THE JOURNAL OF CHEMICAL PHYSICS VOLUME 30, NUMBER 3 MARCH, 1959

Energy Levels of Bound Electrons in Liquid Ammonia

JOSHUA JORTNER

Department of Physical Chemistry, The Hebrew University, Jerusalem, Israel

(Received July 17, 1958)

The properties of infinitely dilute metal ammonia solutions are interpreted on the basis of Landau's model for electron binding by polarization of the dielectric medium. The electrons are bound in cavities of radius 3.2–3.45 A. The energy levels of the trapped electrons are computed by the variation method using one-parameter wave functions. It is possible to obtain theoretical values for the heat of solution of the electron and the energy of the $1s \rightarrow 2p$ transition in agreement with experimental data.

The susceptibility of the energy of the electronic transition to temperature cannot be interpreted by the temperature dependence of the dielectric constant only, and it is presumed that the electron cavity radius is temperature dependent.

INTRODUCTION

THE physical and chemical properties of the solutions of alkali metals in liquid ammonia and ammines have been studied for many years. Although the available experimental data concerning these systems is extensive, the nature of the binding of the electrons in these solutions is still a matter of controversy. The currently proposed theories for these systems are the electron cavity and the cluster theory.

The cluster theory was recently proposed by Alder *et al.*[1] It was postulated that the main unit in the solution is a solvated metal cation with the valence electron localized on the protons of the ammonia molecules of the primary solvation layer. This species may dissociate, or may combine with dimer formation.

The electron cavity model postulates the binding of the electrons, which are removed from the alkali ions, in cavities in the liquid. This model was essentially proposed by Ogg.[2] The cavity radius and the binding energy of the electron were computed using an oversimplified model of an electron in a box. This model was refined by Lipscomb.[3] Kaplan and Kittel[4] postulated the binding of the electron in a molecular orbital formed by the protons of the ammonia molecules adjacent to the cavity. The electron cavity model was recently applied[5] to interpret the absorption spectra of alkali metals in ammonia as electronic transition within the e centers and the absorption spectra of electrons in ammine solutions as due to e_2 center absorption bands.

An experimental evidence for the possibility of binding of electrons in nonprotonic solvents was recently obtained by Wilkinson *et al.*[6] who obtained solutions of electrons in certain ethers. These results indicate that proton-electron exchange forces are not essential for the electron binding in solutions. Recently a model[7] was proposed for the binding of electrons in solutions which is an improved form of the electron cavity model. This model is based on Landau's ideas on the possibility of binding of electrons in a dielectric medium.[8] Landau's model was mathematically formulated in the work of Pekar[9] who used the term "polaron" for the state of an electron bound by the polarized medium. Dawydow[10] and Deigen[10] attempted to apply Pekar's model to liquid ammonia solutions. The comparison between the work of these authors and our results is presented in the last section of this work. An application of this model to electron capture in liquid systems was made by Platzman and Franck[11] who discussed the nature of the photoexcited state of the halide anions, and also indicated the possibility of the application of this model to metal-ammonia solutions. It was previously shown[7] that the absorption spectra of metal ammonia solutions can be interpreted on the basis of a refined form of Landau's model, using the experimental data for the solvation energy of the electron. The purpose of this work is to present more elaborate calculations of the energy levels of bound electrons in liquid ammonia.

SUMMARY OF EXPERIMENTAL RESULTS

The present summary will be limited to the properties of dilute metal ammonia solutions which are relevant to the presentation of the model.

(1) The volume expansion of a dilute sodium ammonia solution is 72 A^3 per alkali atom. With Kituki's[12] density measurements, Lipscomb[3] suggested that the electrostriction due to the Na$^+$ ion is about 35 A^3/ion. A more accurate treatment will be presented similar

---

[1] Becker, Lindquist, and Alder, J. Chem. Phys. **25**, 971 (1956).

[2] R. A. Ogg, Phys. Rev. **69**, 669 (1946).

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

[4] J. Kaplan and C. Kittel, J. Chem. Phys. **21**, 1429 (1953).

[5] Fowles, McGregor, and Symons, J. Chem. Soc. 3329 (1957).

[6] Down, Lewis, Moore, and Wilkinson, Proc. Chem. Soc. 209 (1957).

[7] J. Jortner, J. Chem. Phys. **27**, 823 (1957).

[8] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), p. 86.

[9] S. Pekar, J. Phys. (U.S.S.R.) **10**, 341, 347 (1946).

[10] (a) A. S. Dawydow, J. Exptl. Theoret. Phys. U.S.S.R. **18**, 913 (1948); (b) M. F. Deigen, Trudy Inst. Fiz. Akad. Nauk, Ukr. S.S.R. **5**, 119 (1954); Zhur. Eksptl. i Theoret. Fiz. **26**, 300 (1954). I am grateful to the referee for drawing my attention to these papers.

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

[12] S. Kituki, J. Soc. Chem. Ind. Japan, **42** (Suppl. Binding), 15 (1939).

TABLE I. Calculation of the heat of solution of an electron in liquid ammonia.

