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Application of Liquid Theory to Sodium-Ammonia Solution

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The significant structure theory of liquids has been successfully applied to the sodium ammonia solution. In applying the theory to sodium ammonia solution, we assumed there were four species in solution, *i.e.*, sodium cation, solvated electron, triple ion, and free electron and equilibria existed between them. Based on these assumptions, we set up the model explaining the anomalous properties of sodium ammonia solution. The partition function for sodium ammonia solution is composed of the partition functions for the above four species and also for the Debye-Hückel excess free energy term. Agreements between calculated and experimental values of the thermodynamic quantities, such as molar volume, vapor pressure, partial molar enthalpy and entropy, and chemical potential as well as viscosity are quite satisfactory.

Introduction

Since Weyl[1] has reported in 1864 that the alkali and alkaline earth metals can dissolve in liquid ammonia, ample studies have been performed to understand the anomalies of the metal ammonia solution.

An international conference in 1963, Colloque Weyl I[2], to celebrate the centenary of Weyl's discovery was convened at Lille, France and thereafter, the anomalies in physical and chemical properties of metal ammonia solutions were hot issues through four more times of conferences[3-6]. But none of the theories and the models could explain all the phenomena of metal ammonia solutions well.

These peculiar and important properties of metal ammonia solutions may be summarized as follows.

Color and Liquid-Liquid Phase Separation. Very dilute solutions of all alkali and alkaline earth metals in liquid ammonia exhibit the blue color which is considered due to the presence of the solvated electrons. Optical spectroscopy[7,8] shows that there are two intense absorption bands at 7,000 and 15,000 cm^{-1}. Using the polaron model (cavity model), Jortner[9] calculated the energy levels of the solvated electron and explained the absorption band very well.

As the metal dissolves more into the solution, the blue color fades out and the concentrated solution displays the metallic bronze color.

On the other hand, as the temperature lowers, the liquid-liquid phase separation takes place. Here, the upper phase is the concentrated solution (metallic bronze color) and the lower is the dilute solution (blue color).

Volume Expansion and Vapor Pressure. When metals dissolve in liquid ammonia, there is a remarkable increase in molar volume, amounting about 65 ml/mol which is greater that the sum of the volumes of the pure components[10,11]. This large increase in apparent molar volume must be due to the particular state of the electrons in solution and confirms the presence of the previously mentioned solvated electrons which form cavities. The average radius of the cavity calculated from the molar volume is about 3.2 Å.

In ordinary case, as the solutes(salts) dissolve into solution the vapor pressure drops continuously. But in the case of metal ammonia solution, the vapor pressure remains nearly constant until the mole ratio, $r=(\text{moles NH}_3)/(\text{moles metal})$, becomes about 10 and below this value the vapor pressure drops rapidly.

Magnetic and Electrical Properties. Very dilute solutions show the paramagnetism[13] caused by the unpaired electrons. The molar paramagnetic susceptibility decreases rapidly with increasing the concentration because of the formation of the diamagnetic species. The temperatures dependence of the molar magnetic susceptibility is positive, *i.e.*, with rising temperature the diamagentic species dissociate into the paramagnetic species and hence, the molar susceptibility increases.

The limiting value of the equivalent conductance of highly dilute sodium ammonia solution is about 1,020 Ω^{-1}cm^{2}mol^{-1}, at −33 °C[14]. When the concentration is increased to the range in which electron pairs are formed, the equivalent conductivity decreases slightly. However, the transition to the metallic state is marked by the strong increase in conductivity above 0.5 *M*. The equivalent conductivity of a saturated sodium ammonia solution is comparable to that of mercury or of pure sodium metal. This metallic conductivity is considered due to the transition of the solvated electrons to the free electron state. Over the entire concentration range, the conductivity increases with rising temperaute and decreases with rising pressure.

From the magnetic susceptibility and conductivity behaviors, electrons formed by dissociation of metals in ammonia could exist in three different states[15] and following equilibria might be formulated describing the transition from one state to another where the metal cations might be involved.

$$\underset{\text{paramagnetic}}{e_s^-} \rightleftarrows \underset{\text{diamagnetic}}{\frac{1}{2}e_2^=} \rightleftarrows \underset{\text{metallic}}{e_f^-} \qquad (1)$$

In Eq. (1), the suffix *s* and *f* indicate "solvated" and "free", respectively.

