules around the cavity. Hence, he calculated $h\nu = 1{\cdot}1$ ev for the $2p \leftarrow 1s$ transition. This value should be compared with the experimental result of 0·8 ev.

Lipscomb concluded that a further attraction potential was required and suggested that interactions between the electrons and the protons of the oriented polarised solvent molecules might be responsible for this dis-

[40] Hill, *ibid.*, 1948, **16**, 394.
[41] Stairs, *ibid.*, 1957, **27**, 1431.
[42] Platzman, unpublished results, quoted in footnote to p. 423 of ref. 43.
[43] Platzman and Frank, *Z. Physik*, 1954, **138**, 411.
[44] Jortner, *J. Chem. Phys.*, 1957, **27**, 823.

crepancy. Kaplan and Kittel[45] have developed this idea and presented a model in which the unpaired electrons exist entirely in delocalised molecular orbitals on all of the protons which define the cavities. The N–H bonds are considered to be partially ionic, thus permitting the electron to occupy the 1*s* level, though higher levels are also considered. This model, which was based on the highly successful model for *F*-centres proposed by Kip *et al.*,[46] was used to explain the results of electron spin resonance studies.[21] One aspect of this work is that the authors assumed that the electrons occupy cavities which are already present in the liquid rather than cavities which are built up around the electrons in the same way as ions become solvated. They considered the line-width of the electron spin resonance spectra and assumed that only the protons contribute to this by hyperfine interactions. Their result is of the right order of magnitude only if they take into account the narrowing effect caused by rotation of the ammonia molecules, the value for the width estimated when this motion is neglected being 13 ξ gauss, where ξ is a measure of the effective *s* character of the molecular orbital on hydrogen. In view of the many approximations involved, the numerical results can only be taken to mean that the model is reasonable for mobile solutions. The experimental result of 3·5 gauss for $\triangle H_{\mathrm{MS}}$ for rigid solutions[23] is appreciably less than the predicted value, however, unless ξ is very much less than unity, which seems unlikely.

3. Discussion

The various alternative models outlined in section 2 are based upon well-authenticated analogues in the solid state, and it is helpful to make certain comparisons. In the case of phosphorus-doped silicon mentioned above, the electron is trapped at the cation centre because there is no alternative centre of any binding power in the crystal. However, in an alkali-halide crystal the trap is an anion vacancy rather than a cation. In solution one can say that the electron can choose between solvated cations and the potential wells formed by oriented solvent molecules which can be formed in bulk solvent as the result of polarisation by the electron. Both alternatives seem reasonable. The mathematical descriptions outlined above have been used, together with a variety of others, to describe colour centres in solids, with varying success. The results of electron spin resonance and double resonance studies on *F*-centres suggest that those models in which the orbital for the unpaired electron is considered to be diffusely spread over a large volume of solid are unacceptable.[47,48] The same argument may well be true for solutions.

Concentrated Solutions.—The isolation of solids such as $Ca(NH_3)_6$, which have all the properties of a metal, suggest that the expanded-metal theory must be substantially correct for concentrated solutions. That is,

---

[45] Kaplan and Kittel, *ibid.*, 1953, **21**, 1429.
[46] Kip, Kittel, Levy, and Portis, *Phys. Rev.*, 1953, **91**, 1066.
[47] Wertz, Auzins, Weeks, and Silskee, *ibid.*, 1957, **107**, 1535.
[48] Feher, *ibid.*, 1957, **105**, 1122.

that the weakly held valency electrons bind together units consisting of metal ion and about six solvent molecules oriented around them. Pitzer has given an interesting treatment of these solutions and has shown how this model may be used to explain most of the known properties including the phenomenon of phase separation in concentrated solutions.[49]

In this way the properties of concentrated solutions are at least qualitatively explained. The marked volume changes are a natural outcome: just as when sodium ions become sodium metal there is an apparent radius increase of about 1·2 Å for each ion, so when solvated sodium ions [say, $Na(NH_3)_6^+$] become "expanded metal" made up of $Na(NH_3)_6$ units, an apparent increase in radius of 0·9 Å would account for the experimentally observed expansion.

Medium Solutions.—In this range (1M—0·05M), the solute valency electrons remain almost completely paired, but the metallic properties of concentrated solutions give way to salt-like properties. The "expanded-metal" theory gives a picture in which dimer units predominate (see Figure). The conductivity falls rapidly as the average distance between dimers becomes too great for effective electron tunnelling, but the change in paramagnetism is small since dissociation into monomer units or metal ions and electrons is still unimportant.