Metal	λ[a] ev	I[b,c] ev	$H_S(M^{Z+})$[d] ev	H_SM[e] ev	H_S[e] ev
Li	1.61	5.39	5.62	−0.42	1.81
Na	1.13	5.14	4.47	0.061	1.74
K	0.94	4.34	3.52	0	1.76
Rb	0.89	4.18	3.31	0	1.76
Cs	0.82	3.89	3.04	0	1.67
Ca	2.00	$I_1=6.11$ $I_2=11.87$	17.3	−0.86	1.78
Sr	1.71	$I_1=5.69$ $I_2=10.98$	15.7	−0.90	1.81
Ba	1.83	$I_1=5.21$ $I_2=9.95$	14.4	−0.83	1.72

[a] Rossini, Wagman, Evans, Levine, and Jaffe, U. S. Natl. Bur. Standards, Circ. No. 500 (1952).

[b] J. Sherman, Chem. Revs. **11**, 93 (1932).

[c] C. E. Moore, Atomic Energy Levels, U. S. Natl. Bur. Standards, Circ. No. 467 (1949).

[d] Heats of solution of monovalent cations were calculated from heats of solution of salts in ammonia (references 19, 20). Heats of solution of divalent cations were calculated from the heat of the reaction $M(s)+ZH^+am \rightarrow M^{Z+}(am)+(Z/2)H_2$ (reference 19).

[e] References 19, 20.

to that proposed for the calculations of partial molar volumes of ions in water.[13,14]

By using the method of Hepler[14] we introduce the ionic molar volume in the form

$$V=\tfrac{4}{3}\pi N(ar_c)^3-B/ar_c, \tag{1}$$

where N is Avogadro's number and r_c is the ionic crystal radius. The ionic cavity radius in solution r_i is greater than the crystal radius and is presented by

$$r_i=ar_c, \tag{2}$$

where a is a numerical factor greater than unity. The main contribution to a arises from the loose packing of the ions and the solvent molecules. Robinson and Stokes showed that allowance for this effect yields $a=1.22$.[15] The electrostriction constant B is presented assuming the validity of Born's model and neglecting the effects of dielectric saturation

$$B/N=(Z^2e^2/2D_s^2)(dD_s/dP) \\ -(Z^2e^2/2)[1-(1/D_s)](1/r_i)(dr_i/dP) \tag{3}$$

where Ze is the ionic charge, D_s the dielectric constant of the medium.

With Kituki's[12] data we obtain

$$V_{\mathrm{NaCl}}=-0.4\ \mathrm{cm^3/mole} \qquad V_{\mathrm{NH_4Cl}}=27.7\ \mathrm{cm^3/mole}$$

If we assume that the values of a and B are the same for both monovalent anions and cations, we obtain for an ion pair the equation,

$$\frac{V_1+V_2}{(1/r_{c_1})+(1/r_{c_2})}=\frac{\frac{4}{3}\pi a^3(r_{c1}^3+r_{c2}^3)}{(1/r_{c_1})+(1/r_{c_2})}-\frac{B}{a}, \tag{1'}$$

where the index 1 and 2 represent the cation and the anion, respectively.

Solving for a and B, using the experimental values for NH_4Cl and NaCl we obtained

$$a=1.42; \qquad B/a=32.10^{-8}\ \mathrm{cm^4/mole}.$$

The radius of the electron cavity is calculated from the following cycle:

	$\Delta V(\mathrm{A}^3)$
$\mathrm{Na}(s)\rightarrow \mathrm{Na}^+(am)+e(g)$	$\frac{4}{3}\pi(ar_{c\mathrm{Na}^+})^3-(B/ar_{c\mathrm{Na}^+})-V_m$
$e(g)\rightarrow e(am)$	$\frac{4}{3}\pi R_0^3-(B/R_0)$
$\mathrm{Na}(s)\rightarrow \mathrm{Na}^+(am)+e(am)$	72,

where $V_m=39.4$ A^3/atom is the volume of the sodium atom in the solid state. Hence we obtain $\frac{4}{3}\pi R_0^3-(B/R_0)=155$ A^3.

Solving for R_0 we get $R_0=3.45$ A. This result is somewhat higher than that obtained by Lipscomb. The electrostriction term is probably somewhat overestimated, as it is assumed that the electron is confined in the cavity.

(2) The solvation energy of an electron in ammonia is calculated from the heats of solution of alkali metals in ammonia.[16–19] In order to obtain from these data the heat of solution of the electron, the heats of solution of the individual cations have to be calculated. The heats of solution are defined by the enthalpy change ΔH for the process,

$$A^Z{}_{(\mathrm{am})}\rightarrow A^Z(g),$$

where $\Delta H=H_S(A^Z)-Zev$. Here $H_S(A^Z)$ is the heat of solution of the ion A^Z of charge Ze and v is the inner potential of ammonia. The heats of solution of individual cations were calculated using the data for heats of solution of salts in liquid ammonia as tabulated by Jolly.[20] The calculation was carried out using Verwey's method.[21] These values for the ionic heats of solution are based on the value $H_{S}{}^{H+}=286$ kcal for the heat of solution of the proton. These results are presented in Table I.

---

[13] A. M. Couture and K. J. Laidler, Can. J. Chem. **34**, 1209 (1956).

[14] L. G. Hepler, J. Phys. Chem. **61**, 1426 (1957).

[15] R. A. Robinson and R. H. Stokes, Trans. Faraday Soc. **53**, 301 (1957).