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Theory

Model. As mentioned previously the conduction behavior of the metal ammonia solution over the metal–nonmetal transition region can be explained by the equilibrium between the solvated electrons and the metallic free electrons. On the other hand, there are two experimental observations such that (i) electrons photoinjected from a cathode into liquid amonia exist in two different states, which exhibit low and high mobility[16] and which might be characterized as solvated and free electrons, and (ii) the absorption spectrum of solvated electrons persistes still in higher concentrated solutions, *i.e.*, that solvated electrons are present in solutions of metallic character[17]. Hahne *et al.*[18] proposed an equilibrium model for the interpretation of the conduction behavior of metal ammonia solution from the above two observations. The proposed quilibrium is written in the form

$$e_s^-(\mathrm{NH_3})_j \overset{K_e}{\rightleftharpoons} e_f^- + j\cdot\mathrm{NH_3} \tag{2}$$

with j the solvation number of the solvated electrons.

The equilibrium constant, K_e, is

$$K_e = \frac{[e_f^-]\,[\mathrm{NH_3}]^j}{[e_s^-(\mathrm{NH_3})_j]} \tag{3}$$

The charge and material balances are

$$[e_s^-(\mathrm{NH_3})_j] + [e_f^-] = [\mathrm{M^+(NH_3)}_l] = c_M \tag{4}$$

$$j\cdot[e_s^-(\mathrm{NH_3})_j] + l\cdot[\mathrm{M^+(NH_3)}_l] + [\mathrm{NH_3}] = c_A \tag{5}$$

where c_A, c_M, l, and $[\mathrm{NH_3}]$ are the overall concentrations of the ammonia and the dissolved metal, the solvation number of the metal cation, and the concentration of the free ammonia molecules, respectively. From the Eqs. (3) to (5), we can obtain the concentration of free electrons as a function of the concentration of dissolved metal. The data used in the calculation are given in Table 1 and compared with those of Hahne *et al.*[18]

The degree of dissociation of the dissolved metal into paramagnetic solvated electrons, as obtained from magnetic measurements[13], is plotted against the mole fraction of dissolved metal in Figure 1. The data indicate that for the mole fraction of metal, $x_M < 10^{-3}$ the paramagnetic solvated electrons predominate, while for $x_M > 10^{-3}$ the spin compensated diamagnetic species are predominant. The equilibrium between the above two species could be described by the equilibrium in Eq. (1), but it is more reasonable that some metal cations should be involved to reduce the Coulombic repulsion between the two electrons. Therefore, this diamagnetic species is rather the solvent–shared triple–ion than metal anion. Then the equilibrium can be written as

TABLE 1: Thermodynamic Data for the Equilibrium in Eq. (2) at 240 °K

	Ours	Hahne *et al.*[a]
K_e[b]	5×10^4	2.5×10^6
ΔG, cal/mole	−4420	−7000
ΔH, cal/mole	4500	50000
ΔS, cal/mole·K	37.2	50.

[a]Data at 200 bar. [b]We used molal concentration while Hahne *et al.*[18] used mole concentration.

$$2e^- + \mathrm{M^+} \overset{K_M}{\rightleftharpoons} (e^-\cdot\mathrm{M^+}\cdot e^-)\,(=\mathrm{M^-}) \tag{6}$$

$\mathrm{M^-}$ is used as abbreviation for the triple–ion for convenience sake.

The equilibrium constant K_M is

$$K_M = \frac{[\mathrm{M^-}]}{[e^-]^2\,[\mathrm{M^+}]} \tag{7}$$

And the charge and material balances are

$$[e^-] + [\mathrm{M^-}] = [\mathrm{M^+}] \tag{8}$$

$$[\mathrm{M^+}] + [\mathrm{M^-}] = c_M \tag{9}$$

The concentrations of all species were calculated using the above three equations and the degree of dissociation was represented by solid curve in Figure 1. The data used in above calculations are given in Table 2.

Figure 2 represents the concentration changes (depicted in fraction) of all species using the equilibria in Eqs. (2) and (6). Also, we regarded all the species except free electron were solvated and that there were following equilibria between the bound and free ammonia molecules.

$$M_i + \mathrm{NH_3} \overset{K_i}{\rightleftharpoons} (M_i\cdot\mathrm{NH_3}) \tag{10}$$

Here subscript i stands for i–th species.

Thus the fraction of the ammonia molecules bound to i–th species is $K_i/(1+K_i)$, and if n_i is the number of sites available for ammonia molecules bound to i–th species, the solvation number becomes $n_iK_i/(1+K_i)$.