This theory adequately explains the results of *X*-ray scattering studies,[32] but, if Schmidt's conclusions are correct, the cavity theory does not. The latter theory tells us that on dilution the concentrated solutions break down to give simple solvated sodium ions together with electron-pairs in separate solvent cavities (e_2 cavities).

The electronic absorption band in the 15,000 cm.$^{-1}$ region must be ascribed to dimer units if the expanded-metal theory is correct. Becker *et al.* have estimated that this unit should absorb in the 7000 cm.$^{-1}$ region, but the model used is very crude, and the lack of agreement can hardly be used as an effective argument against the theory. If the e_2 cavity theory is correct, then the visible band must be caused by the excitation of one of the electrons to a higher level in the cavity.

Whilst this explanation may be satisfactory for solutions in ammonia, it is less so for solutions in solvents with very low dielectric constants. That is because in this concentration range the e_2 cavity theory is modelled upon a solution of a 1:2 electrolyte. Such electrolytes are generally only sparingly soluble even in ammonia, and when they dissolve ion-pair formation is extensive. In ammonia this does not necessarily mean that the ions are adjacent, but in solvents of very low dielectric constant the ions are probably solvated as dipoles except in very dilute solutions.[11,50] This phenomenon, which will be described as dipolar contact, has been

[49] Pitzer, *J. Amer. Chem. Soc.*, 1958, **80**, 5046.
[50] Hughes, Ingold, Patai, and Pocker, *J.*, 1957, 1206.

detected by spectrophotometry for salts such as tetra-n-butylammonium iodide even with concentrations as small as 10^{-4}M.[51] It is probable, therefore, that in ethers dipolar contact would be almost complete for 1:2 electrolytes. As Kraus has pointed out,[2] one cannot picture such ion-pair formation in the usual way for metal solutions: it is quite impossible to construct a solvated-dipole model from sodium ions and electron-pairs. One is forced to conclude that under these conditions the electrons will move in an orbital centred on the sodium ion. If we go further and postulate that the equilibrium

$$\mathrm{Na^{+}(solv.)} + \mathrm{Na^{-}(solv.)} \rightleftharpoons \mathrm{2Na(solv.)} \quad \ldots\ldots\ldots \quad (3)$$

lies well to the right, then we have returned to the "expanded-metal" model for these solutions.

In that case, the band at 15,000 cm.$^{-1}$ found in metal–ether solutions must be ascribed to the dimer, and it is a logical, though not compelling, extrapolation to suggest that the band in this region found for medium solutions in ammonia is likewise due to "expanded-metal" dimer.[52]

Dilute Solutions.—For solutions in ammonia, this is the region in which electron-pair units break up to give single electron species. For solutions in ethers this does not occur and for solutions in amines it may or may not occur, depending upon conditions. We will examine this process for ammonia solutions in detail.

The picture we have to adopt for the "expanded-metal" theory is that, on dilution, dimers dissociate to give paramagnetic monomer units. While this process, symbolised in the Figure, accounts qualitatively for the magnetic phenomena, it does not explain the great increase in electrical conductivity on dilution. Becker *et al.* overcame this difficulty by postulating equilibrium (4)

$$\mathrm{Monomer} \rightleftharpoons \mathrm{Na^{+}(solv.)} + \mathrm{e} \quad \ldots\ldots\ldots \quad (4)$$

They compared this dissociation with that of a weak electrolyte, and suggested that the electron " becomes associated with other protons of bulk solvent ammonia molecules". It is not clear in what state these "free" electrons are supposed to exist but the authors do not mean to imply that the electron is in a cavity of oriented solvent molecules. Indeed, they consider that the cavity theory is fraught with many shortcomings, and reject it entirely.[3] At one stage in their calculations they assume that the electron has direct access to the entire volume of the solution.

Good evidence for the presence of this monomer unit in small concentration in concentrated and medium solutions comes from the shift in the ^{23}Na nuclear resonance spectrum: indeed it would be very hard to explain this shift in any other way. However, although this result shows

---

[51] Griffiths and Symons, unpublished results.

[52] Symons, *J. Chem. Phys.*, 1959, **30.**

that the monomer unit can exist in metal solutions, it does *not* prove that the unpaired electrons in dilute solutions are bound in this way rather than in cavities constructed of oriented solvent molecules (e_1 cavities).