[16] C. A. Kraus and F. C. Schmidt, J. Am. Chem. Soc. **56**, 2297 (1934).

[17] Schmidt, Studer, and Sottysiak, J. Am. Chem. Soc. **60**, 2780 (1938).

[18] L. V. Coulter and L. Monchick, J. Am. Chem. Soc. **73**, 5867 (1951).

[19] L. V. Coulter, J. Phys. Chem. **57**, 553 (1953).

[20] W. L. Jolly. Chem. Revs. **50**, 351 (1952).

[21] E. J. W. Verwey, Rec. trav. chim. **61**, 127 (1942).

The heat of solution of an electron in ammonia is obtained from the following Born-Haber cycle:

	ΔH
$M(s)\rightarrow M(g)$	λ
$M(g)\rightarrow M^{z+}(g)+Ze(g)$	$\sum_{i=1}^{Z} I_i$
$M^{z+}(am)\rightarrow M^{z+}(g)$	$H_S(M^{z+})-Zev$
$Ze(am)\rightarrow Ze(g)$	ZH_S^e+Zev
$M(s)\rightarrow M^{z+}(am)+Ze(am)$	H_S^M

where I_i are the ionization potentials of the metal atom λ is the sublimation energy of the metal, H_S^M, $H_S(M^{z+})$ and H_S^e are the heat of solution of the alkali metal, the alkali metal cation, and the electron, respectively. Hence we obtain

$$H_S^e=(1/Z)\left(\lambda+\sum_{i=1}^{Z} I_i-H_S(M^{z+})-H_S^M\right). \qquad (4)$$

The values of H_S^e thus obtained are presented in Table I.

The heat of solution of an electron in liquid ammonia is $H_S^e=1.7\pm0.2$ ev and is approximately independent of the cation. These results are in agreement with the data of Jolly[20] but contradict the results of Coulter.[19] Calorimetric measurements[22] on the concentration dependence of heats of solution of alkali metals were interpreted as due to the heat of unpairing of electrons which was determined as 0.2 ± 0.05 ev. This relatively small energy difference is of the order of magnitude of the uncertainty of the heats of solution of individual ions and was not introduced into the calculation of H_S^e.

(3) The absorption spectrum of metal ammonia solutions in the region of 500–750 mμ shows a continuous absorption independent of the alkali metal.[23] The band maximum lies in the near infrared region. Vogt[24] reported that the band maximum lies at 1.8 μ (0.7 ev) for both lithium and sodium solutions. Jolly[25] found the absorption maximum of sodium ammonia solutions at 1.5 μ (0.8 ev). Blades and Hodgins[26] found the absorption maximum at about 1.5 μ for lithium sodium and potassium solutions. Bosch[27] reported for thin films of metal ammonia that the infrared band in these systems lies at $h\nu=1.0$ ev at -253°C.

The place of the absorption band is susceptible to temperature.[26] The temperature coefficient for potassium ammonia solutions reported by these workers is $d(h\nu)/dt=-9$ cm^{-1}/deg in the region -33°C–-70°C.

(4) It is fairly well established that in extremely dilute alkali metal-ammonia solutions the electrons exist as individual unpaired solvated electrons, removed from the alkali metal. This conclusion is consistent with both the electron cavity and the cluster theory. Calorimetric measurements[22] and concentration dependence of paramagnetic susceptibility[4] of these systems were interpreted on the basis of the electron cavity theory by equilibrium between e and e_2 centers. Neglecting the entropy change of this process the equilibrium constant for dissociation of the e_2 centers should be about 0.02. Conductivity and magnetic susceptibility data were interpreted in terms of the cluster theory. Kraus[28] interpreted the conductivity of dilute metal ammonia solutions as being of an electrolytic type and involving ion pair formation. The dissociation constant calculated by him for sodium solutions at -33°C was 0.05. Alder *et al.*[1] showed that the concentration dependence of *para* magnetic susceptibility of potassium-ammonia solutions is consistent with the assumption that the dissociation constant of the "ion pair" is 0.03. It thus appears that in the concentration region below 10^{-3} mole/liter the degree of dissociation is greater than 0.95. Thus we feel that the treatment of the electrons, as bound to the dielectric medium in this extremely dilute concentration region, is justified.

PRESENTATION OF THE MODEL

The proposed model for metal ammonia solutions postulates that in the limiting case of extremely dilute solutions the electron is removed from the metal cation, and is located in a cavity in the liquid. The electron is trapped by polarization of the medium by the electron itself. This picture of "an electron trapped by digging its own hole"[8] was introduced by Landau.[29] No experimental evidence was found for trapping of electrons in crystals by this mechanism, but this picture may be applied to liquid systems.

The form of the potential well formed by the polarized medium will be calculated. We assume that the electron is bound in a spherical cavity of a mean radius Ro. At relatively large distances from the cavity center the medium may be treated as a continuous dielectric medium. In that region the total polarization $-P_t-$ of the medium formed by a spherically symmetrical charge distribution within the cavity is presented by

$$P_t=(e/4\pi r^2)[1-(1/D_S)]. \qquad (5)$$

The electronic polarization is given by

$$P_e=(e/4\pi r^2)[1-(1/D_{0p})]. \qquad (6)$$

D_S and D_{0p} are the static and optical dielectric constant.