Partition Function. According to the significant structure theory of liquids[19,20], the partition function for N molecules is generally written as

$$f_N = f_s^{\,N\frac{V_s}{V}} \cdot f_g^{\,N\left(\frac{V-V_s}{V}\right)} \tag{11}$$

in which f_s and f_g are the partition functions of the solid–like and gas–like molecules, respectively. N, V_s, and V are the Avogadro's number and the molar volumes of the solid–like molecules and liquid, respectively.

The partition function for liquid ammonia is adopted from the previous work[21].

On the other hand, the equilibrium constant, K_i, for the solvation to i–th species in equilibrium in Eq. (10) can be written as the ratio of the partition functions by

$$K_i = \frac{f_{M_i}\cdot f_{\text{bound NH}_3}}{f_{M_i}\cdot f_{\text{free NH}_3}} = \frac{f_{\text{bound NH}_3}}{f_{\text{free NH}_3}} \tag{12}$$

TABLE 2. Thermodynamic Data for the Spin Pairing Reaction in Eq. (6)

	Ours (240 °K)	Schindewolf *et al.* (238.15 °K)
K[a]	7×10^3	6.25×10^4
ΔG, cal/mole	−4223	−5020
ΔH, cal/mole	−6142	−7146
ΔS, cal/mole·K	−8	−7.6

[a]We used molal concentration while Schindewolf *et al.*[28] used molar concentration.

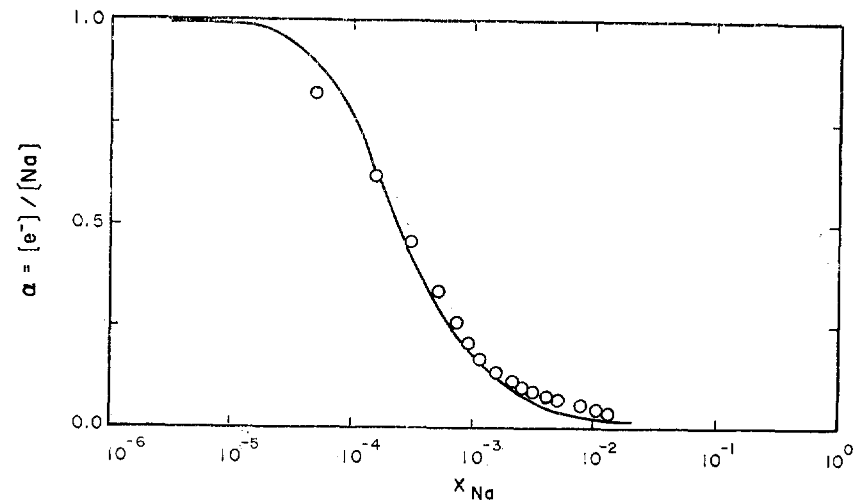

Figure 1. Relative concentration of the paramagnetic solvations from magnetic measurements. o, experimental[13]; ——, calculated.

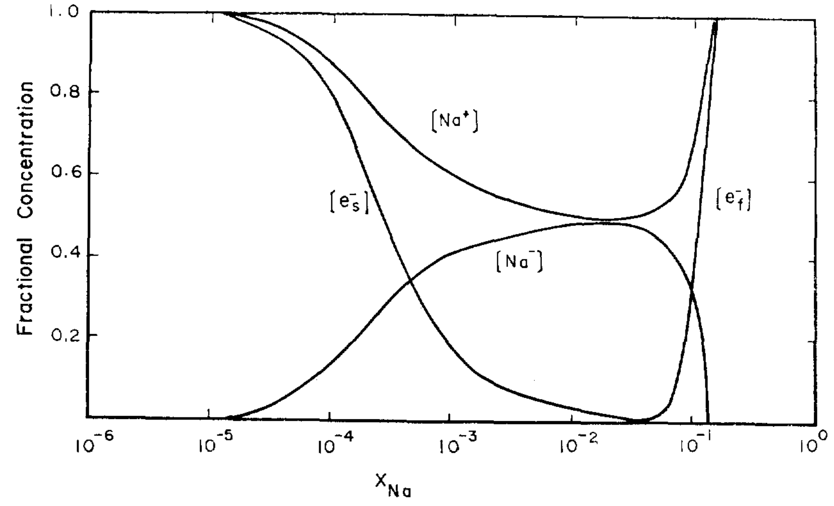

Figure 2. Relative concetrations of the four species in sodium ammonia solution.

