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I. Pressure Effects in Metal-Ammonia Solutions
II. Effect of Pressure and Metal Concentration on Magnetic Properties of Metal-Ammonia Solutions

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PRESSURE EFFECTS IN METAL–AMMONIA SOLUTIONS*

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A study of the pressure and temperature variation of the equilibrium constant or the molar volume of a system can be used to obtain an insight into the nature of the species present. A detailed description of two experiments (compressibility and optical measurements) is presented to illustrate the techniques and operating principles employed in the high-pressure study of metal–ammonia solutions. The results of (1) measurements of the isothermal compressibility of K– and KI–NH_3 solutions, (2) an optical study of the reaction of solvated electrons with ammonia, (3) the absorption spectrum of dilute K– and KI–NH_3 solutions, (4) electrical conductivity experiments, (5) reflectivity measurements, (6) experiments on the miscibility gap, and (7) studies of the reaction of the solvated electron in water–ammonia mixtures are used to discuss the nature of metal–ammonia solutions.

THE temperature dependence of the properties of metal–ammonia solutions[1] in a relatively restricted temperature interval is well known. In contrast, little has been reported on the pressure dependence of the properties of the solutions. In principle, however, pressure dependences should give as valuable information as do temperature dependences; compare, for example, the temperature- and pressure-dependence of the equilibrium constant, K, and the rate constant, k, of chemical reactions (equations 1 to 4),

$$\mathrm{d}(\ln K)/\mathrm{d}T = \Delta H/RT^2 \tag{1}$$

$$\mathrm{d}(\ln K)/\mathrm{d}p = Q - \Delta V/RT \tag{2}$$

$$\mathrm{d}(\ln k)/\mathrm{d}T = \Delta H^{\ddagger}/RT^2 \tag{3}$$

$$\mathrm{d}(\ln k)/\mathrm{d}p = -\Delta V^{\ddagger}/RT \tag{4}$$

which yield the reaction and activation enthalpy (ΔH and $\Delta H^{\ddagger}$) and the reaction and activation volume (ΔV and $\Delta V^{\ddagger}$). The reaction and the activation volume are defined as the differences in volume between products or activated complex and the reactants. These quantities in general have the same significance as the reaction enthalpy and the activation enthalpy in chemical reactions.

The pressure dependence of the properties of the metal–ammonia solutions should be particularly pronounced in view of the large apparent volume of the solvated electron. With versatile high pressure equipment one should also be able to obtain data over a wider temperature range extending beyond the

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* A review based on the experimental work performed in collaboration with K. W. Böddeker, H. Kohrmann, G. Lang, K. Maurer, R. Olinger and R. Vogelsgesang.

critical point of ammonia, so that the solvated electrons can be studied even in a dense gaseous phase.

During the last four years we have investigated the more important properties of some metal–ammonia solutions under pressure. The techniques of modern high pressure research start at 5000 to 10000 atm, and extend to hundreds of thousands or even millions of atmospheres. Metal–ammonia solutions possess the highest pressure coefficients observed in condensed phases; accordingly pressures of at most 2000 atm are sufficient for most experiments. The experimental apparatus to achieve these pressures costs only a few hundred dollars, but the techniques still require some skill.

The high pressure experiments reported here involve the following areas of metal–ammonia chemistry: (1) isothermal compressibility; (2) chemical equilibria; (3) absorption spectrum; (4) electrical conductivity; (5) reflection spectrum; (6) miscibility gap; (7) magnetic properties; and (8) ammonia–water mixtures. In addition we have conducted some experiments on electrolyte solutions for comparison purposes.

In the interpretations of the experimental results we were guided by the following simple model. Unpaired solvated electrons (e^-_{sol}) exist in dilute solutions ($c < 0{\cdot}001$ mole/l.). At higher concentrations the electrons form pairs e^{2-}_{2sol}.

$$2e^-_{sol} \rightleftharpoons e^{2-}_{2sol} \qquad (5)$$

The diamagnetic pair e^{2-}_{2sol} might include cations to compensate for the electrostatic repulsion. With a further increase in concentration ($c > 0{\cdot}5$ mole/l.) the transition to the metallic state occurs.

$$\tfrac{1}{2}e^{2-}_{2sol} \rightleftharpoons e^-_{met} \qquad (6)$$

Magnetic data give evidence for equilibrium 5. Electric conductivity and reflectivity data give evidence for the transition 6, which, according to the theory, is interrelated to the miscibility gap.

In dilute solutions the electrons are thought to be trapped in a cavity, the size of which determines the position of the light absorption maximum[2]. The molar volume of the spin-paired and metallic electrons obtained from density measurements of medium to concentrated solutions is 60 to 90 ml[1–3]. Unfortunately, the molar volume of the unpaired solvated electron is not known because density measurements on the dilute solutions have not been carried out with the required precision. According to Ogg[4] the molar volume of electrons in the highly dilute metal solutions might be as high as 800 ml. Data obtained by Evers and his group[5] indicate that the molar volume is concentration dependent, going through a pronounced minimum at about 0·01 mole/l.; Gunn's results[6] on the other hand indicate that the volume in concentrated solutions is little changed from that in dilute solution.

The results of our experiments, in terms of this model, can be summarized as follows. The metal–ammonia solutions are more compressible than pure ammonia[7], and the absorption spectrum of the dilute solutions is shifted to the blue with increasing pressure[7, 8]. Both phenomena arise from a compression of the solvent structure associated with dissolved electrons. In concentrated solutions the increased compressibility may partly be caused by a shift of equilibrium 6 from the metallic to the non-metallic state since the latter requires less volume. Evidence for this shift is derived from the decrease in conductivity[9] and reflectivity[7]; in addition the displacement of the miscibility gap[10] to higher concentrations with increasing pressure also supports this suggestion. Equilibrium 5 is not affected by pressure[11], indicating equal volumes for the paramagnetic and diamagnetic species. However, other possible equilibria involving solvated electrons[12, 13] are strongly affected by pressure because of the high molar volume of the solvated electrons. Using the position of the near infra-red absorption band as a criterion, the volume of the solvated electron in water–ammonia mixtures increases with increasing ammonia content[14]. The mean lifetime of the electron increases exponentially with ammonia content in these mixtures. The results suggest a correlation between the molar volume of the solvated electron and its reactivity which has been confirmed by kinetic measurements under pressure.

EXPERIMENTAL EQUIPMENT

Two typical examples will suffice to demonstrate the operating principles of high pressure equipment applied to liquid ammonia work: the high pressure apparatus for (1) determining the isothermal compressibility of metal–ammonia solutions and (2) for the radiolytic formation and optical detection of solvated electrons[14] under pressure.

(1) Compressibility measurements[7]

Figure 1 shows the apparatus employed for the compressibility measurements. All essential parts are fabricated of stainless steel and, as far as possible, are electroplated with gold to decrease the rate of decomposition of the metal solutions. The autoclave is 320 mm long and has an outer diameter of 70 mm. The autoclave contains a piston (1) which is ground and fitted with two O-rings to provide for complete sealing, in the upper portion (10 mm diameter by 130 mm long). The upper end of the piston rod (2) extends through a 3 mm hole in the autoclave lid (3). A ferritic magnet (5) is attached to the end of this rod. The upper part of the autoclave is connected to the pressure generator and to the manometer which are filled with pentane as the pressure transmitting fluid. The lower part of the autoclave (20 mm in diameter by 80 mm long) is connected to the storage autoclaves containing the solution to be investigated and pure ammonia respectively in glass cylinders.

Connections are made with steel capillary tubing with conical ends screwed into corresponding conical bores. The storage autoclaves are maintained under a low overpressure to ensure fast and complete filling of the evacuated compression autoclave. By increasing the pressure in the upper chamber of the compression autoclave the piston moves downward and compresses the solution.

The displacement of the piston is followed with a differential transformer which surrounds the capillary (4) in which the ferrite magnet moves. The differential transformer consists of three coils; an alternating current (5 kHz) flows through the central primary coil. The voltage induced in the two outer secondary coils is rectified and is fed via a differential amplifier to a null

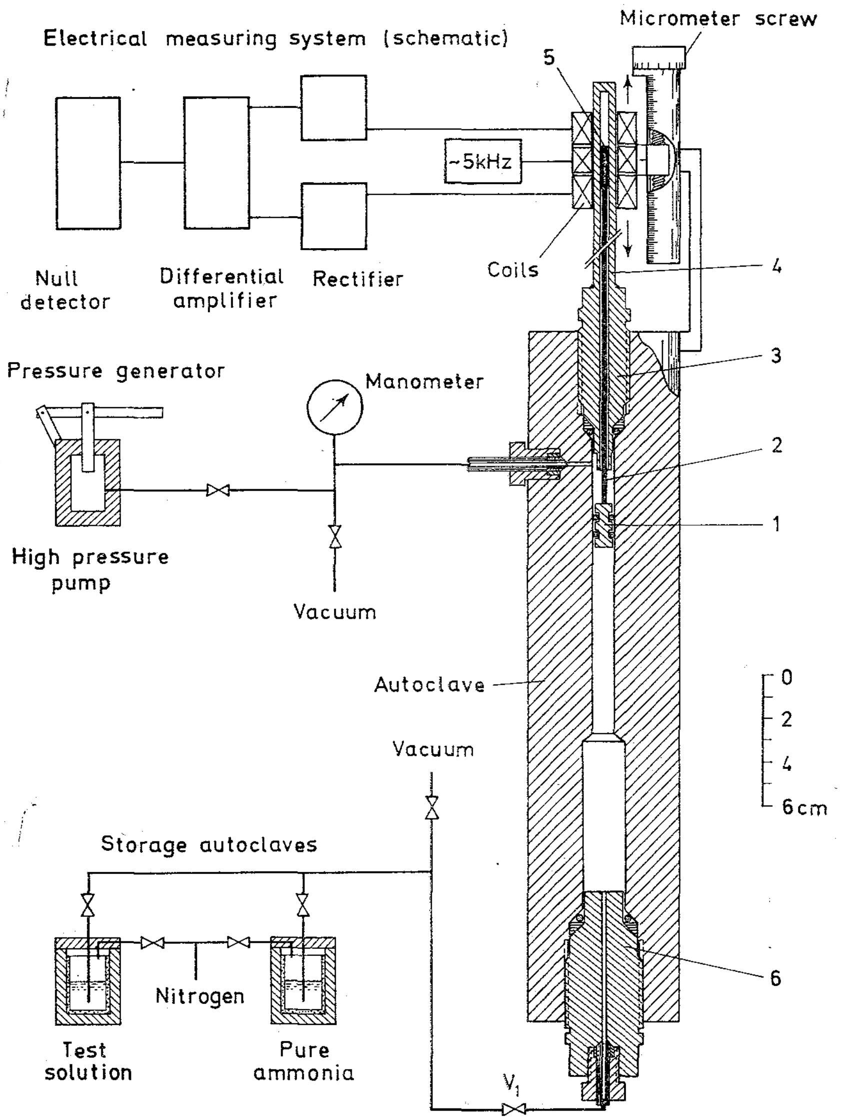

FIGURE 1. Experimental apparatus for compressibility measurements[7]