The part of the polarization which cannot follow the

---

[22] Coulter, Wolsky, Zdanuk, and Monchik, 119th meeting Am. Chem. Soc. (1951), Abstr. 101, p. 500.

[23] G. E. Gibson and W. L. Argo, J. Am. Chem. Soc. **40,** 1327 (1918).

[24] E. Vogt, Z. Elektrochem. **45,** 597 (1939).

[25] W. L. Jolly, University of California Radiation Laboratory Rept. No. UCRL 2008 (1952).

[26] H. Blades and J. W. Hodgins, Can. J. Chem. **33,** 411 (1955).

[27] E. Bosch, Z. Physik. **137,** 89 (1954).

[28] C. A. Kraus, J. Chem. Educ. **30,** 83 (1953).

[29] L. Landau, Physik. Z. Sowjetunion **3,** 664 (1933).

TABLE II. Calculations for the 1*s* energy level of an electron in liquid ammonia.

R_0 A	μ A^{-1}	W_{1s} ev	r_B^{1s} A
3.00	0.360	−1.415	2.78
3.20	0.347	−1.356	2.88
3.45	0.330	−1.281	3.03

motion of the electron is presented by

$$P_D = P_t - P_e, \tag{7}$$

$$P_D = (e/4\pi r^2)[1/D_{0p}) - (1/D_S)]. \tag{7'}$$

This "permanent polarization" represented by 7′ creates the potential well. This separation of the total polarization to electronic and permanent polarization can be approximately achieved if the frequency of the bound electron is much greater than the period of nuclear vibrations, and is of the order of magnitude of the electronic frequencies. In this case $D_{0p} = n^2$ where n is the refractive index of ammonia. Thus the permanent polarization consists of the atomic and dipole polarization. The electrostatic potential resulting from this polarization is given by

$$\phi = \int_r^\infty (P_D/r^2)4\pi r^2 dr. \tag{8}$$

In the vicinity of the cavity the atomic structure of the medium is of primary importance. The first layer of the solvent molecules surrounding the cavity may create a discontinuity of the potential function which is roughly similar to that across a spherical double layer. The potential function will still be a decreasing function of r but deviations from spherical symmetry may be appreciable.

Our treatment involves an extrapolation of the simple form of Landau's potential presented by (8) up to the cavity radius. It is presumed that ϕ is continuous up to R_0 and that within the cavity ϕ is constant. The liquid is treated as a continuous isotropic dielectric medium where the electron is confined in a spherical cavity. The effects of proton-electron exchange forces are not introduced. Another approximation involved is that the electronic wave function may extend beyond the cavity radius and some of the nearest molecules will be acted by a field due to less than one electronic charge.

The potential energy of the electron is $-e\phi$, thus the following expression for the potential energy $V(r)$ is obtained

$$V(r) = -\beta e^2/r \quad \text{for} \quad r > R_0,$$

$$V(r) = -\beta e^2/R_0 \quad \text{for} \quad r < R_0, \tag{9}$$

where $\beta = [(1/D_{0p}) - (1/D_S)]$. The reference state is that of a nonpolarizing electron located in the medium at infinity from the cavity.

CALCULATION OF THE ENERGY LEVELS OF A TRAPPED ELECTRON

A calculation of the energy levels of an electron bound in the potential well $V(r)$ is presented. Considering the approximations involved in the derivation of Eq. (9), these calculations intend to show that the right orders of magnitude for the experimental quantities can be obtained from the proposed model.

The calculations were carried out using the variation method. As the potential for $r > R_0$ is approximated by a hydrogen-like form the one parameter function introduced for the ground state was of the form

$$\psi_{1s} = A \exp(-\mu r), \tag{10}$$

where $A^2 = \mu^3/\pi$.

The energy of the ground state was calculated from the variation integral

$$W_{1s} = \int_v \psi_{1s}[-h^2\Delta/8\pi^2 m + V(r)]\psi_{1s} dv, \tag{11}$$

where Δ is the Laplacian operator and v is the total volume.

From (11) the energy is obtained as a function of μ. The best value of μ is obtained by putting $\partial W_{1s}/\partial\mu = 0$ and solving for μ. By substitution of this value of μ into (10) and (11) the energy and the wave function for this state are obtained.

Expression (11) is presented in the explicit form:

$$W_{1s} = -\int_0^\infty \psi_{1s}(1/r^2)(d/dr)[r^2(d\psi_{1s}/dr)]4\pi r^2 dr$$
$$-(\beta e^2/R_0)\int_0^{R_0} \psi_{1s}{}^2 4\pi r^2 dr - \beta e^2 \int_{R_0}^\infty \psi_{1s}(1/r)\psi_{1s}4\pi r^2 dr. \tag{11'}$$

Introduction of (10) into (11′) yields

$$W_{1s} = (h^2\mu^2/8\pi^2 m) - (\beta e^2/R_0)$$
$$+ (\beta e^2/R_0)(1+\mu R_0)\exp(-2\mu R_0) \tag{12}$$

and

$$\partial W_{1s}/\partial\mu = (\mu h^2/4\pi^2 m) - \beta e^2(1+2\mu R_0)\exp(-2\mu R_0). \tag{13}$$

The Bohr radius for the 1*s* level is approximately presented by $r_B{}^{1s} = 1/\mu$ and the mean radius by $\bar{r}_{1s} = 3/2\mu$. Calculations for ammonia at −33°C were carried out setting $D_S = 22$, $D_{0p} = n^2 = 1.756$, and $\beta = 0.523$. The results of these calculations for several values of R_0 are presented in Table II.