The equilibrium constant K_M in equilibrium in Eq. (6) is

$$K_M=\frac{f_{M^-}}{f_{M^+}\cdot(f_{e_s^-})^2} \tag{13}$$

In the similar manner, K_e, in equilibrium in Eq. (1) is represented as

$$K_e=\frac{f_{e_f^-}}{f_{e_s^-}} \tag{14}$$

Now, consider a metal ammonia solution system containing m molal concentration of dissolved metal. And let the concentrations of the metal cations, triple–ions, solvated electrons, and free electrons be m_1, m_2, m_3, and m_4, respectively. Then the total partition function, f, of the system is written as

$$f=\left(f_{\mathrm{M}^+}^{m_1}\cdot f_{\mathrm{M}^-}^{m_2}\cdot f_{e_s^-}^{m_3}\cdot f_{e_f^-}^{m_4}\right)^N\cdot f_{\text{free NH}_3}^{\left(\frac{1000}{17}-\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}\right)N}$$
$$\cdot\prod_{i=1}^{3}(f_{\text{bound NH}_3})_i^{\frac{n_iK_i}{1+K_i}m_iN}\cdot f_{\text{D–H}}^{\left(\frac{1000}{17}-\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}m_i+\sum_{i=1}^{4}m\right)}\cdot f_{conf} \tag{15–a}$$

where $\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}m_iN$ is the total number of ammonia molecules bound to the ions; $\left(\frac{1000}{17}-\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}\cdot m_i+\sum_{i=1}^{4}m_i\right)N$ are the total number of free ammonia molecules and that of the entities in the system considering the ions and free ammonia molecules as independent entities. Substituting Eqs. (12) to (14) into Eq.(15–a) and using the charge and material balances, one obtains.

$$f=\left(f_M^{m}\cdot K_M^{m_2}\cdot K_e^{m_4-m}\right)^N\cdot f_{free\ \mathrm{NH}_3}^{\frac{1000}{17}N}\cdot$$
$$\prod_{i=1}^{3}K_i^{\frac{n_iK_i}{1+K_i}m_iN}\cdot f^{\left(\frac{1000}{17}\ \sum_{i=1}^{3}\frac{n_iK_i}{1+K_j}m_i+\sum_{i=1}^{4}m_i\right)}\cdot f_{\mathrm{conf}} \tag{15–b}$$

where $f_M=f_M+f_{e_f^-}$ and $m=m_1+m_2=2m_2+m_3+m_4$ ·

Here, the dissolved metal in solution is regarded as having only the solid–like degree of freedom, therefore, the partition function, f_M, for metal is given by[22]

$$f_M=e^{E_{s,M}/RT}\cdot(1-e^{-\theta_M/T})^{-3} \tag{16}$$

in which the subscript M stands for metal. And partition functions for configuration and Debye–Hückel excess free energy[23] term are given by

$$f_{\mathrm{conf}}=\frac{\left[\left(\frac{1000}{17}-\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}m_i+\sum_{i=1}^{4}m_i\right)N\right]!}{\left[\left(\frac{1000}{17}-\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}m_i\right)N\right]!\ \prod_{i=1}^{4}(m_iN)!} \tag{17}$$

and

$$f_{\mathrm{D-H}}=\exp\left\{\frac{V}{8\pi a'^3}\left[\frac{a'^3\kappa^3-1}{1+a'\kappa}+1+a'\kappa-2\ln(1+a'\kappa)\right]\right\} \tag{18}$$

where

$$\kappa^2=\frac{4\pi Ne_0^2}{\varepsilon kT}\sum_{i=1}^{4}c_iz_i^2 \tag{19}$$

$$a'=\left[\frac{3}{4\pi}\left(V_{\mathrm{M}^+}+V_{e^-}+\sum_{i=1}^{3}\frac{n_iK_i}{1+K_i}V_{s,\mathrm{NH}_3}\right)\right]^{\frac{1}{3}} \tag{20}$$

in which κ and a' are the ionic atmosphere and the mean radius of the solvated ion; e_0 and ε are the charge of electron and dielectric constant of ammonia; c_i and z_i are the concentration and valence of the i–th species.

However, the solid–like molar volume, V_s, of the system is written as assuming the additivity rule

$$V_s=V_{s,\mathrm{NH}_3}\cdot x_{\mathrm{NH}_3}+V_{s,\mathrm{M}}\cdot x_{\mathrm{M}}+V_{s,e^-}\cdot x_{e^-} \tag{21}$$

where subscripts stand for the species and x's are the mole fractions of the corresponding species. Here, the free electrons contribute to V_s as same as the solvated electrons do.