detector. As long as the ferrite magnet is exactly positioned in the centre of the differential transformer the null detector shows no deflection. A displacement of the magnet brought about by a compression of the solution results in a deflection of the null indicator which can be compensated for by a downward displacement of the transformer along a micrometer screw until a new null position is attained. The volume decrease of the solution, ΔV, obtained from the application of a pressure difference, Δp, can be obtained from the displacement of the piston. The isothermal compressibility, β, of the solution is given by equation 7, where V_0 is the inner volume of the autoclave (32·8 ml). The volume change of the autoclave due to expansion (about 0·1 per cent per 1 000 atm)

$$\beta = \Delta V/V_0 \Delta p \tag{7}$$

is negligible compared to the volume change of the solution (3 to 10 per cent per 1 000 atm). The apparatus can be used for pressures up to 4 000 atm. This equipment was calibrated with water at temperatures between 30° and 90°C, the measured compressibility being in good agreement with literature data.

(2) Optical measurements[15]

Figure 2 gives the experimental apparatus for optical studies of solvated electrons produced by pulse radiolysis under high pressure. The equipment consists of the high pressure section, the optical section, and the linear electron accelerator.

The optical section is a modified conventional spectrophotometer with lamp, lenses, monochromator and a fast responding light detector. The light detector is connected to a wideband oscilloscope which is triggered by the linear electron accelerator. The accelerator delivers up to 300 pulses per second of electrons (5 μsec, 10 MeV, 0·5 A) which induce the formation of solvated electrons in the solution contained in the high pressure cell. The high pressure optical cell is connected to the pressure generator and to the storage autoclave via capillary tubing. A compromise had to be made with respect to the wall thickness of the optical cell. The walls, on the one hand, had to be sufficiently thick to withstand a pressure of at least 1 000 atm, but they had to be transparent to the electrons from the accelerator. The range of 10 MeV electrons in steel is about 6 mm. To ensure even exposure of the solution to the electron beam, a wall thickness of only 2 mm was used. With this thickness and a twofold factor of safety the outer diameter of the cell must not exceed 14 mm. Since it is impossible to incorporate optical windows and capillaries into a steel tube of given diameter and wall thickness, only the 70 mm long centre portion (1) of the cell which is exposed to the electron beam has the critical dimensions. Two axially bored steel blocks (2) housing the window holders (3) were welded to both sides of this tube; conically formed sapphire windows (4) were ground into the holders. The window holders and washers (5) are tightened into the housings with hollow screws (6). The cell was tested at pressures up to 1 500 atm.

This apparatus is useful for photometric studies of the solutions of electrons with concentrations up to approximately 3×10^{-5} mole/l. that are easily produced by pulse radiolysis. For the study of metal–ammonia solutions with metal concentrations up to 3×10^{-2} mole/l. another similarly constructed autoclave[7] was used; however, the optical path length could be adjusted to between 20 and 0·1 mm. Other parts of the high pressure hardware used in these studies have been described elsewhere[9, 13].

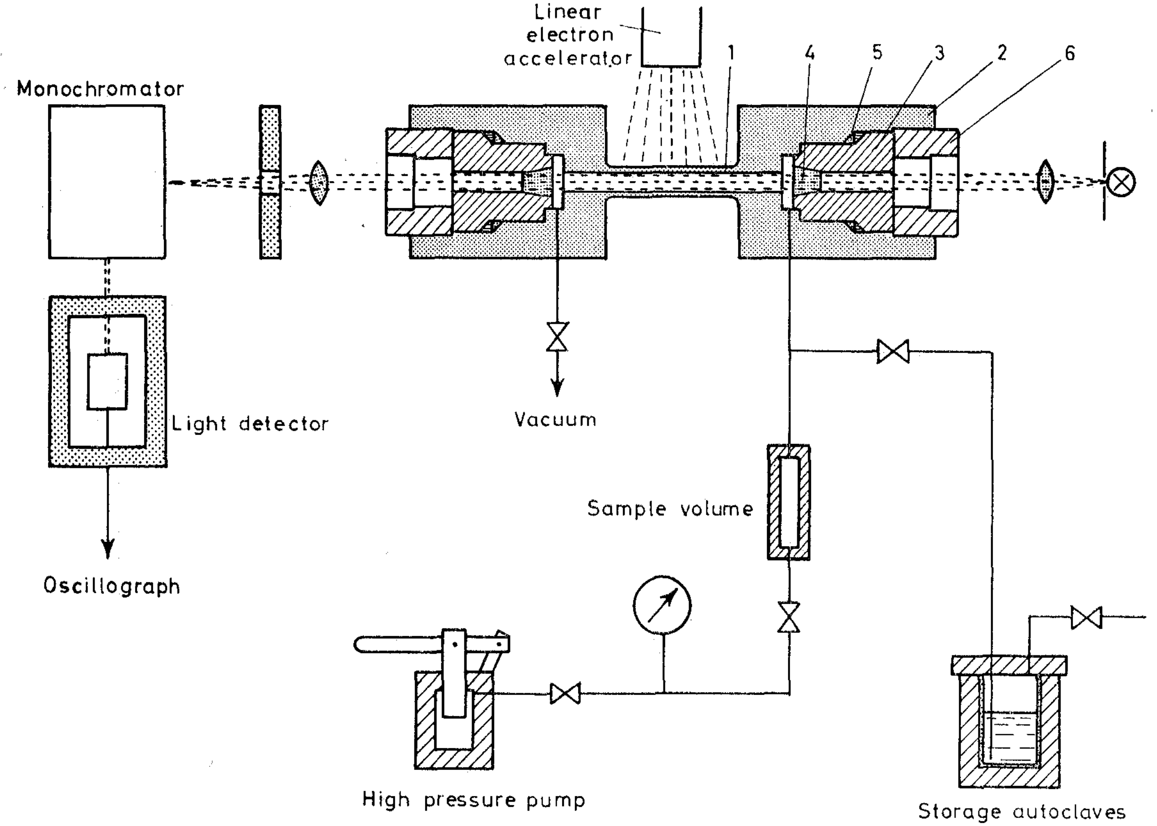

FIGURE 2. Experimental apparatus for the optical detection of solvated electrons produced by pulse radiolysis under pressure[15]

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

(1) Isothermal compressibility of potassium- and potassium iodide–ammonia solutions[7]

Figure 3 shows the compressibility of potassium–ammonia solutions and, for comparison, of potassium iodide–ammonia solutions at −30°C and 100–500 atm. The isothermal compressibility of pure ammonia, also at −30°C, is indicated by the broken line. Obviously the dissolved metal and the electrolyte have an adverse effect on the compressibility. The compressibility of the iodide solution decreases with increasing concentration, which is to be expected for 'normal' electrolytes in which the reorientation of the solvent molecules by the electrostatic field of the ions (electrostriction) gives rise to a more compact, i.e. less compressible, structure of the solvent. In the metal solution this effect of the cations is overcompensated by the volume expansion of the solvated electrons present which leads to an increased compressibility with increasing concentration. The trend of the isothermal compressibility with concentration is the same as that of the adiabatic compressibility measured by Maybury and Coulter[16]. However, the isothermal data are, as expected, higher (by about 60 per cent) than the adiabatic data.

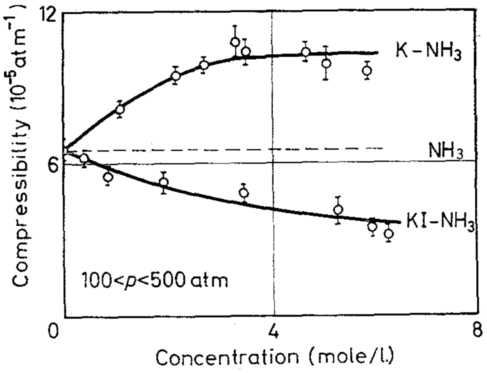

FIGURE 3. The isothermal compressibility of K–NH_3 and KI–NH_3 solutions determined at −30°C between 100 and 500 atm[7]

(2) Equilibrium reaction of solvated electrons with ammonia[12]

An equilibrium easily investigated using high pressure techniques is that of the reaction of solvated electrons with ammonia which leads to molecular hydrogen and amide ions

$$e^-_{sol} + NH_3 \rightleftharpoons \tfrac{1}{2}H_2 + NH^- \qquad (8)$$

According to general experience, the metal–ammonia solutions tend to decay completely, equilibrium 8 being displaced far to the right. However, Jolly and Kirschke[17] showed that the concentration of solvated electrons is still measurable with an equilibrium constant of ~70 (mole/l.)$^{1/2}$ and a reaction enthalpy of −16 kcal/mole. The reaction is exothermic as written.

Reaction 8 was studied by observing the absorption spectrum of a 0·23 mole/l. potassium amide–ammonia solution with and without added hydrogen (solution saturated at 100 atm) in the optical high pressure cell (path length, 4 mm); these experiments were conducted at static pressures of 200 to 1 100 atm and at temperatures of 23° to 147°C. The difference between the spectra of the two solutions shows the broad absorption spectrum characteristic of solvated electrons with a maximum at 1·6 to 1·8 μ (Figure 4). The intensity of this band increases with temperature and decreases with pressure. The equilibrium concentration, *C*, of solvated electrons as calculated from the intensity as a function of pressure for seven different temperatures is plotted in Figure 5. In these calculations it is assumed that the extinction coefficient for solvated electrons ($\epsilon = 48000$ l./mole-cm) is independent of temperature and pressure.