From Eqs. (12) and (13) we obtain the best approximation to W_{1s} which the form of the trial function (10) would allow. The adequacy of this variation function was tested by repeating the calculation using the function $\psi_{1s} = A(1+\gamma r)e^{-\gamma r}$ where $A^2 = \gamma^3/7\pi$. The value of W_{1s} thus obtained is -1.415 ev for $R_0=3.20$ A, which is only 4.5% lower than the result obtained using the simple one parameter function.

The energy of the $2p$ level was calculated using the one parameter functions

$$2p_x=\mathrm{B}r\sin\theta\cos\varphi\exp(-\alpha r),$$
$$2p_y=\mathrm{B}r\sin\theta\sin\varphi\exp(-\alpha r),$$
$$2p_z=\mathrm{B}r\cos\theta\exp(-\alpha r),\qquad(14)$$

where $B^2=\alpha^5/\pi$.

The energy is presented by

$$W_{2p}=(h^2\alpha^2/8\pi^2m)-(\beta e^2/R_0)+(\beta e^2/R_0)(1+\tfrac{3}{2}\alpha R_0+\alpha^2R_0^2+\tfrac{1}{3}\alpha^3R_0^3)\exp(-2\alpha R_0).\qquad(15)$$

and

$$\partial W_{2p}/\partial\alpha=(h^2\alpha/4\pi^2m)-\beta e^2(\tfrac{1}{2}+\alpha R_0+\alpha^2R_0^2+\tfrac{2}{3}\alpha^3R_0^3)\exp(-2\alpha R_0).\qquad(16)$$

The numerical value for R_0 and the form of the potential well selected for the $2p$ state are the same as those for the ground state. The $2p$ energy level thus obtained is not an equilibrium state but is used for the calculation of the energy of the $1s\rightarrow 2p$ electron transition. During the electronic transition the position of the nuclei remains unchanged according to the Franck-Condon principle. Thus we have to consider the energy of the $2p$ state acted by a field corresponding to the ground state. By using the oversimplified picture of a cavity in a continuous dielectric medium this restriction is equivalent to the assumption that R_0 remains constant and that the permanent polarization of the medium did not change.

The Bohr radius for the $2p$ state is given by $r_B^{2p}=2/\alpha$ and the mean radius by $\bar{r}_{2p}=5/2\alpha$.

Considering the relatively great extension of the $2p$ wave function the energy of this state is not very susceptible to the behavior of $V(r)$ at small distances. The energy of an electron bound in the $2p$ state in a hydrogen-like potential well of the form $-\beta e^2/r$ is 0.925 ev.

Table III presents the results of the calculations for the $2p$ state.

CORRELATION WITH EXPERIMENTAL RESULTS

The calculation of the energy levels of an electron in the potential well formed by the polarized dielectric medium did not include the effect of the electronic polarization. When an electron is trapped in this potential well the electronic polarization will lower this state by an additional amount. The actual binding energy of the electron will be presented by the expression

$$E_i=W_i+S_i^e,\qquad(17)$$

where S_i^e is the contribution of the electronic polarization to the energy of i state. E_i is the total binding energy of the electron in this state.

TABLE III. Calculations for the $2p$ energy level of an electron in liquid ammonia.

R_0 A	α A^{-1}	W_{2p} ev	r_B^{2p} A
3.00	0.390	−0.826	5.14
3.20	0.381	−0.790	5.25
3.45	0.370	−0.769	5.39

The total binding energy in the ground state E_{1s} can be correlated with the experimental solvation energy of the electron. Consider the hypothetical process of the transfer of the bound electron to the gaseous phase within a period which is much shorter than the relaxation and vibration period of the solvent molecules,

$$(e_{am})\rightarrow(\quad)+e_g\quad\text{where}\quad\Delta E=-E_{1s}+ev$$

the symbol ( ) represents the electron cavity surrounded by the polarized solvent. This process is equivalent to the following sequence:

	ΔE
$(e_{am})\rightarrow e_g+\mathrm{NH_3(l)}$	H_S^e+ev
$\mathrm{NH_3(l)}\rightarrow(\quad)$	Π.

Π is the rearrangement energy required for the formation of the potential well. Hence we obtain

$$H_S^e=-E_{1s}-\Pi.\qquad(18)$$

The polarization energy Π was estimated from an electrostatic model.

$$\Pi=\tfrac{1}{2}\int_{v'}\rho\phi dv'=\tfrac{1}{2}\int_{R_0}^{\infty}e\psi_{1s}^2\phi 4\pi r^2dr\qquad(19)$$

where ρ is the charge density, v' is the volume occupied by the dielectric medium; and by using (9) and (10) Π is then presented by

$$\Pi=(\beta e^2/2R_0)(\mu R_0+2\mu^2R_0^2)\exp(-2\mu R_0).\qquad(19')$$

Π was calculated by Platzman and Franck[11,30] for uninegative anions by using the expression

$$\Pi=\tfrac{1}{2}\int_{R_0}^{\infty}EP_D4\pi r^2dr$$

where E is the electric field. This expression is incorrect as in that case E should be replaced by D—the electric displacement.