More information can be obtained from a consideration of the spectra of dilute solutions in ammonia. In order to explain adequately the conductivity of dilute sodium solutions, Kraus has estimated a dissociation constant of 0·05 for the "ion pairs" at —33°.[2] This is about the same as the value estimated from magnetic data by Becker *et al.* for the dissociation of monomer.[3] The latter authors suggest that the infrared band found in dilute solutions is due to excitation of the unpaired electrons to a higher level around the sodium ions. The important feature of this argument is that the monomer unit is responsible for the colour. A calculation using the equilibrium constants quoted[3] shows that, when the overall concentration of metal is less than 10^{-3}M, the concentration of monomer is negligible compared with that of "free" electrons. For example, for an overall concentration of 10^{-4}M, the concentration of monomer is about 10^{-7}M.[23] Nevertheless, such a solution is still blue and, since the molar extinction coefficient at 6700 cm.$^{-1}$ is about 4×10^4, the optical density of such a solution in a 1 cm. cell would be 4 at the peak. The oscillator strength of this band is[23] about 0·7 if one assumes that *all* the unpaired electrons are responsible for the absorption: the very small amount of monomer supposed to be present in these solutions could not possibly be the cause of this band, and it would be necessary to postulate that practically all the electrons were still bound to sodium ions before such a situation could be entertained. In other words, one would have to reject the value of 0·05 for the dissociation constant and the negligibly small concentration of "free" electrons would have to have extremely high mobilities to account for the conductivity of these solutions.

Against this conclusion is the definite decrease on dilution in the value of P_{Na} deduced from the Knight shift for ^{23}Na.[26] Also the results from electron spin resonance studies on rigid glasses are not in accord with this possibility. If most of the paramagnetic centres are monomer units it is hard to understand why the spectrum is devoid of hyperfine structure.[23] The spectrum was recorded as the first derivative of the absorption curve and would be very sensitive to the presence of poorly resolved hyperfine lines. McConnell and Holm's values[26] of P_{Na} and $P_{Na}{}^{\circ}$ being used, it can be shown that splitting between outermost lines of the quartet expected for ^{23}Na would be about 5 gauss. Interaction with neighbouring magnetic nuclei (^{1}H and ^{14}N) could broaden these four lines beyond the point of resolution, but it is hard to see how a single symmetrical line of width 3 gauss could result. Indeed, since this quartet is clearly resolved for fluid solutions containing $Ph_2CO^-Na^+$, one might expect to have detected a quartet in fluid solutions of sodium in ammonia.

There is another argument against the monomer theory. The addition of a sodium salt to a dilute solution of sodium in ammonia should have little effect upon monomer units and, if the infrared band were due to electronic transitions of the monomer, then the only change expected would be a slight shift or broadening. On the other hand, if the band were due to excitation of electrons in solvent cavities then excess of sodium ion could shift the equilibrium depicted in Fig. 2 to favour monomer, and hence one might hope to observe a new band characteristic of the monomer. When sodium iodide is added, a new band is observed in the 12,500 cm.$^{-1}$ region in addition to the 6700 cm.$^{-1}$ band.[23] This band is therefore tentatively assigned to monomer.

The band at 15,000 cm.$^{-1}$ has already been assigned to dimer units. To check the reasonableness of these suggestions one can compare these spectra with the well-established spectra of alkali-metal atoms and molecules.[23] The atoms have a doublet with very small separation in the 14,000 cm.$^{-1}$ region ($P \leftarrow S$) and the molecules have two bands, one on either side of this (${}^1\Sigma_u{}^+ \leftarrow {}^1\Sigma_g{}^+$ and ${}^1\Pi_u \leftarrow {}^1\Sigma_g{}^+$). There is a trend to lower energies on going from sodium to cæsium for all bands, and the separation between the two bands for the molecules decreases. For example, the bands for K and K_2 are at 13,000 cm.$^{-1}$ (average) and 11,671 and 15,370 cm.$^{-1}$ respectively. The allocation for the solution bands, therefore, seems reasonable except that one might have expected a doublet for the dimer. However, the 15,000 cm.$^{-1}$ band is broad and asymmetric and may well be both bands. It would not seem reasonable to assign the 6700 cm.$^{-1}$ band to monomer and the 15,000 cm.$^{-1}$ band to dimer if this analogy is good.