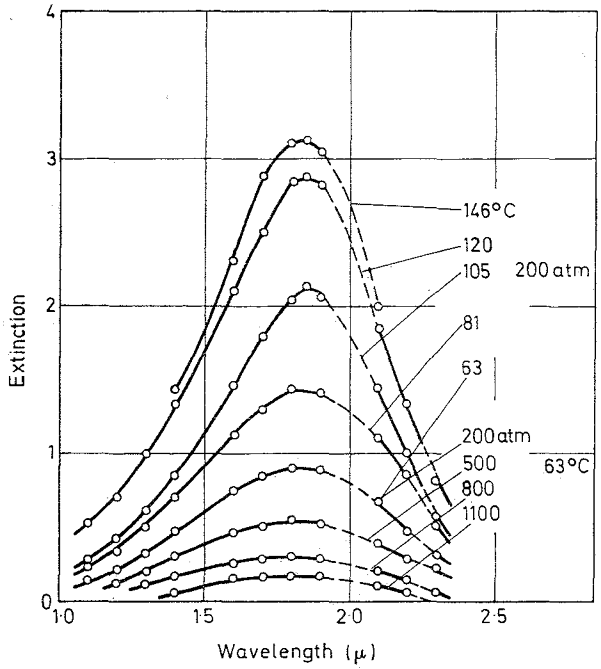

FIGURE 4. The absorption spectrum of solvated electrons in a 0·23 mole/l. KNH_2–NH_3 solution saturated under 100 atm with hydrogen at various pressures and temperatures[12]

Depending on the conditions, the equilibrium concentration of solvated electrons ranges between 5×10^{-7} and 2×10^{-4} mole/l., i.e. the concentration is so low that unpaired electrons predominate rather than spin-compensated electron pairs. From the temperature and pressure dependence of the equilibrium concentration (equations 1 and 2) a reaction enthalpy of -12 ± 1 kcal can be calculated using the data obtained between 23° and 63°C at 200 atm, which is somewhat less negative than the value reported by Jolly and Kirschke[17]. A reaction volume, ΔV, of -64 ± 3 ml is obtained from the data between 200 and 1 100 atm at 23°C. With increasing temperature and increasing pressures both ΔH and ΔV become less negative.

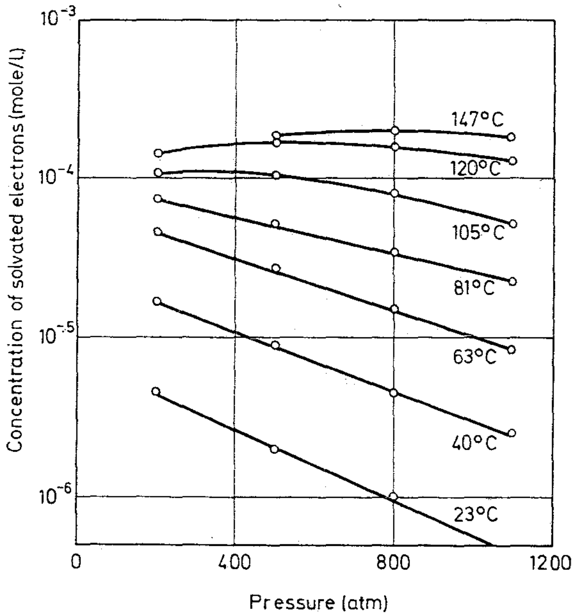

FIGURE 5. Pressure and temperature dependence of the equilibrium concentration of solvated electrons in a KNH_2–H_2–NH_3 mixture[12]. The concentrations correspond to those in Figure 4

The large reaction volume reflects the large molar volume of the solvated electron. From the reaction volume and the molar volume of the other species present the molar volume of the solvated electrons can be calculated as 98 ± 15 ml at 23°C, which, taking into consideration the thermal expansion (see below), can be reduced to about 75 ± 13 ml at −33°C. This value, within the limits of error, is the same as that obtained from density measurements on more concentrated solutions in which spin compensated electron pairs are predominant. So we conclude that solvated electrons in the spin compensated state and in the single state have about the same molar volume. A corroboration of the result using magnetic measurements will be given in a subsequent paper in this colloquium by Dr Böddeker[11].

(3) Absorption spectrum of dilute potassium- and potassium iodide-ammonia solutions[7,8]

The absorption spectrum of a dilute potassium–ammonia solution is shifted to shorter wavelengths with increasing pressure and, as has been known for some time[18], to longer wavelengths with increasing temperature. The experimental data are displayed in Figure 6 in which the position of the absorption maximum is plotted against the temperature and the pressure, respectively. According to the simple model of an electron-in-a-cavity with a square well potential the wavelength of maximum light absorption is proportional to the square of the cavity radius (equation 9).

$$\lambda_{\text{max.}} \propto R^2 \tag{9}$$

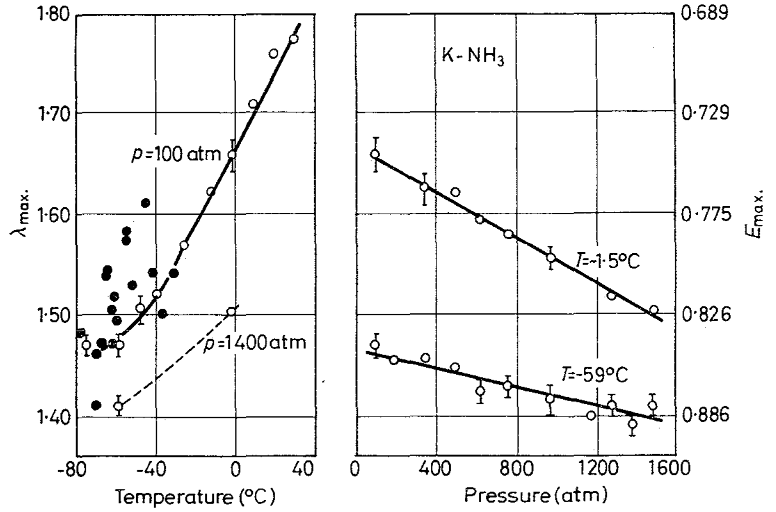

FIGURE 6. Position of the absorption maximum of solvated electrons in dilute K–NH_3 solutions as a function of pressure and temperature: ○ data from this laboratory[7], • data from the literature[18]

The more sophisticated models due to Jortner[2] lead to a more complex relationship but still show the same tendency. Thus the blue shift of the spectrum with increasing pressure and the red shift of the spectrum with increasing temperature can be interpreted in terms of a compression and a thermal expansion of the electron cavity.

Differentiation of equation 9 with respect to pressure and temperature, respectively, and replacement of the cavity radius R by the cube root of the cavity volume V leads to equations 10 and 11:

$$\alpha = \frac{\mathrm{d}V}{\mathrm{d}T \times V} = \frac{3}{2}\frac{\mathrm{d}\lambda}{\lambda \times \mathrm{d}T} \tag{10}$$

$$\beta = -\frac{\mathrm{d}V}{V \times \mathrm{d}p} = -\frac{3}{2} \times \frac{\mathrm{d}\lambda}{\lambda \times \mathrm{d}T_p} \tag{11}$$

where β and α are the coefficients of the isothermal compressibility and thermal expansion, respectively. Thus the shifts of the absorption band are a measure of the volume changes of solvated electrons. The numerical factor $\frac{1}{2}$ arises from the square well potential, and the factor 3 comes from the *cubic* co-efficients of compressibility and thermal expansion. Using these equations and the data in Figure 6 we obtain values for α and β of $(3{\cdot}4$ to $4{\cdot}1) \times 10^{-3}$ deg^{-1} and $(4{\cdot}4$ to $5{\cdot}9) \times 10^{-5}$ atm^{-1}, respectively, which are of the same magnitude as for pure ammonia ($1{\cdot}7 \times 10^{-3}$ deg^{-1}, $7{\cdot}5 \times 10^{-5}$ atm^{-1}). This coincidence of the α and β values for ammonia and for solvated electrons in ammonia, however, probably is accidental. The corresponding data for hydrated electrons and water do not agree.

The absorption spectra of the halide ions and of a number of other ions, like those of the solvated electrons, depend strongly on the solvent. The light absorption of these ions, according to the theory of Platzman and Frank[19] arises from a transition of an electron from the ion to the solvent molecules of the solvation shell (charge-transfer-to solvent: ctts). The radius of the solvation shell required determines the position of the absorption maximum (cf. equation 9). As with solvated electrons we may expect a blue shift of the spectrum with increasing pressure and a red shift with increasing temperature. The experimental results for iodide ions in Figure 7, and for amide ions (not shown) comply with these ideas and show that there is close parallelism in the optical behaviour of solvated electrons and ions possessing ctts-spectra.

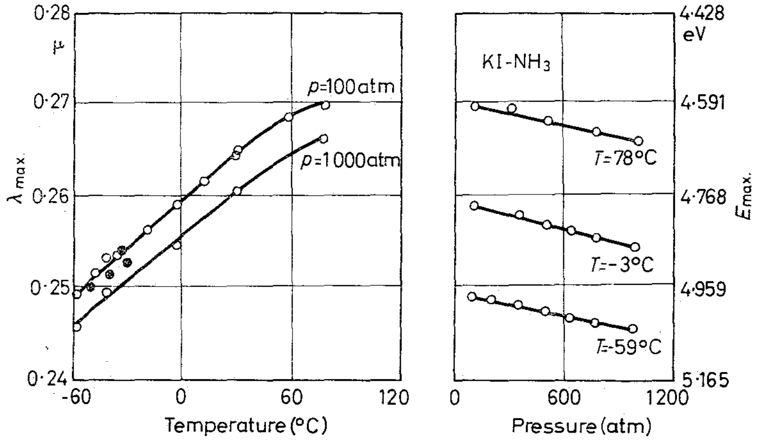

FIGURE 7. Position of the absorption maximum of iodide ions in dilute KI–NH_3 solutions at various pressures and temperatures: ○ data from this laboratory, • data from the literature[20]

(4) Electrical conductivity[9]

When pressure is applied to a solution of a strong electrolyte, the specific conductivity changes only slightly because the major effects more or less compensate each other; that is the increase in ion concentration arising from a compression of the solution is offset by a decrease of ion mobility due to the increased viscosity of the solvent. Potassium nitrate in ammonia is a typical strong electrolyte in this respect; up to 1 500 atm, only a small change in specific conductivity occurs (Figure 8)[21]. Potassium amide on the other hand shows a substantial increase in conductivity with pressure[21]. The latter behaviour is typical of weak electrolytes (the dissociation constant for $KNH_2 \rightleftharpoons K^+ + NH_2^-$ is given[22] as $K = 7{\cdot}3 \times 10^{-5}$) for which the dissociation constant increases with increasing pressure. Dissociation leads, because of electrostriction, to a volume decrease of the system ($\Delta V < 0$; cf. equation 2).