We assume the ammonia molecules are divided into three classes as follows:

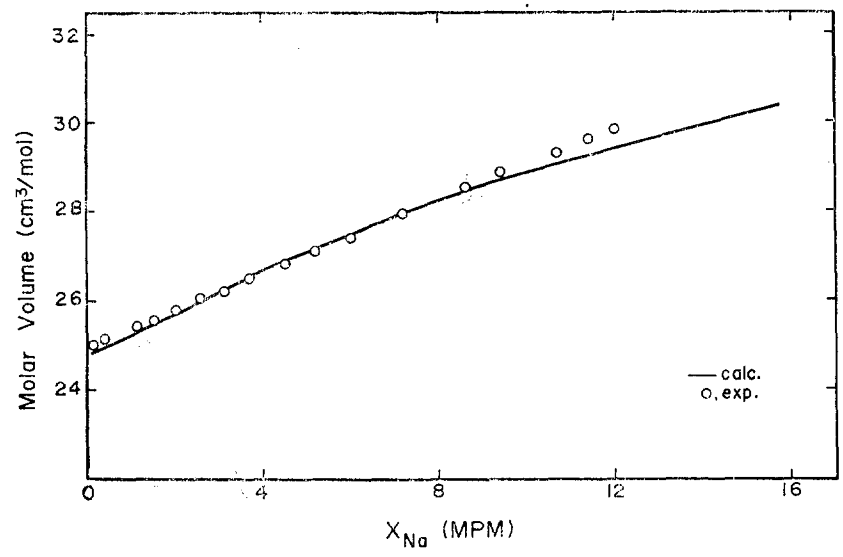

Figure 3. Molar volume of the sodium ammonia at 140 °K[26].

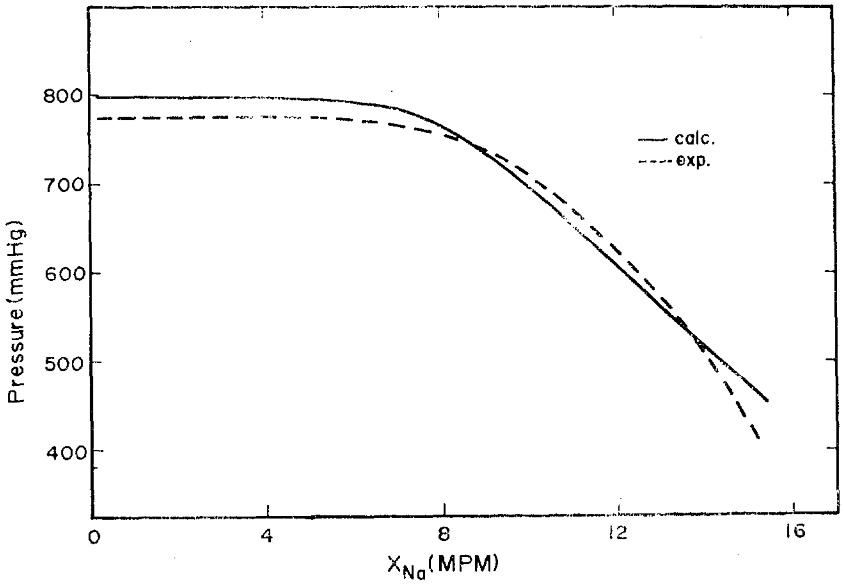

Figure 4. Vapor of the sodium ammonia solution at 240 °K[27].

TABLE 3: Thermodynamic Data for the Equilibria of Solvations of the Species in Solution at 240 °K

Species	Na$^+$	Na$^-$	e_s^-
K_i	5.	2.6	4.
ΔG, cal/mole	−767.9	−455.7	−661.2
ΔH, cal/mole	−983.9	1679.1	4100.
ΔS, cal/mole·K	−0.9	8.9	19.8
n_i, site number	6.	18.	5.
$\frac{n_iK_i}{(l+K_i)}$, solvation umber	5.	13.	4.

TABLE 4: Parametric Values used in Partition Functions

Species	NH$_3$	Na	e_s^-
E_s°, cal/mole	6332.0	25750.0	
E_s', cal/mole	6632.	—	—
E_s'', cal/mole	5932.	—	—
V_s, m*l*/mole	22.4	24.7	47.
θ, °K	142.63	93.75	—
n	11.543	—	—
a	9.236×10^{-3}	—	—

(i) free ammonia molecules which have the normal sublimation energy of ammonia, E_s°

(ii) ammonia molecules participating in solvation of metal cations, which have somewhat higher sublimation energy, E_s' $(<E_s^\circ)$, due to the structure making effect of the metal cations[24]

(iii) ammonia molecules participating in solvation of solvated electrons, which have lower sublimation energy, $E_s''(<E_s^\circ)$, due to the structure breaking effect of the solvated electrons[25].

