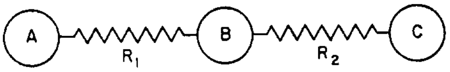

FIG. 1.

achieved at an infinite distance from any surface step, the Nernst equation can only be used for those areas. At the kinks, equilibrium is maintained not between the adsorbed atoms and the solution but between the interior of the metal and the adsorbed atoms, and all of the overvoltage is used to make deposition occur. At intermediate distances from the kinks the concentration of adsorbed atoms rises just enough to decrease the rate of deposition until it equals the divergence of the diffusive flux along the surface.

Figure 1 represents a helpful analogy. A, B, and C are conductors representing respectively the metal, the adsorbed atoms, and the solution, while R_1 and R_2 are resistances representing the resistance to diffusion to a kink and the resistance to deposition respectively. If a potential representing the overvoltage is applied between A and C, the potential of B will represent the chemical potential of the adsorbed atoms. At the kinks, R_1 is small compared to R_2 because of the short diffusion distance; the potential of B is therefore about the same as that of A; almost all the voltage drop occurs in R_2 and causes a current flow (corresponding to deposition). At an infinite distance from any step R_1 is infinite because of the long diffusion distance, so that the potential of B equals that of C and no current flows. At intermediate distances the value of R_1 and the potential of B are intermediate, and some current less than that at the kinks flows through R_1 and R_2.

* Free energy means electrochemical free energy.

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Errata: Radiolysis of Mixtures: Cyclohexane-Benzene-Iodine

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THE last words of the third paragraph should read: G (cyclohexene) = 2.3.

Units of benzene concentration in Fig. 2 are moles/liter (not 10^{-1} moles liter). The discussion employs the correct units. The legend of Fig. 2 is marred by the absence of commas. It should read: ◐$[I_2]=0$, C_6H_6. ○$[I_2]=3\times10^{-2}M$, C_6H_6. ●$[I_2]=3\times10^{-2}M$, C_6D_6.

Notes

Model for Metal Ammonia Solutions

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THE purpose of this note is to show that certain photochemical and energetic data for metal ammonia solutions can be semiquantitatively interpreted on the basis of an improved form of the electron cavity (e.c.) model.[1] The model of Alder *et al.*[2] does not provide an adequate explanation for these results.

The solvation energy H_e^s of an electron in ammonia calculated from heats of solution of alkali metals,[3] according to Verwey's method[4] is 1.7±0.1 ev. The energy for the thermal process $e_{(am)}\rightarrow e_{(g)}$ is H_e^s+ev, where v is the inner potential of ammonia. Thus H_e^s+ev has to be correlated with the photoelectric threshold a, while H_e^s is relevant to electronic transitions of the bound electron. The available experimental data on absorption spectra of these systems are presented in Table I.

The proposed model is based on Landau's model for electron capture.[5] An electron may be bound in a potential well formed by polarization of the medium by the electron itself. This picture is probably applicable to liquid systems. This model is in essence similar to that proposed for absorption spectra of anions.[6]

Considering electrostatic interactions and neglecting proton-electron exchange forces we postulate the following form for the potential energy $V(r)$. The reference state is that of a nonpolarizing electron in the medium,

TABLE I. Spectroscopic investigation of electrons in ammonia and in amines.

System	Results	Reference
Alkali metals in liquid NH_3	Continuous absorption in 500–750 mμ region	a
Na in liquid NH_3	(a) $h\nu=0.8$ ev	b, c
Films of alkali metals and NH_3 at 20°K–75°K	Li 20–50°K	
	(b) $h\nu=1$ ev	
	(c) $h\nu=2$ ev	
	Na 20–50°K	
	(d) $h\nu=1$ ev	d
	(e) $h\nu=2$ ev	
	K 20°K	
	(f) $h\nu=1$ ev	
	(g) $h\nu=1.6$ ev	
Alkali metals in $MeNH_2$	(h) $h\nu=1.9$ ev	a
Li in rigid solvent containing $MeNH_2$	(i) $h\nu=1.9$ ev	
	(j) $h\nu=2.9$ ev(weak)	
	(k) diffuse band in infrared region	e

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[d] E. Bosch, Z. Physik **137**, 89 (1954).
[e] Reference 7.