The conductivity of metal solutions shows rather complex behaviour when they are compressed. In dilute solutions ($c < 0{\cdot}5$ mole/l.) the conductivity changes only slightly with pressure (10 per cent decrease at 1 500 atm), but in the concentration range where the conductivity increases rapidly with concentration, i.e. 0·5 to 2 mole/l., the conductivity decreases markedly with

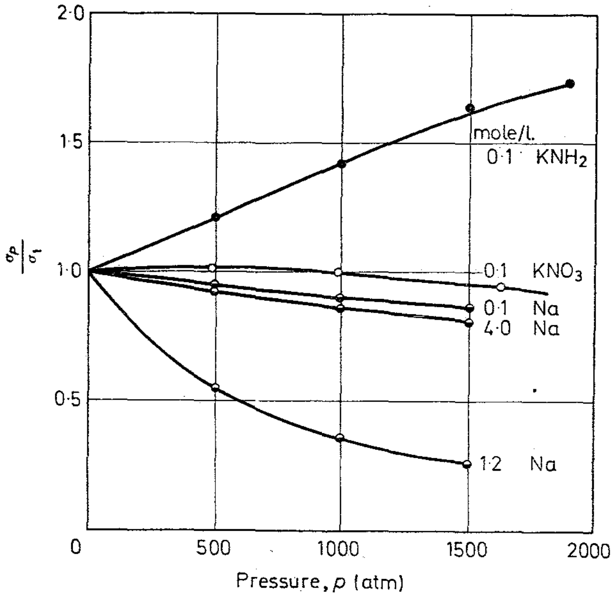

FIGURE 8. The change in specific conductivity with pressure of 0·1 mole/l. KNO_3 and KNH_2–NH_3 solutions[21] and of Na–NH_3 solutions at various concentrations[9]

increasing pressure (a factor of three at 1 500 atm). At higher metal concentrations an increase in pressure again yields only a small conductivity decrease. The data collected for sodium–ammonia solutions are displayed in Figure 9, where the pressure coefficient of the conductivity $k_p = \Delta\sigma/\sigma \times \Delta p$ is plotted against the concentration. The coefficient is negative for all concentrations and has a minimum at a concentration of about 1 mole/l. Comparison with the temperature coefficient[23] of the conductivity in Figure 9 reveals that pressure and temperature have adverse effects on the conductivity of the metal solutions. Evaluation of the data shows that the steep conductivity increase in the conductivity versus concentration diagram (or the nonmetal–metal transition described by equation 6) is shifted to smaller concentrations with increasing temperature and to higher concentrations with increasing pressure. That is, a solution of given concentration becomes more metallic with increasing temperature and less metallic with increasing pressure. Whereas the temperature dependence of the equilibrium expressed in equation 6 is known[24] and is understood on the basis of the Mott theory[25] of metallic transition, the pressure dependence of the equilibrium is surprising. One might expect that the increase of concentration as a result of the compression should make the solutions more metallic instead of less so. The results obtained can be explained on the basis of equation 6 if it is assumed that the dissolved metal in the metallic state occupies a larger volume than when it is in the nonmetallic state; and, therefore, the system, according to the principle of Brown and Le Chatelier, tries to compensate for the applied pressure by reverting to the nonmetallic state.

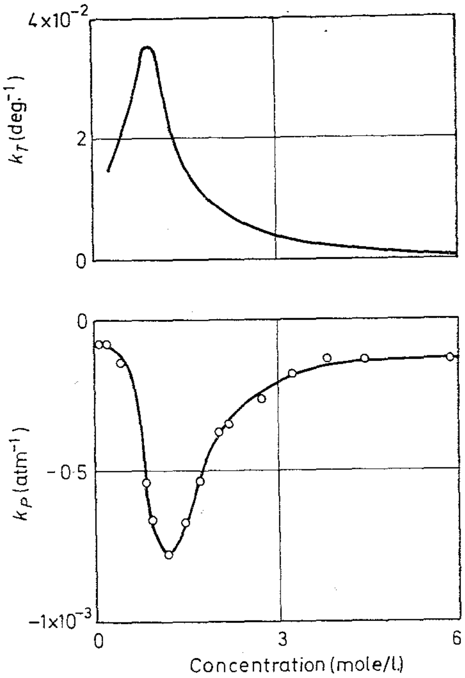

FIGURE 9. Pressure[9] and temperature[23] coefficients of the electrical conductivity of Na–NH_3 solutions, calculated from conductivity data at 1 and 500 atm (−40°C) and −34° and 50°C (1 atm)

(5) Reflectivity[7]

The bronze lustre of concentrated metal–ammonia solutions which agrees with their metallic behaviour is caused by the high reflectivity of these systems to red light. In agreement with data from the literature we find that the reflectivity (measured at an angle of nearly 90°) decreases with decreasing metal concentration[26, 27] and approaches the value for pure ammonia with increasing dilution. The concentration dependence of the reflectivity corresponds qualitatively to the theory which relates the reflectivity to the free electron concentration or to the electrical conductivity. Consequently we may expect the reflectivity to change with temperature and pressure in the same manner as does the conductivity. This expectation is borne out by the experiments which show an increase of reflectivity with temperature and a decrease with pressure. The temperature and pressure coefficients of the reflectivity are plotted versus concentration in Figure 10. The curves with maxima or minima around 1 mole/l., that is, in the concentration range of the nonmetal $\rightleftharpoons$ metal transition, parallel those of the conductivity and, like these, can be explained by the corresponding equilibrium.

(6) Miscibility gap[10]

According to the hypothesis of Mott[25] the miscibility gap of metal–ammonia solutions is closely related to the nonmetal $\rightleftharpoons$ metal transition. Since the

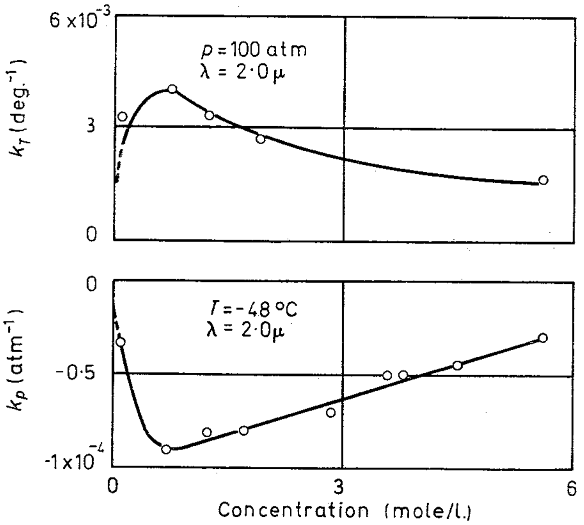

Figure 10. Pressure and temperature coefficients[7] of the reflectivity (wavelength 2 μ) o K–NH_3 solutions, calculated from experimental data at 100 and 1000 atm (−48°C) and at 0° and −48°C (100 atm)

position of this transition is shifted to higher concentrations by pressure the miscibility gap also should be shifted to higher concentrations with increasing pressure. This behaviour is, indeed, found in the results of experiments in which the pressure influence on the miscibility gap was investigated using conductivity measurements. Figure 11 shows the results of these experiments;

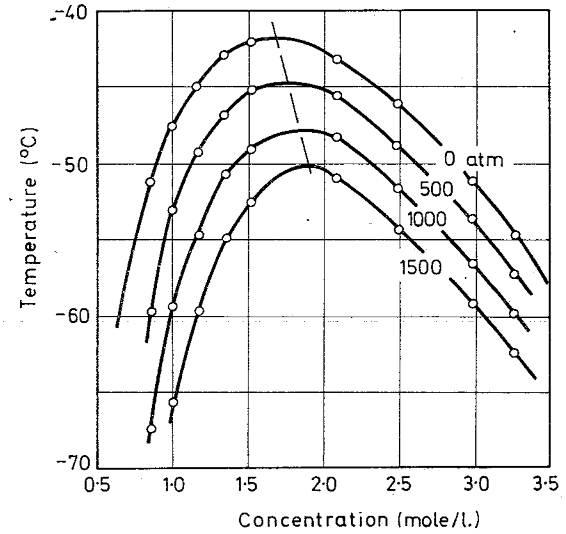

Figure 11. Influence of pressure on the miscibility gap of Na–NH_3 solutions[10]

the critical concentration of the miscibility gap increases with increasing pressure and the critical temperature decreases.

The change of critical temperature with pressure warrants further discussion. The thermodynamics of binary mixtures yields, for a miscibility gap[28] with upper consolate point, equation 12 as the relationship between the critical temperature, T_c, pressure, p, the molar volume, V, and concentration expressed as the mole fraction, x.

$$dT_c/dp \sim -d^2V/dx^2 \tag{12}$$

The molar volume is expressed as

$$V = x_1V_{01}+x_2V_{02}+\Delta V(x) \tag{13}$$

where V_{01} is the molar volume of the pure component 1 and $\Delta V(x)$ the volume change caused by mixing. Since dT_c/dp in our system is negative, d^2V/dx^2 must be positive. According to density measurements[29] $\Delta V(x)$ is positive at all concentrations. Therefore $\Delta V(x)/x$ or the apparent molar volume of the metal, $\Delta V(x)/x+V_0$, must increase with concentration in the concentration range of the miscibility gap. Thus the pressure shift of the critical temperature of the miscibility gap represents an independent proof of the hypothesis that the transition to the metallic state is connected with a volume increase of the system, as deduced earlier from the pressure dependences of the electrical conductivity and reflectivity.