Hence, the sublimation energy, E_s, of ammonia in this system can be additively written as

$$E_s=E_s^\circ\cdot x_{\text{free NH}_3}+E_s'\cdot x_{\text{NH}_3,\text{M}^+}+E_s''\cdot x_{\text{NH}_3,e_s^-} \tag{22}$$

where x's are the fractions of three kinds of ammonia molecules against the total amonia molecules.

Calculations and Results

All the calculations are carried out for the sodium ammonia solution over the whole concentration range at 240 °K. The parametric values used in calculations are listed in Tables 3 and 4.

Molar Volume and Vapor Pressure. The Helmholtz free energy, A, is given by $A=-kT\ln f$. If A is plotted as a function of molar volume V at constant temperature and a common tangent to the points corresponding to the liquid phase and vapor phase is drawn, vapor pressure equals to the slope of the common tangent and the abscissas of the two tangential points are the molar volumes of liquid and vapor phases, respectively. The results are shown in Figures 3 and 4, and compared with the observed values of the molar volume[26] and vapor pressure[27]. The solid curves (calculated) in Figures 10 and 11 explain the large increase in molar volume and anomalous vapor pressure behavior of sodium ammonia solution very well.

Partial Molar Entropy, Enthalpy, and Chemical Potential. The entropy, enthalpy, and Gibbs free energy of the system are represented in terms of partition function as follows

$$S=-\left(\frac{\partial A}{\partial T}\right)_V=k\left(\frac{\partial(T\ln f)}{\partial T}\right)_V \tag{23}$$

$$H=kT^2\left(\frac{\partial\ln f}{\partial T}\right)_V+VkT\left(\frac{\partial\ln f}{\partial V}\right)_T \tag{24}$$

$$G=-kT\ln f+VkT\left(\frac{\partial\ln f}{\partial V}\right)_T \tag{25}$$

Consider a binary mixture system, then the excess properties of a mixture can be written by the relation[19].

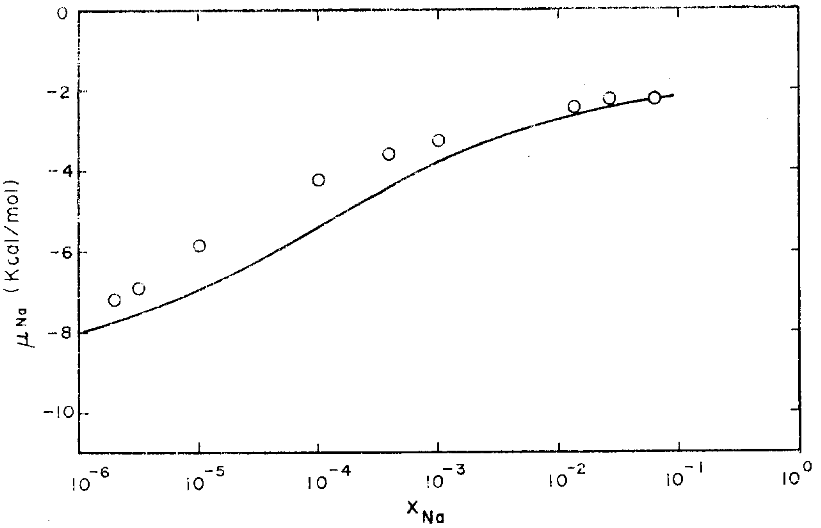

Figure 5. Chemical potential of sodium in ammonia solution at 240 °K. o, experimental[28]; ——, calculated.