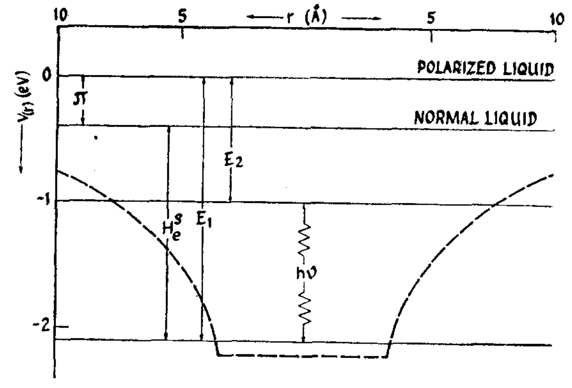

FIG. 1. $1s \rightarrow 2p$ transition of an electron in liquid ammonia.

placed at infinity from the cavity center.

$$V(r) = -\frac{s\mu e}{r_0^2} - \frac{s\alpha e^2}{2r_0^4} - \frac{2\pi N\alpha e^2}{r_0+2r_{\mathrm{NH_3}}} \qquad r<r_0 \quad \text{(1a)}$$

$$V(r) = -\frac{e^2}{r}\left(\frac{1}{D_{0p}} - \frac{1}{D_s}\right) \qquad r>r_0 \quad \text{(1b)}$$

where r_0 is the e.c. radius, $r_{\mathrm{NH_3}}$ radius of solvent molecules, s number of solvent molecules surrounding the e.c., α polarizability of solvent molecule, μ dipole moment of solvent molecule, N number of solvent molecules per cc in the bulk, and D_{0p} and D_s optical and static dielectric constants.

Equation (1a) is based on a rough structural model. The third term was obtained from the expression

$$\int_{r_0+2r_{\mathrm{NH_3}}}^{\infty} \frac{\alpha e^2}{2r^4} 4\pi N r^2 dr.$$

Equation (1b) is Landau's expression for a potential well formed by directed dipoles surrounding a negative charge. The approximate value of $r_0 = 3.6$ A is calculated assuming continuity of $V(r)$, setting $s=4$.

The dipole rearrangement energy-Π-required for formation of the potential well was calculated from an electrostatic model. The value $\Pi = 0.45$ ev was obtained.

In the potential well (1) an infinite number of stationary states ($W_1 W_2 \cdots$) exists. For the higher states:

$$W_n = \frac{me^4}{2\hbar^2 n^2}\left(\frac{1}{D_{0p}} - \frac{1}{D_s}\right)^2 \qquad n=2, 3\cdots. \quad (2)$$

For the ground (1s) state W_1 is obtained from

$$H_e^s = W_1 - \Pi \quad (3)$$

hence $W_1 = 2.1$ ev $W_2 = 1$ ev.

During the electronic transition the dipole arrangement is not changed. Hence we get

$$h\nu_{1\rightarrow n} = W_1 - W_n = H_e^s + \Pi - W_n. \quad (4)$$

We assume that these numerical results are applicable to all systems of Table I. For the $1s \rightarrow 2p$ transition $h\nu = 1.1$ ev (see Fig. 1). The intense bands a, b, d, f, h, i refer to this transition. For transitions to higher states the series limit is 2.1 ev. The bands c, e, g, j are attributed to these transitions. The experimental results for ammonia are in agreement with these calculations.

Spectrophotometric evidence for the existence of e_2 centers[1] may be found in the k band. This assumption is supported by the observation[7] that irradiation at the i band wavelengths gives rise to a reversible change in the k band intensity, indicating that at low temperatures an e.c. may possibly act as an electron trap.

Our results make possible the calculation of v for liquid ammonia.

Setting[8] $a = 1.6$ ev from

$$a = H_e^s + \Pi + ev \quad (5)$$

we get $v = -0.5$ volt.

The author wishes to thank Professor G. Stein for his help and encouragement.

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Plasma Augmentation of the Surface Conductivity of Glasses

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THE purpose of this note is to call attention to an effect which we have observed when highly ionized gases are in contact with normally nonconducting surfaces, especially glasses. Superficial conductivity is then observed over the nonconductor, and its magnitude seems to be a function of the ion (presumably electron) concentration in the plasma. At a plasma concentration of 10^{16} to 10^{17} ions/cc, superficial conductances of the order of 1 mho or less have been estimated.

The technique of the experiments was as follows: a flowing hydrogen plasma was passed down a tube through a transverse magnetic field, and probes were introduced into the plasma through holes in the glass walls. Normally the plasma resistances observed are of the order of 1000 ohms, but when the probes are allowed to touch the glass walls on both sides, the indicated resistance between the probes (while normally