(7) Solvated electrons in ammonia–water mixtures[14]

Because of its fast reaction with water, the solvated electron in ammonia–water mixtures cannot be studied by dissolving alkali metal. In this system solvated electrons can, however, very conveniently be produced by radiolysis. Preliminary results of some optical and kinetic studies of solvated electrons in ammonia–water mixtures will be outlined briefly.

(a) *Absorption spectrum*

The position of the electron absorption band shifts linearly with increasing ammonia content from the position in water (0·7 μ[1b,e]) to that in pure ammonia (1·7 μ). On the basis of equation 9 this means that the size of the solvent cavity associated with electrons increases with increasing ammonia content of the mixtures. The magnitude of the red and blue shifts of the spectra in the solvent mixtures which occurs with increasing temperature and pressure, respectively, lies between the corresponding shifts observed in the pure solvents.

(b) *Lifetime*

Due to the slow reaction 8 the lifetime of solvated electrons in pure ammonia is larger than 10^6 sec. In water it is less than 100 μsec[1b,e] because of the fast reaction with water, formally described by equation 14.

$$e^- + H_2O \rightleftharpoons \tfrac{1}{2}H_2 + OH^- \tag{14}$$

In ammonia–water mixtures the lifetime of solvated electrons increases essentially exponentially with increasing mole fraction of ammonia; e.g. in a

20 per cent water–80 per cent ammonia mixture we observe a lifetime of about 100 sec. Thus a fivefold dilution of the more reactive water species with relatively inert ammonia leads approximately to a millionfold decrease of the rate of reaction 14. Similar results were obtained by Dewald[30]. The rate constant of the reaction, $\varkappa$, is given by equation 15 according to transition state theory,

$$\varkappa = (kT/h) \exp(\Delta S^{\neq}/R) \exp(-\Delta H^{\neq}/RT) \tag{15}$$

where $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are entropy and energy of activation, respectively. The energy of activation of reaction 14 occurring in pure water is about 4 kcal/mole[1b,e]. For mixtures with an ammonia content between 20 and 80 mol-per cent energies of activation are 1 ± 3 kcal/mole. Thus the decrease in reaction rate with increasing ammonia content must be due to a decrease in activation entropy. Since the entropy is a function of volume in the sense that the entropy of a system increases when its volume increases, the reactivity of solvated electrons with water can be related to their molar volume. As the ammonia content of the mixtures increases, the volume associated with the solvated electron increases, the volume of activation becomes more negative, the entropy of activation becomes more negative, and the reaction rate decreases. As a consequence of this relationship we expect (equation 4) little change in the reaction rate with increasing pressure for the fast reaction of solvated electrons in water-rich mixtures (in which the electrons occupy a relatively small volume). A higher increase in the reaction rate with increasing pressure would be expected for the slower reaction of solvated electrons in the ammonia-rich mixtures, in which the electrons occupy a large volume. Indeed we find that there is no pressure influence[31] and the volume of activation is close to zero for the rate of reaction 14 in water, whereas in some preliminary experiments with ammonia–water mixtures the rate of disappearance of solvated electrons is accelerated two- to four-fold by a pressure increase of 1 000 atm yielding an activation volume of 17 to 35 ml/mole.

REFERENCES

[1] For recent reviews see:
  (a) G. Lepoutre and M. J. Sienco (Eds.), *Métal–Ammonia Solutions*. W. A. Benjamin: New York (1964).
  (b) R. F. Gould (Ed.), Advances in Chemistry Series No. 50, *Solvated Electron*, American Chemical Society: Washington, D.C. (1965).
  (c) J. Jander in *Chemie in nichtwässrigen ionisierenden Lösungsmitteln*, Vol. I, Part 1, G. Jander, H. Spandau and C. C. Addison (Eds.), Vieweg: Braunschweig (1966).
  (d) J. C. Thompson in *The Chemistry of Non-Aqueous Solvents*, Vol. II, J. J. Lagowski (Ed.), Academic Press: New York (1967).
  (e) U. Schindewolf, *Angew. Chemie*, **80**, 165 (1968); *Angew. Chem.* (*Internat. Ed.*), **7**, 190 (1968).

[2] J. Jortner, *J. Chem. Phys.* **30**, 839 (1959); *Radiation Res. Suppl.* **4**, 24 (1964).
J. Jortner, S. A. Rice and E. G. Wilson, p 222 in Ref. 1a.

[3] W. N. Lipscomb, *J. Chem. Phys.* **21**, 52 (1953).

[4] R. A. Ogg, *J. Am. Chem. Soc.* **68**, 155 (1946).

[5] C. W. Orgell, A. M. Filbert and E. C. Evers, p 67 in ref. 1a; W. H. Brendley and E. C. Evers, p 111 in ref. 1b.

[6] S. R. Gunn, p 76 in ref. 1a; *J. Chem. Phys.* **47**, 1174 (1967).

[7] R. Vogelsgesang, *Dissertation*, University of Karlsruhe (1969).

[8] U. Schindewolf, *Angew. Chem.* **79**, 585 (1967); *Angew. Chem.* (*Internat. Ed.*), **6**, 575 (1967).

[9] U. Schindewolf, K. W. Böddeker and R. Vogelsgesang, *Ber. Bunsenges. phys. Chem.* **70**, 1161 (1966).

[10] U. Schindewolf, G. Lang and K. W. Böddeker, *Z. phys. Chem.*, N.F., **66**, 86 (1969).

[11] K. W. Böddeker, G. Lang and U. Schindewolf, this volume, page 219.

[12] U. Schindewolf, R. Vogelsgesang and K. W. Böddeker, *Angew. Chem.* **79**, 1064 (1967); *Angew. Chem. (Internat. Ed.)*, **6**, 1076 (1967).

[13] K. W. Böddeker, G. Lang and U. Schindewolf, *Angew. Chem.* **81**, 118 (1969); *Angew. Chem. (Internat. Ed.)*, **8**, 138 (1969).

[14] U. Schindewolf and R. Olinger, Bunsentagung 1969, Frankfurt.

[15] U. Schindewolf, G. Lang and H. Kohrmann, *Chem. Ing. Tech.*, **41**, 830 (1969),

[16] R. H. Maybury and L. V. Coulter, *J. Chem. Phys.* **19**, 1326 (1951).

[17] E. J. Kirschke and W. J. Jolly, *Science*, **147**, 45 (1965); *Inorg. Chem.* **6**, 855 (1967).

[18] H. Blades and J. W. Hodgins, *Canad. J. Chem.* **33**, 411 (1955); R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.* **82**, 4472 (1960); M. Gold and W. L. Jolly, *Inorg. Chem.* **1**, 818 (1962).

[19] R. Platzman and J. Frank, *Z. Physik*, **138**, 411 (1954).

[20] M. Smith and M. C. R. Symons, *Trans. Faraday Soc.* **54**, 338, 346 (1958);
J. T. Nelson, R. E. Cuthrell and J. J. Lagowski, *J. Phys. Chem.* **70**, 1492 (1966).

[21] R. Vogelsgesang, *Thesis*, University of Karlsruhe (1965).

[22] W. W. Hawes, *J. Am. Chem. Soc.* **55**, 4422 (1933).

[23] C. A. Kraus, *J. Am. Chem. Soc.* **43**, 758 (1921);
C. A. Kraus and W. W. Lucasse, *J. Am. Chem. Soc.* **44**, 1946 (1922).

[24] R. Catterall, *J. Chem. Phys.* **43**, 2262 (1965).

[25] N. F. Mott, *Phil. Mag.* **6**, 287 (1961);
N. F. Mott *et al. Physica Status Solidi (Berlin)*, **21**, 343 (1967).

[26] T. A. Beckman and K. S. Pitzer, *J. Phys. Chem.* **65**, 1527 (1961).

[27] J. C. Thompson, unpublished results.

[28] R. Rehage, *Z. Naturforsch.* **10a**, 316 (1955);
R. Haase, *Thermodynamik der Mischphasen*, Springer: Berlin (1956); G. Schneider, *Ber. Bunsenges. phys. Chem.* **70**, 497 (1966).

[29] E. Huster, *Ann. Physik*, **33**, 477 (1938).

[30] R. Dewald and R. V. Tsina, *Chem. Commun.* 647 (1967).

[31] U. Schindewolf, H. Kohrmann and G. Lang, *Angew. Chem.* **81**, 496 (1969); *Angew. Chem. (Internat. Ed.)*, 8, 512 (1969).

GENERAL DISCUSSION

J. Jortner—About the transition to the metallic state, the first reaction is that when you compress the system you should get the effect in the direction opposite to what you found. However, the localized state, whether it is an electron, bielectron, or whatever, is very sensitive to medium change. You change the density by about 10 to 20 per cent under a few thousand atmospheres pressure. What increases in the first place is the repulsive part of the potential, so the electron is pressed more into the cavity. Now you can use both arguments, that you need a great deal of overlap between centres and obviously you need a higher density in order to achieve this critical overlap. It shows a very important thing to all the people interested in species in metal-ammonia. If these were proper M^- ions, this effect would not have been observed. It demonstrates what Cohen and Thompson recently wrote in *Advances in Physics*—that the transition to the metallic state occurs through some aggregates, ionic aggregates which still contain electron cavities.

M. J. Sienko—I should like to second what Dr Jortner said in terms of the importance of the clusters. I think we have here an effect on the medium which is the main reason for shifting the phase separation at high pressure. From the shift to higher concentration one would infer that the medium has been stabilized and the clusters are smaller. It would be interesting if you had a better definition of the shape of the coexistence curve at the high pressure, particularly at the top. From our study of phase separation (page 405) we have been led to deduce a strong dependence of shape on cluster formation. If, at high pressure, cluster formation is less probable, i.e. clusters are smaller, the forces leading to phase separation would be of shorter range. This would mean that the deviation from parabolic behaviour should set in further away from the critical temperature. The top of the coexistence curve would then be cubic instead of parabolic as it apparently is at low pressure.

U. Schindewolf—We probe the curve by conductivity measurements. At the top you get two coexisting solutions of about equal concentration which differ only very little in conductivity, so we had difficulty in obtaining the top of the curve precisely enough to distinguish between parabolic and cubic form.

J. C. Thompson—There is a fly in the ointment. As the ion gets bigger, the consolute temperature is depressed. Now Jortner is saying, I think correctly, that the solvated electron gets smaller, but that also had the effect of depressing the consolute temperature.