The electronic polarization energy was approximately evaluated assuming that the electron is a sphere

---

[30] R. Platzman and J. Franck, *Farkas Memorial Volume* (Research Council of Israel, Jerusalem, 1953), Special Publication No. 1, p. 21.

TABLE IV. Theoretical calculation of H_S^e and $h\nu$ for an electron in liquid ammonia at −33°C.

R_0 A	S_{1s}^e ev	S_{2p}^e ev	E_{1s} ev	E_{2p} ev	π ev	H_S^e (calc) ev	H_S^e (exptl) ev	$h\nu$ (calc) ev	$h\nu$ (exptl) ev
3.00	−0.745	−0.480	−2.160	−1.306	0.494	1.67	...	0.85	...
3.20	−0.717	−0.472	−2.073	−1.262	0.475	1.60	1.7	0.81	0.8
3.45	−0.682	−0.459	−1.963	−1.228	0.418	1.55	...	0.74	...

of radius $\bar{r}_i$. The interaction energy is approximately given by

$$S_i^e=-\tfrac{1}{2}\int_{\bar{r}_i}^{\infty}(eP_e/r^2)4\pi r^2dr. \qquad (20)$$

Thus the electronic polarization energies for the 1*s* and 2*p* states are

$$S_{1s}^e=-(e^2\mu/3)[1-(1/D_{0p})];$$

$$S_{2p}^e=-(e^2\alpha/5)[1-(1/D_{0p})]. \qquad (20')$$

The near infrared absorption band of metal ammonia solutions is interpreted by us as rising from the $1s\rightarrow 2p$ transition of the bound electron. The nature of the excited state is still a matter of controversy. Jolly[25] proposed that this transition corresponds to the transition of the electron to the conduction band. This idea was also presented by Stairs.[31] Fowles *et al.*[5] postulated that in the excited state the electron is still bound in the cavity. This interpretation is similar to that proposed by us, although as we shall show later their arguments are open to criticism. This problem will probably be finally settled by investigation of the photoconductivity of these systems.

The energy of the $1s\rightarrow 2p$ transition will be given by

$$h\nu=E_{2p}-E_{1s}. \qquad (21)$$

The results obtained from this model can be compared with the available experimental data for the heat of solvation of the electron and the energy of the electronic transition of the bound electron. The agreement with the experimental results is reasonable (Table IV).

The diagrammatic representation of the Landau's potential well, the energy levels of the bound electron and the charge distribution is presented in Fig. 1.

TEMPERATURE DEPENDENCE OF THE POSITION OF THE ABSORPTION BAND

Any model proposed for metal ammonia solutions has to present an adequate interpretation for second-order effects of temperature dependence of the band maximum.

The experiments of Blades and Hodgins[26] indicate that environment changes have a marked effect on the position of the band maximum. The band maximum is susceptible to temperature changes and increase of temperature causes shifts of the band maximum to longer wavelengths. The energy shift presents the difference between the change of the energy of the ground and excited states,

$$d(h\nu)/dt=dE_{2p}/dt-dE_{1s}/dt, \qquad (22)$$

where t is the temperature.

This pronounced effect of temperature on the position of the absorption band is typical also for other cases of electron transfer spectra. The analogy between the temperature effect on the absorption spectrum of metal-ammonia solutions and the ultraviolet absorption spectrum of anions was recently pointed out.[5] It was shown by Stein and Treinin[32] that the temperature effect on the absorption spectrum of anions cannot be interpreted by using the Franck-Platzman equation[30] and assuming that D_{0p} and D_S are temperature dependent. Smith and Symons[33,34] interpreted the absorption spectrum of the iodide ion using the model of a particle in a spherical box for the excited state. The temperature effect was interpreted in terms of the temperature dependence of the cavity radius. Recently the Franck Platzman model was refined by Stein and Treinin to include the temperature dependence of the ionic radius.[32] This picture yielded satisfactory agreement with experimental data. These results will be published in the near future.

The energy levels calculated from Eqs. (12) and (15) are dependent on β and on R_0. For the ground level $E_{1s}=E_{1s}(\beta, R_0, \mu)$ μ itself is calculated from Eq. (13) setting the left side equal to zero; hence $\mu=\mu(\beta, R_0)$. Thus we may write

$$dE_{1s}/dt=(\partial E_{1s}/\partial\beta)(d\beta/dt)+(\partial E_{1s}/\partial R_0)(dR/dt)$$
$$+(\partial E_{1s}/\partial\mu)[(\partial\mu/\partial\beta)(d\beta/dt)+(\partial\mu/\partial R_0)(dR_0/dt)]. \qquad (23)$$

By using Eq. (13) we obtain

$$\partial E_{1s}/\partial\mu=\partial S_{1s}^e/\partial\mu, \qquad (24)$$

$$\frac{\partial\mu}{\partial\beta}=-\frac{(\partial^2W_{1s}/\partial\beta\partial\mu)}{(\partial^2W_{1s}/\partial\mu^2)},$$

$$\frac{\partial\mu}{\partial R_0}=-\frac{(\partial^2W_{1s}/\partial R_0\partial\mu)}{(\partial^2W_{1s}/\partial\mu^2)}. \qquad (25)$$

---

[31] R. A. Stairs, J. Chem. Phys. **27**, 1431 (1957).