These considerations lead to the conclusion that the blue paramagnetic unit in dilute solutions is an electron in a solvent cavity and not the "expanded-metal" monomer.[52] This being combined with conclusions drawn in the previous section, it appears that of the four possible units (expanded-metal dimer and monomer; e_2 and e_1 cavities) only two, expanded-metal dimers and e_1 cavities, need be considered as major components.[52] There is good evidence for the existence of monomer units but these do not seem to be major components under any conditions.

No good evidence for e_2 cavities has been found. It has been postulated that the absorption band in the visible region was due to excitation of electrons in e_2 cavities.[24] It was mentioned in section 2 that these units are comparable with *F′* centres in alkali halide crystals. However, the band characterising *F′* centres is of lower energy than the *F* centre band and, by analogy, one might predict that the band associated with e_2 cavities would be of *lower* energy than that due to single electrons in similar solvent cavities. It is hard to see why the energy of the e_2 transition should be more than double that of the e_1 transition.

Consequences.—This hybrid model should be examined in the light of those properties not so far considered.

The large volume increment found for dilute solutions is accommodated more satisfactorily than by the "expanded-metal" monomer theory, Lipscomb's arguments[14] are not invalidated.

The Knight shift for ^{23}Na nuclei are satisfactorily accommodated. Although the concentration of monomer units is always small, it is quite sufficient to account for the shifts reported: the only modification required is that the orbitals for the unpaired electron must be somewhat less diffuse than postulated by McConnell and Holm.[26] The lack of shift for protons is a puzzling feature, whatever model is adopted. One definite conclusion is that Kaplan and Kittel's detailed picture cannot be correct: that is, the unpaired electron does not spend its time moving in *s* orbitals on the protons of the cavity. One can equally well reject the mathematical description given by Becker *et al.*[3] when discussing spectra.

Absence of a Knight shift for protons does not mean that protons and electrons do not interact. The shift expected for normal dipolar interaction is to high fields, and therefore opposite to the shift caused by hyperfine contact interaction. If these effects are comparable, then no shift would be observed.[52] Just this sort of cancellation was found by Phillips, Looney, and Ikeda for the effect of paramagnetic salts on the hydroxyl proton resonance of certain alcohols.[53]

The large Knight shift for nitrogen is also hard to understand on any of the models described. The explanation given by Pitzer[39] is satisfactory provided that one postulates normal solvation for NH_3^-, but the major bonding forces must still be the same as for the cavity model, and a possible alternative explanation would be that the electrons move, in part, around those oriented solvent molecules which define the cavities, in orbitals of the type postulated by Pitzer.[39] The net effect would then be similar to that expected for NH_3^-, and the model would resemble that for *F* centres in alkali-halide crystals.[46]

4. Future developments

Most of the reasoning given in section 3 is based upon magnetic and spectrophotometric data, and many of the postulates made could be tested by applying these techniques, simultaneously, to a variety of solutions. Electron spin double resonance[48] might well solve many problems if applied to frozen glasses of various concentrations, and magnetic studies of photolysed glasses in which the 15,000 cm.$^{-1}$ band has been bleached would be of great interest. The effect of added salts on the conductivity would be worth investigating: if our tentative conclusions are correct there should be a decrease in conductivity with increase in concentration of added salt.

In conclusion, brief reference will be made to the postulate that the first excited state of solvated iodide ions may be compared with an electron in a cavity having an iodine atom at its centre.[54] The radius of the

---

[53] Phillips, Looney, and Ikeda, *ibid.*, 1957, **27**, 1435.

[54] Smith and Symons, *Trans. Faraday Soc.*, 1958, **54**, 339, 346.

solvent shell will not be precisely that expected for an e_1 cavity in the given solvent since it is predetermined by the size of the iodide ion. Nevertheless, it should provide a potential well capable of binding the electron, and the fact that an excited state exists for solvated iodide ions means that such preformed cavities can retain electrons. Since the formation of the cavity in the first instance is primarily a function of the negative charge, this means, at least, that the e_1 cavity model is reasonable.

Of the two models proposed for this excited state, the square-well model[54] seems to fit the data better than the hydrogen atom-like *s*-orbital model.[43] However, it is most probable that neither model does justice to the problem, and the same is true of the simplified description of e_1 cavities.[41,44] These mathematical descriptions are, however, fairly simple, and provided that the experimental data are reasonably well explained, they are of considerable utility.

Thanks are offered to Dr. H. C. Clark, Dr. W. Doyle, and Dr. G. W. A. Fowles for enjoyable discussion.