J. Jortner—What I was saying is that the charge is getting more localized because the medium background energy is getting more positive.

J. C. Thompson—What does that say with respect to the cavity size? It would seem to me that the cavity itself would be compressed to some extent. If larger species produce a lower consolute point, then there would seem to be a competition between a smaller species which lets the consolute point go up and the effect of the Mott transition that would push it down again.

J. Jortner—I think the dramatic effect is changing the background energy. You saw those curves that had high background energies: the cavity is a little bit more expanded. This will be a compensating effect, so I am not ready to commit myself. I still think the cavity will be a little bit compressed.

J. L. Dye—Leon Dorfman and I at Ohio State have recently determined the absorption spectrum of the solvated electron in ammonia–water mixtures as a function of composition. Both the peak position and the halfwidth show similar variations with composition. In the region of either pure solvent the variation is smaller than in the intermediate region.

W. L. Jolly—Most salts in liquid ammonia are weak electrolytes. Why would you expect a difference between the conductivity behaviour of KNH_2 and KNO_3 under pressure?

L. Onsager—KNO_3 is a stronger electrolyte so that a comparable change in the free energy of dissociation entails a smaller relative change of the conductivity.

A. Patterson—Have you tried KI or NaI by this pressure measurement technique? I think NaI is the strongest electrolyte one knows.

W. L. Jolly—Is the spectrum of the aqueous electron shifted with pressure? Would you expect it to be appreciable given the fact it has zero volume?

U. Schindewolf—There is a distinct blue shift of about 200 to 250 Å in the solvated electron spectrum in water at 1 000 atm pressure. (see ref. 31 above). The relative shift is about the same for electrons in ammonia as for electrons in water. Even if the cavity is zero, the charge distribution of the electron in water is finite. Compression of the solution may lead to a closer confinement of the charge sphere.

J. Jortner—In the continuum model when we say the cavity radius is zero we really mean that the void does not exceed the size of a single solvent molecule. We have here solvent molecules, say with a hard core of 1 Å, that will make a void for the electron. Smaller changes in the region of small R values will induce larger changes in the excitation energy. My picture of the electron in water is that the coordination number is four as in pure water or in ice. You can take the void size in water to be of the order of 1·5 Å. The $\mathrm{d}hD/\mathrm{d}R$ will be larger for water than for ammonia.

L. Onsager—There is a change in the dipole moment with decreasing distance between the different molecules. On the other hand, there may be some disorganization of the water with increasing pressure. However, the dielectric constants of the solid phases increase with increasing pressure.

R. Catterall—I would like to recall an observation by Compton (D. M. J. Compton, *Pulse Radiolysis*, ed. M. Ebert, 1965) on the pulse radiolysis of Na–NH_3 solutions. The i.r. band was bleached by the pulse and then recovered slowly. Have you pulsed metal–ammonia solutions?

J. L. Dye—I have. They do bleach but there is no recovery.

R. Catterall—The band widths taken from your published spectra are appreciably narrower for solvated electrons produced by the $NH_2^- + \frac{1}{2}H_2 \rightleftarrows e^-_{solv} + NH_3$ equilibrium (2 500 cm^{-1}) than for Na–NH_3 solutions (3 500 cm^{-1}). It looks like it is beyond experimental error. Do you have any comment?

U. Schindewolf—The electron concentration formed in the 'Jolly reaction' is rather low. For electron concentration from 10^{-7} to 10^{-5} mole/litre we need a window distance of at least 20 mm. Since ammonia has a very strong absorption around 1·5 and 2·1μ, the data there are apt not to be too good. If you are calculating with the spectral width, you should do it with the data on metal–ammonia solutions.

I would like to make one other comment on this work. We have gone up to a temperature of 150° to 160°, which means far above the critical point of the ammonia, so we can observe electrons in the supercritical state. It is a remarkable fact that the spectrum hardly changes when we go from liquid ammonia to supercritical ammonia. Dr Hart has found the same thing in water.

E. Hart—I would like to remark on the lifetime of the hydrated electron in connection with Dr Schindewolf's remarks about e$^-$ in ammonia–water mixtures. The millisecond that he mentions is actually the lifetime of the hydrated electron when it reacts with water

$$e^-_{aq} + H_2O \rightleftarrows H + OH^-$$

In other words, if we remove the hydroxide ion, then only the forward reaction with water occurs. The hydrated electron lives for tens of milliseconds in an alkaline solution where the reverse reaction regenerates it. What eliminates the electrons from water under these conditions is the diffusion-controlled reaction

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$$

In ammonia, this reaction does not take place. I don't know what the rate constant is for the forward reaction of the equilibrium

$$e^- + NH_3 \rightleftarrows H + NH_2^-$$

but I suggest that it is low and the lifetime of the electron is long because the reverse reaction that reforms it is relatively rapid. In pure alkaline solutions the theoretical half-life of e^-_{aq} is >1 sec at concentrations $<10^{-10}$ M e^-_{aq}.

U. Schindewolf—I do not know anything about the mechanism of the reaction we observed. Therefore I just noted lifetimes which describe the rate of disappearance of electrons no matter what the mechanism might be.

P. Chieux—The volume expansion in concentrated metal–ammonia solution is attributed to free electrons only. Do you have any comments on that?

U. Schindewolf—It probably also comes from the so-called spin-paired electrons. Reliable density measurements are made down to a concentration of about 10^{-2}, far below the metallic state, the state where you have predominently spin-paired electrons.

P. Chieux—Do you consider also the structural effect on the solvent due to the solvation shell around the ion?

U. Schindewolf—I believe it is taken care of. You mean the electrostriction due to the cations in the solution. Dr Jortner in his 1959 paper took care of the electrostriction effect and got a volume expansion of the order of 80 to 90 ml per mole of electrons.

J. Jortner—The lack of change in the absorption spectra of the electron in ammonia and water near the critical point should help assess the role of short range and long range interactions in the stabilization of the electron. You have changed the density tremendously and, of course, also the dielectric constant. Close by the molecular field will not be very much affected but what happens outside is very appreciably changed. The spectrum of iodide you showed may be the first indication that the stabilization of the excited state of the iodide ion is really pushed up when you start decreasing the density. The interesting question is how do the energy versus density curves look for the solvated electron. Here of course you have both the ground and excited levels moving up, so there is more compensation. The other interesting point is what is the critical density where electrons will still be localized in a polar medium.

U. Schindewolf—The aim of our experiments in the supercritical state was to get an answer to this. We did not get it because when we decreased the density of the solution potassium amide, which in reaction with hydrogen forms solvated electrons, was precipitated. It should be done, perhaps, by pulse radiolysis.

EFFECT OF PRESSURE AND METAL CONCENTRATION ON MAGNETIC PROPERTIES OF METAL–AMMONIA SOLUTIONS

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An apparatus for e.s.r.-spectroscopic investigations at elevated pressures is described and applied to several equilibria involving solvated electrons. Large pressure effects are found in the reactions with ammonia and with aromatic hydrocarbons, as well as in the nonmetal–metal transition region of Na–NH_3 solutions, while the pairing equilibrium of the solvated electrons is not affected by pressure. The catalytic para-hydrogen conversion is shown to be a useful probe for the equilibria interrelating the paramagnetic species in metal–ammonia solutions.

Depending above all on the total metal concentration, the dissolved electrons in alkali metal–ammonia solutions occur in several different states which may be described as

$$e^-_{sol}\,[c_m < 10^{-3}\,\text{mole/l.}] \rightleftharpoons \tfrac{1}{2}e_2^{2-} \rightleftharpoons e^-_{met}\,[c_m > 0{\cdot}5\,\text{mole/l.}] \qquad (1a, 1b)$$

Least understood of these is the diamagnetic 'electron pair' (no specific model implied) preceding the transition to the metallic state, while the least accessible is the unpaired 'solvated electron' predominating only at concentrations below 10^{-3} mole/l.

Both the 'solvated' and the 'metallic' electrons being paramagnetic, e.s.r. spectroscopy can be employed to gain information about these states as well as the equilibria interrelating them. A second phenomenon related directly to the paramagnetism of metal–ammonia solutions is the catalytic para-hydrogen conversion. Experiments exploring both effects are reported below.

(A) ESR MEASUREMENTS UNDER PRESSURE

The application of pressure techniques is suggested by the unusual volume effects of metal–ammonia solutions; it also extends the temperature range available for investigation[1]. For e.s.r. measurements at pressures up to 500 atm at variable temperature the apparatus shown in Figure 1(a) was used[2]. The sample cell, a length of quartz capillary extending through the temperature-controlled cavity of the e.s.r. spectrometer, is connected to the pressure generator and the storage autoclaves via steel capillaries by means of the pressure coupling shown in Figure 1(b). Pressure generator and manometer are filled with pentane as pressure-transmitting fluid and can be closed to the remaining apparatus at valve 1. The storage autoclaves contain in glass

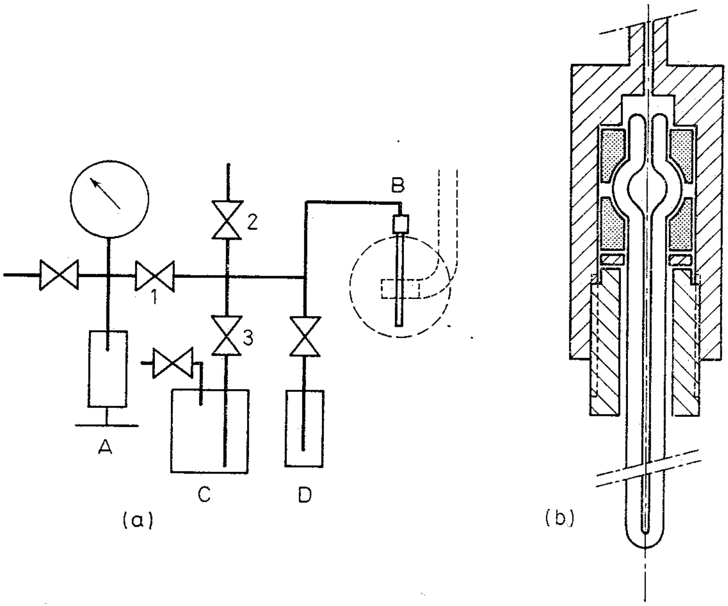

FIGURE 1. (a) Apparatus for e.s.r. measurements under pressure. A: pressure generator with manometer; B: sample cell with pressure coupling; C, D: storage autoclaves for solution and pure solvent; 1–3: valves; magnet and microwave guide of the e.s.r. spectrometer are indicated by dotted lines. (b) Pressure coupling with Teflon packings connecting the quartz capillary[2]

vessels (i) the solution to be investigated (this autoclave can be cooled to $-80°C$) and (ii) pure solvent used to clean the apparatus. The quartz capillaries (i.d. 0·5 to 1 mm; o.d. 5 mm) withstand pressures of up to 500 atm. The solutions are prepared under vacuum conditions in a graduated dropping funnel with cooling jacket, attached by a glass-to-steel taper joint to the storage autoclave.