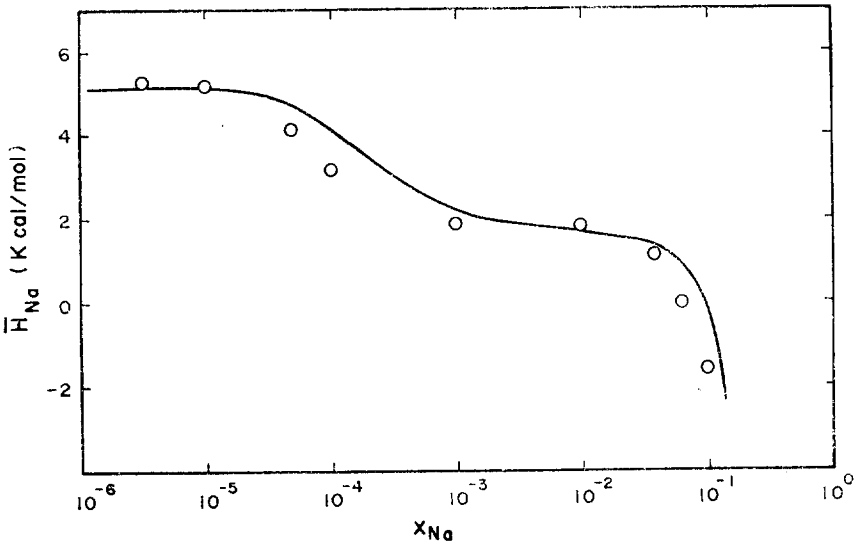

Figure 6. Partial molar enthalpy of sodium in ammonia solution at 240 °K. o, experimental[28]; ——, calcuated.

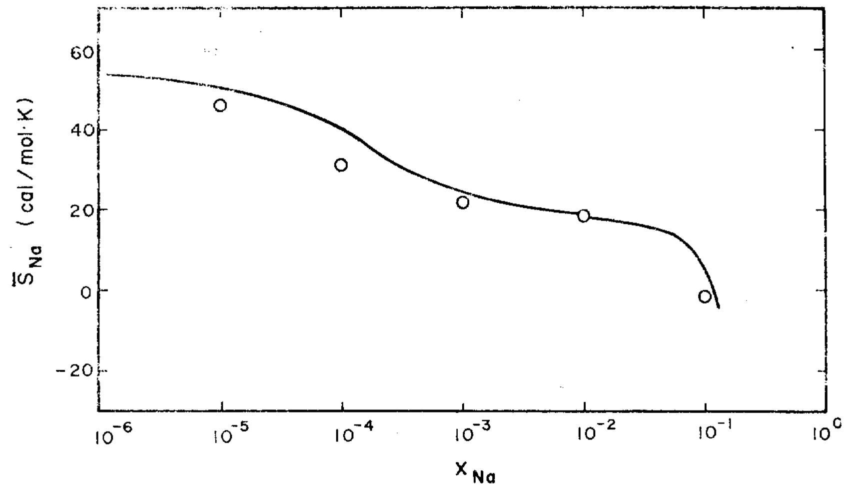

Figure 7. Partial molar entropy of sodium in ammonia solution at 240 °K. o, experimental[28]; ——, calculated.

$$S^E=S-(x_1S_1^\circ+x_2S_2^\circ)+R(x_1\ln x_1+x_2\ln x_2) \tag{26}$$

$$H^E=H-(x_1H_1^\circ+x_2H_2^\circ) \tag{22}$$

$$G^E=G-(x_1G_1^\circ+x_2G_2^\circ)-RT(x_1\ln x_1+x_2\ln x_2) \tag{28}$$

where subscript i shows the i-th component; x's are the mole fractions of the corresponding components; superscript o stands for the pure component. The third terms in Eqs. (26) and (28) represent the mixing terms for entropy and free energy. Then, the partial molar quantities, $\bar{Y}_i$'s, are obtained using the relation of $\bar{Y}_i=Y_i^E/m_i$. The results are shown in Figures 5 to 7 with the experimental values[28]. The agreement between two curves in each case is satisfactory.

Viscosity. The visocosity, n, is given by the sum of two terms

$$\eta=\frac{V_s}{V}\eta_s+\frac{V-V_s}{V}\eta_g \tag{29}$$

where η_s and η_g are the visocosities contributed by solid-like and gas-like molecules. Assuming that solutes (sodium cations) do not contribute to the viscosity, the viscosity equation for solid-like molecules is simply derived from Eyring's earlier procedure[29]

$$\eta_s=\frac{Nh}{Z\kappa}\frac{V}{V_s}\frac{6}{\sqrt{2}}\frac{1}{V-V_s}\cdot\frac{1}{1-e^{-\theta/T}}\exp\left[\frac{a'E_sV_s}{(V-V_s)RT}\right] \tag{30}$$

in which Z and κ are the site number of nearest neighbors and the transmission coefficient.

The term η_g is derived from the kinetic theory of gases[30] and is given by

$$\eta_g=\frac{2}{3d^2}\left(\frac{mRT}{\pi^3}\right)^{\frac{1}{2}} \tag{31}$$

where d is the diameter of the molecules. The calculated and experimental[31] results are shown in Figure 8 and the agreement between two curves is satisfactory.