[32] G. Stein and A. Treinin (to be published).

[33] M. Smith and M. C. R. Symons, Trans. Faraday Soc. **54**, 338 (1958).

[34] M. Smith and M. C. R. Symons, Discussions Faraday Soc. **24**, (1957).

The temperature coefficient of the energy of the ground level is thus obtained in the form,

$$\frac{dE_{1s}}{dt}=\left[\frac{\partial E_{1s}}{\partial\beta}-\frac{\partial S_{1s}{}^{e}}{\partial\mu}\cdot\frac{(\partial^2W_{1s}/\partial\beta\partial\mu)}{(\partial^2W_{1s}/\partial\mu^2)}\right]\frac{d\beta}{dt}+\left[\frac{\partial E_{1s}}{\partial R_0}-\frac{\partial S_{1s}{}^{e}}{\partial\mu}\frac{(\partial^2W_{1s}/\partial R_0\partial\mu)}{(\partial^2W_{1s}/\partial\mu^2)}\right]\frac{dR_0}{dt}. \quad (26)$$

The temperature coefficient for the $2p$ state is given by Eq. (26) with E_{2p} substituted for E_{1s}, $S_{2p}{}^{e}$ substituted for $S_{1s}{}^{e}$, and α substituted for μ.

The calculations were carried out for $R_0=3.20$ A, $\beta=0.523$. The temperature dependence of the ground and the first-excited level are presented by Eqs. (27) and (28) where E is expressed in ev and R_0 is expressed in A.

$$dE_{1s}/dt=-4.00(d\beta/dt)+0.409(dR_0/dt), \quad (27)$$

$$dE_{2p}/dt=-3.12(d\beta/dt)+0.132(dR_0/dt). \quad (28)$$

From Eq. (22) we obtain

$$d(h\nu)/dt=0.88(d\beta/dt)-0.277(dR_0/dt). \quad (29)$$

The temperature dependence of the energy levels and of $h\nu$ is thus attributed to the temperature dependence of the properties of the dielectric medium, which are roughly expressed by the temperature dependence of D_S and D_{0p}, and to the temperature dependence of the mean cavity radius.

For liquid ammonia at -33°C $d\ln D_S/dt=0.0046$ deg^{-1}(20) and $D_S=22$. The temperature dependence of D_S can be represented by $D_S=66.2\exp(-T/217)$, where T is the absolute temperature.

No experimental data are available for the temperature dependence of D_{0p}. For liquid water using the available experimental data[35] we calculated

$$d(1/D_{0p})/dt=-7.10^{-5}\text{ deg}^{-1}\,{}^{(35)}$$

compared with $d(1/D_S)/dt=2.1\times10^{-4}$ deg^{-1} for ammonia at -33°C. Thus we assume that the changes of D_S with temperature is greater than that of D_{0p}, and the temperature dependence of β at -33°C is approximately presented by

$$d\beta/dt=-\frac{d(1/D_S)}{dt}=-6.95\times10^{-5}\exp(T/217).$$

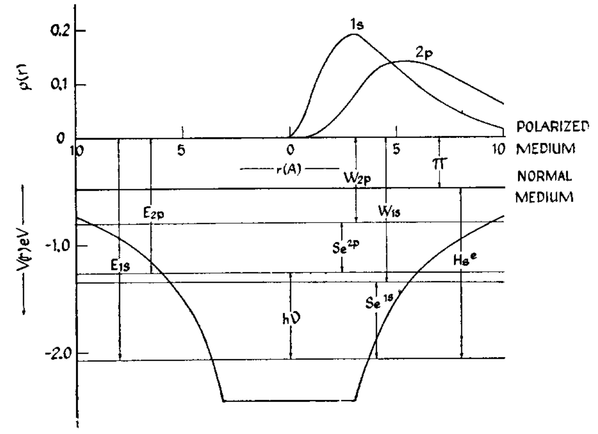

FIG. 1. Energy-level diagram for a bound electron in liquid ammonia.

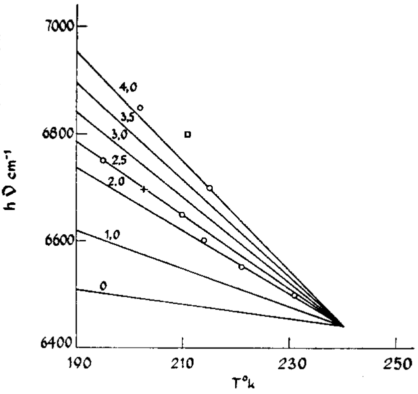

FIG. 2. The temperature dependence of the position of the band maximum of metal ammonia solutions. The experimental results of Blades and Hodgins[26] are compared with the calculated data [Eq. (30)]. Experimental points: +Li; □Na; ○K. Theoretical curves: ——. The numbers represent the values of dR_0/dt in 10^{-3} A/deg.