(B) PRESSURE DEPENDENCE OF EQUILIBRIA INVOLVING SOLVATED ELECTRONS

Stable solutions of solvated electrons of concentration low enough to exclude the presence of spin-compensated electron pairs ($< 10^{-3}$ mole/l.) can be obtained through the reversible reaction of alkali amides with hydrogen in liquid ammonia[3, 4]

$$\tfrac{1}{2}H_2 + KNH_2 \rightleftharpoons e^-_{sol} + NH_3 + K^+ \qquad (2)$$

The equilibrium concentration of solvated electrons in a 1 mole/l. potassium amide solution saturated with hydrogen at a pressure of 100 atm at room temperature is about 10^{-6} mole/l. The intensity of the e.s.r. signal of this system decreases with increasing pressure (Figure 2), reflecting a displacement of equilibrium 2 to the left. The corresponding volume change associated

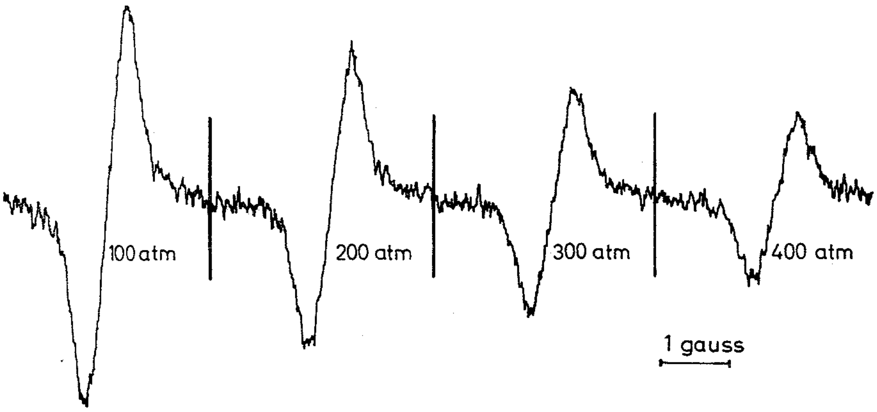

FIGURE 2. The e.s.r. signal of the solvated electrons in a hydrogen-saturated (100 atm) solution of potassium amide (1 mole/l.) in ammonia at varying pressures at room temperature[2]

with the reaction[2] of -63 ± 5 ml/mole agrees well with the result of optical studies[4].

The exceptionally large volume change associated with reactions involving solvated electrons is also exemplified in the equilibrium between solvated electrons and benzene radical anions,

$$e^-_{sol} + C_6H_6 \rightleftharpoons C_6H_6^- \quad (3)$$

both of which are paramagnetic. The effect of pressure on this reaction in methylamine/ammonia 2:1 at -110°C ($c_K = 10^{-2}$ mole/l.; $c_{C_6H_6} = 10^{-1}$ mole/l.) is shown in Figure 3. The decrease in electron concentration is accompanied by an increase in concentration of benzene radical anions, the displacement corresponding to a volume change[2] of -71 ± 5 ml/mole.

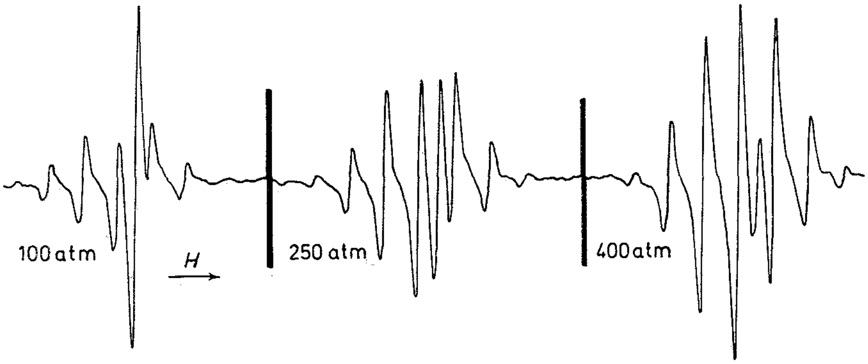

FIGURE 3. Effect of pressure on the equilibrium 3 in methylamine–ammonia (2:1) at -110°C. The electron signal appears superimposed on the e.s.r. septet of the benzene radical anions[2].

(C) EFFECT OF PRESSURE ON THE EQUILIBRIA (1a, 1b)

The e.s.r. signals of 'solvated' and 'metallic' electrons in ammonia differ with respect to linewidth and line symmetry. The intensity of the narrow symmetrical signal of dilute Na–NH_3 solutions ($\leqslant 0{\cdot}2$ mole/l.) does not vary with pressure to within ± 5 per cent/100 atm at −33°C. The apparent volume of the electrons in dilute metal–ammonia solutions is thus practically independent of their degree of association according to equilibrium 1a. Considering that the only property observed to change drastically with the position of this equilibrium is the spin-paramagnetism of the solutions, we picture the 'electron pair' as a spin-oriented association of 'solvated electrons' which otherwise retain their identity.

As the metal concentration is raised from about 0·2 to 6 mole/l. (−33°C) the linewidth (distance between points of maximum slope irrespective of line

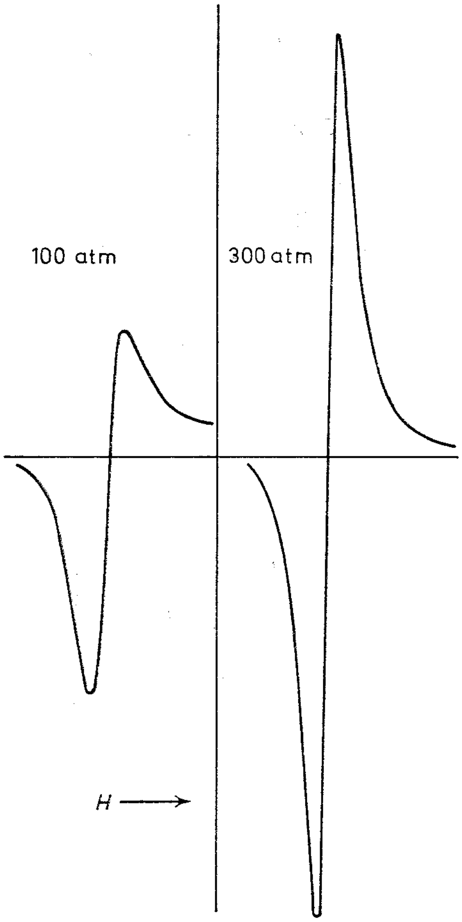

FIGURE 4. Effect of pressure on the asymmetrically broadened e.s.r. signal of a 0·4 mole/l. sodium–ammonia solution at −33°C

symmetry) increases by a factor of 50. In addition, the line becomes asymmetrical[5], the onset of asymmetry at about 0·3 mole/l. (−33°C) presumably marking the appearance of 'metallic' electrons according to equilibrium 1b. The effect of pressure on the asymmetrically broadened e.s.r. signal of a 0·4 mole/l. Na–NH_3 solution at −33°C is shown in Figure 4. With increasing pressure the asymmetry is reduced and the linewidth decreases, both effects, which diminish with increasing metal concentration, indicating a displacement of equilibrium 1b to the left. This implies that the nonmetal–metal transition is shifted towards higher sodium concentrations with increasing pressure, as has also been deduced from the effect of pressure on the electrical conductivity[6] and on the miscibility gap[7] of the Na–NH_3 system.

(D) THE PARA-HYDROGEN CONVERSION IN SODIUM-AMMONIA SOLUTIONS

Like all paramagnetic systems, metal–ammonia solutions catalyse the para-hydrogen conversion[8]. The specific rate (rate referred to concentration of paramagnetic species, derived as the ratio of rate and paramagnetic susceptibility[9]) of the para-hydrogen conversion in sodium–ammonia solutions is independent of the total sodium concentration up to about 0·5 mole/l. [−33°C; Figure 5(a)], i.e. throughout the spin-paramagnetic region. For dilute solutions, therefore, the reaction is of first order with respect to the concentration of unpaired solvated electrons, and the following rate law applies

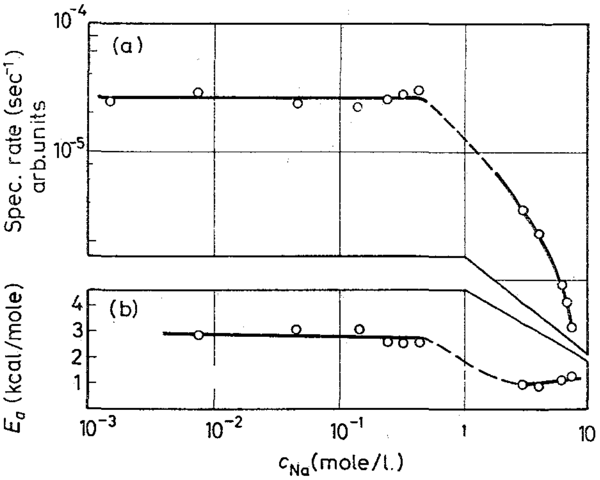

FIGURE 5. (a) Specific rate of the para-hydrogen conversion in sodium–ammonia solutions (−33°C) as a function of total metal concentration. (b) Activation energy of the para-hydrogen conversion in sodium–ammonia solutions (−65° to −45°C) as a function of total metal concentration.

$$\text{rate} = k[p\text{-}H_2][e^-_{sol}] \qquad \text{(mole/l. sec)} \qquad (4)$$

Above a sodium concentration of about 0·5 mole/l. the specific rate decreases abruptly, indicating a change in conversion mechanism with the onset of metallic paramagnetism.

The activation energy of the reaction [$-65°$ to $-45°$C; Figure 5(b)] remains nearly constant throughout the dilute concentration range, then falls off, seemingly to assume a constant value again for metallic solutions. Since the homogeneous para-hydrogen conversion by paramagnetic species is nearly independent of temperature[10], the observed activation energies must reflect the effect of temperature on the equilibria 1a and 1b, both being shifted at the expense of the spin-paired state with increasing temperature. The value of $2{\cdot}8 \pm 0{\cdot}5$ kcal/mole for dilute Na–NH_3 solutions agrees reasonably well with the dissociation energy of electron pairs ($3{\cdot}2 \pm 0{\cdot}5$ kcal per half mole of pairs) derived from susceptibility data[9].

REFERENCES

[1] U. Schindewolf, this volume, page 199.

[2] K. W. Böddeker, G. Lang and U. Schindewolf, *Angew. Chem.* **81**, 118 (1969); *Angew. Chem.* (*Internat. Ed.*), **8**, 138 (1969).

[3] E. J. Kirschke and W. L. Jolly, *Science*, **147**, 45 (1965); *Inorg. Chem.* **6**, 855 (1967).

[4] U. Schindewolf, R. Vogelsgesang and K. W. Böddeker, *Angew. Chem.* **79**, 1064 (1967); *Angew. Chem.* (*Internat. Ed.*), **6**, 1076 (1967).

[5] R. Catterall and M. C. R. Symons, *J. Chem. Soc.* 4342 (1964); R. Catterall, *J. Chem. Phys.* **43**, 2262 (1965).

[6] U. Schindewolf, K. W. Böddeker and R. Vogelsgesang, *Ber. Bunsenges. Phys. Chem.* **70**, 1161 (1966).

[7] U. Schindewolf, G. Lang and K. W. Böddeker, *Z. Phys. Chem.* N. F., **66**, 86 (1969).

[8] Y. M. Claeys, C. F. Baes and W. K. Wilmarth, *J. Chem. Phys.* **16**, 425 (1948).

[9] After data by C. A. Hutchison and R. C. Pastor, *J. Chem. Phys.* **21**, 1959 (1953), and E. Huster, *Ann. Physik*, **33**, 477 (1938). The exact course of the susceptibility at $c_{Na} > 0{\cdot}5$ M is not known; cf. J. C. Thompson, *Advances in Chemistry Series No. 50*, 96 (1965).

[10] L. Farkas and H. Sachsse, *Z. Phys. Chem. B*, **23**, 1 (1933).

GENERAL DISCUSSION

U. Schindewolf—As Dr Böddeker mentioned, we have thought of the possibility of the p-H_2 conversion being catalysed by the spin-paired species too. The observed rate law, however, is in accordance with the interpretation given by Dr Böddeker. But something might nevertheless be wrong. The rate constant found for the conversion according to Wigner's theory is too large by a factor of 100 to 1 000 for a paramagnetic particle of the size of the solvated electron.

To be sure that the p-H_2 conversion was due only to the dissolved metal and not to amide ions formed by decomposition ($NaNH_2$ and KNH_2 are powerful catalysts for the p-H_2 conversion and for the D_2–NH_3–isotope exchange [Y. Claeys, J. Dayton and W. K. Wilmarth, *J. Chem. Phys.* **18**, 759 (1950)]), the p-H_2 was, in some runs, enriched to about 1 000 p.p.m. HD. Parallel to the p-H_2 conversion, isotope exchange was followed by mass spectroscopy. In no case did the rate of isotope exchange exceed the rate of p-H_2 conversion by more than a few per cent. So conversion could not be due to amide catalysis (which has an activation energy of 10 to 12 kcal/mole).

W. H. Koehler—You made the statement that there is no apparent volume change when the spin-pairing process takes place. Could you observe a volume change of say ten per cent?

K. W. Böddeker—We place the limit at ±5 per cent. Within this limit there seems to be no volume change.

T. Tuttle—In investigating the equilibrium between the solvated electron and the benzene negative ion, was there a conservation of paramagnetic species?

K. W. Böddeker—As judged by the intensities of the overlapping spectra, the apparent concentration of the solvated electrons decreases by a factor of 2·6, while that of the benzene radical anions increases by a factor of 3·2 for $\Delta p \sim 300$ atm at $-110°C$.

R. Catterall—We also looked at the benzene–electron equilibrium $C_6H_6 + e^-_{solv} \rightleftarrows C_6H_6^-$ in dimethoxyethane. The benzene anion grows at low temperature, and the solvated electron is favoured at higher. We observed e.s.r. spectra very similar to those reported by Dr Böddeker.

K. W. Böddeker—We have done that too in ether. We found there is no effect of pressure on the intensity of the simple seven-line spectrum.

R. Catterall—The temperature dependence of the onset of asymmetry of the e.s.r. is just as marked as the pressure dependence [R. Catterall, *J. Chem. Phys.* **43**, 2262 (1965)]. Lowering the temperature restores the symmetry just as increasing the pressure does. These trends are to be compared with the decrease in conductivity with decreasing temperature and increasing pressure. Both e.s.r. and conductivity indicate a localization of electrons from the band as temperature is decreased and pressure is increased.

J. Acrivos—Did you have to do any retuning in going from the asymmetric to symmetric lines?

K. W. Böddeker—No, because the broadening of the line had started much below the onset of asymmetry.

M. J. Sienko—In connection with the ortho–para hydrogen conversion, there is an interesting point to consider. Normally, one thinks that the conversion is catalysed by paramagnetic species only, but it is possible to have catalysis by paired electrons. There is the famous case of the Tchitchibabin hydrocarbons which are diamagnetic but their electrons are so far spread out in the molecule that they catalyse individually the ortho–para hydrogen conversion without showing up in the paramagnetic susceptibility. Your k may then remain constant because you are measuring the effect of the single electron plus the electron pair.

K. W. Böddeker—I do remember this case. I would not think it applies in our circumstances. What we did was to take all available data of paramagnetic susceptibility. In the low concentration region this means the e.s.r. susceptibility. We then divided our rates by the values from the best curve we could put through all the susceptibility data. The constancy of k you saw really referred to e.s.r. single-electron concentration. If the pairs were to play a role, it should no longer be a concentration-independent function.

U. Schindewolf—One thing that Dr Böddeker did not stress is that the specific rate constant as referred to the paramagnetic electron is larger by a factor of 100 or 1 000 than one would expect on the basis of Wigner's theory for a single paramagnetic particle with a spin 1/2 and a size of about 3 Å. We still do not know what does the catalysis. There remains the possibility of spin-flipping by the diamagnetic as well as the paramagnetic species. We hope to investigate this by using other metals such as potassium or caesium and making a comparison with paramagnetic species such as manganese.

L. Onsager—Several effects could complicate the interpretation of the ortho–para hydrogen temperature dependence. The rate will depend on how often the hydrogen gets near the electron and this will probably take place more often at higher temperature, assuming that the interaction between hydrogen and electron is predominantly repulsive. Secondly, the conversion depends on how long the hydrogen stays in the neighbourhood and how fast the hydrogen rotates. This would tend to give a rate that decreases with increasing temperature. As regards the reflection on the activation energy for the dissociation of the dimer the effect on the temperature coefficient depends also on the degree of dissociation.

U. Schindewolf—As to the reliability of Dr Böddeker's data, it is well known that the metal solutions decompose to form amide and that amide is a very good catalyst for the isotope exchange reaction of hydrogen and also the ortho–para hydrogen conversion. To be sure no amide was formed, we did hydrogen isotope exchange experiments.

The parahydrogen was enriched with 1000 p.p.m. of HD. If the HD concentration decreased during the experiment, that would be an indication for KNH_2 catalysis, so we discarded those experiments. The data Dr Böddeker gave were for experiments where only the electron catalyses this reaction.

I. Warshawsky—I am wondering if there is a little bit of ambiguity in thinking of a diamagnetic species. Perhaps there are two kinds of diamagnetic species, one in which two electrons are trapped in a cavity and another in which the wave functions overlap but the electrons are not in the same cavity. Perhaps, as Professor Sienko was discussing, one might be effective as a catalyst and the other might not.

K. W. Böddeker—You are touching on a hot subject there. If you look at typical data such as conductivity, optical absorption, magnetic susceptibility, etc., the only thing that dramatically changes as the equilibrium is shifted is the susceptibility. Quite a few of the properties have in fact been referred to as null properties (page 1 ff). We tend to think that throughout the pairing the solvated electrons appear to retain their identity but somehow just get spin-oriented.

J. C. Thompson—There is another change that accompanies the spin-pairing and that is the shift in the optical spectrum. If you take the kind of curve Dr Koehler found (page 41), where you have the shift in the position of the absorption maximum with concentration, and plot it together with the fraction of paired spins which have been determined by the Hutchison–Pastor experiment, then if you normalize the two curves so that they have the same amplitude you find they lie on top of each other. The absorption maximum goes to longer wavelengths at the same time that the spins pair up.

W. H. Koehler—This is hard to rationalize with the double occupied cavity having a smaller radius.

K. W. Böddeker—We have already heard that theory may give a *larger* and a *smaller* radius.

J. Jortner—As soon as it is measured, the theorists will understand.

R. Catterall—The electron resonance linewidth of about 1 gauss observed by Dr Böddeker is surprising. First of all, we know from the salt effect on simple metal solutions that the potassium cation exchange has almost no effect on electron relaxation. Secondly, the rates of the equilibrium $NH_2^- + \frac{1}{2}H_2 \rightleftarrows e^- + NH_3$ are too slow to affect electron relaxation. Thirdly, we observe no *g*-shift for K solutions containing KNH_2, so there is no reason to expect spin–orbit relaxation. Fourthly, we have no reason to suspect a drastic increase in hyperfine coupling to solvent nuclei. Where does the linewidth increase (from 0·02 gauss) come from? The only reason I can think of is viscosity. Do you have any indication that the viscosity of these solutions shows a dramatic increase with pressure?

K. W. Böddeker—The compressibility in this range is about two per cent for this Δp of 300 atmospheres. It really should not affect the viscosity much either.