No experimental data are available for the temperature dependence of the volume expansion of ammonia solution per alkali atom and for the temperature dependence of the partial molar volume of the alkali ions, so it is impossible at present to calculate dR_0/dt from experimental data. For anions in water the temperature coefficient is about 1.5×10^{-3} A/deg for the iodide ion.[32] The temperature coefficient is inversely proportional to the ionic radius.[36] Assuming that R_0 is a linear function of the temperature, the temperature dependence of the electronic excitation energy can be presented by

$$h\nu(T)=h\nu(240)+1.33\times10^{-2}[\exp(240/217)-\exp(T/217)]+0.277(dR_0/dt)(240-T). \quad (30)$$

Figure 2 represents the comparison of the experimental data of Blades and Hodgins[26] with the theoretical calculations. The best agreement was obtained by setting $R_0=3.25$ A. It appears that the temperature dependence of $h\nu$ cannot be interpreted on the basis of the temperature dependence of the dielectric constant only. This temperature dependence can be adequately interpreted by setting $dR_0/dt=3.0\times10^{-3}$ A/deg. The temperature coefficient of R_0 is of the same order of magnitude as that for anions in water. Considering the rather wide scattering of the experimental points this agreement is reasonable.

Another interesting point is the relative susceptibility of the ground and excited levels to temperature changes. As it appears from Eqs. (27) and (28) increase of temperature diminishes the binding energy

---

[35] *International Critical Tables* (National Research Council of U.S.A.—McGraw-Hill Book Company, Inc., 1933), Vol. 7, p. 12.

[36] K. Fajans and O. Johnson, J. Am. Chem. Soc. 64, 668 (1942).

in the ground level more than in the first excited level, thus the temperature coefficient of $h\nu$ is negative. This conclusion of the theoretical calculation contradicts the arguments of Fowles *et al.*[5] who attempted to compare the ground state of the solvated electron with the excited state of the iodide ion.

The proposed model suggests that the energy levels separation increases as the electron cavity volume is reduced and when the dielectric constant of the medium is increased. These effects should lead to displacement of the band maximum to shorter wavelengths when the solution will be compressed. A model of the electron imprisoned in a steep-walled potential well ("an electron in a box") predicts a similar effect.[34]

DISCUSSION

The application of Landau's model to metal ammonia solutions yields reasonable results for extremely dilute solutions. Assuming that the electrons are bound by polarization of a continuous dielectric medium the values of E_{1s} and Π obtained in this paper are probably somewhat overestimated as the extrapolation of Landau's potential was carried out up to the cavity radius. A more refined treatment using the self consistent field method is now carried out.

Another approximation involved in this treatment is that the static dielectric constant was used in the whole region and the effects of dielectric saturation in the vicinity of the electron cavity were neglected.

The main difference between our approach and the work of Pekar,[6] Dawydow,[10] and Deigen[10] is the form assumed for the potential well. These authors assumed that Landau's potential well is adequate for representation of $V(r)$ for values of r approaching zero. This approach utilizes the concept of continuous dielectric constant for distances smaller than molecular dimensions, and the neglect of atomic structure of matter is driven to an extreme limit. This approach is inconsistent with the experimental results concerning the volume expansion of metal ammonia solutions, and leads also to the overestimation of the rearrangement energy which these workers assume to be half of the potential energy of the bound electron. According to those results[9,10] the thermal dissociation energy of the "polaron" in ammonia which may be identified with the solvation energy of the electron is one third of the binding energy in the ground level, about 0.54 ev, in disagreement with our interpretation of the experimental results. Dawydow's treatment does not present an adequate interpretation for the temperature dependence of the absorption band. For the $1s\rightarrow 2p$ transition Pekar's model[9] yields the result $h\nu=1.95\beta^2$ ev, thus $dh\nu/dt=4\times 10^{-4}$ ev/deg in disagreement with the experimental results. Another difference is that in that treatment the contribution of the electronic polarization to the total binding energy was not introduced.

The proposed model indicates the existence of higher excited states. The higher energy levels are only slightly influenced by the form of the potential well at small distances and can be adequately represented by hydrogen-like states.[37]

$$E_n\ (\text{in ev}) = -(13.56\beta^2/n^2)-(e^2/2r_i)[1-(1/D_{0p})]; \quad n>2. \tag{31}$$

The short wave region of the main absorption band should consist of a series of bands leading to a continuous absorption. This continum corresponds to the ejection of the bound electron into the conduction levels of the liquid. The measurements of Blades and Hodgins[26] indicate that the pronounced asymmetry and the continuous absorption in the short wave region of the main absorption band may represent these higher transitions leading finally to the complete ejection of the electron. The low temperature measurements of Bosch[27] show that Li and Na-ammonia films show at 20°K two bands at 1 ev and 2 ev. Potassium films show two bands at 1 ev and 1.6 ev. The high energy levels may represent transitions to higher states.[7,11]

An alternative explanation may attribute these bands to the effects caused by large concentrations of the alkali metals and the low temperatures. Fowles *et al.*[5] proposed that these conditions favor the formation of e_2 centers. On the other hand, these conditions may favor the cation-electron pair formation and dimerization of these species as proposed by the cluster theory.[1] The problem of the interpretation of the properties of alkali metals solutions at high concentrations and in media of low dielectric constant such as aliphalic ammines is still open.

ACKNOWLEDGMENT

The author wishes to thank Professor G. Stein for his valuable advice and continued interest in this work.

---

[37] Reference 8, p. 82.