Discussion

As known earlier, we have found that the large increase in molar volume is mainly due to the cavity formation of solvated electrons. And also the molar volume of the electrons in sodium ammonia solution is nearly unchanged in spite of the formation of diamagnetic triple-ions or transition to the metallic free electrons[11,32]. Therefore, the triple-ions are considered as the species that

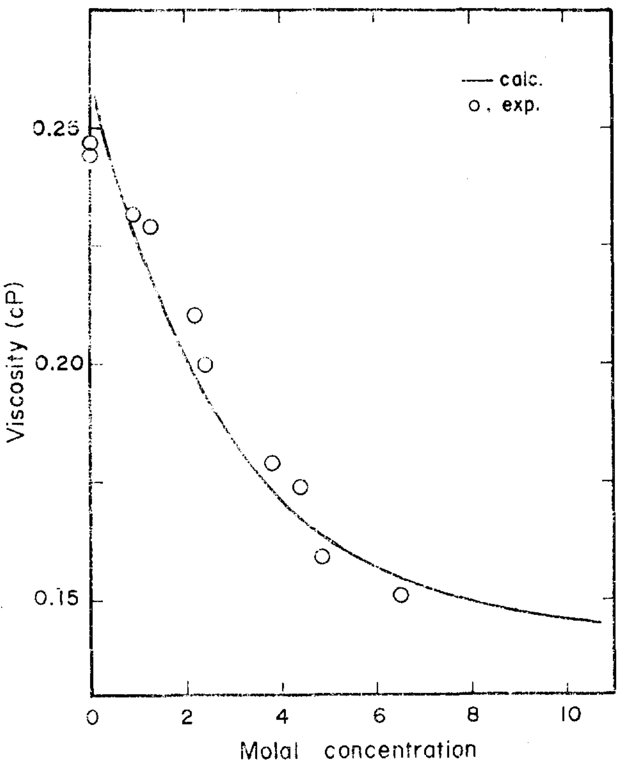

Figure 8. Viscosity against molality of solution at −33 °C[31].

two solvated electrons approach each other to proper distance reducing the repulsion between them by the presence of metal cation and only the electron spins are compensated by spin interaction. From this, we treated the volume of the triple-ions is merely the sum of volumes of two solvated electrons and of solvated sodium cation.

Moreover, the solvated electron interacts with the surrounding ammonia molecules repulsively (ΔH_3=4100 cal/mole) and so has the effect by which the sublimation energy of surrounding ammonia molecules is reduced, while the sodium cation effects the increase in the sublimation energy of neighboring ammmonia molecules by the attractive interaction ($\Delta H_1 = -984$ cal/mole).From these assumptions the pressure behavior of sodium ammonia solution can be interpreted very fwell.

The partial molar enthalpy which is independent of concentration in ideal solution has two plateaus in sodium ammonia solution;one below $x_{Na}=10^{-5}$, the other between $x_{Na}=5\times10^{-4}$ and $x_{Na}=10^{-2}$. The drop between these two plateaus may be related to the enthalpy changes associated with the transition from the paramagnetic to the diamagnetic state, and the other drop below 5×10^{-2} to the transition from the diamagnetic to the metallic state. And above two transitions are both exothermic.

As the free volume of electrons is introduced into solution, the viscosity decreases inversely proportional to the sodium concentration. As assumed in our model, the sodium cations do not contribute to the viscosity behavior in solution while the electrons reduce the viscosity by conferring free volumes.

From the various facts found, the anomalous properties of metal ammonia solution are caused by the behavior of electrons in solution; increasing the volume and decreasing the viscosity by introducing additional free volume into solution; vapor pressure increasing effect of solvated electrons by repulsive interaction with surrounding ammonia molecules and by decrease of the fraction of these solvated electrons according to the transition to metallic free electrons; changing to diamagnetic state or from the diamagnetic to metallic state.

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Molecular Theory of Plastic Deformation (III)*

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(1) The flow data of f (stress) and $\dot{s}$ (strain rate) for Fe and Ti alloys were plotted in the form of f *vs.* $-\ln \dot{s}$ by using the literature values. (2) The plot showed two distinct patterns A and B; Pattern A is a straight line with a negative slope, and Pattern B is a curve of concave upward. (3) According to Kim and Ree's generalized theory of plastic deformation, pattern A & B belong to Case 1 and 2, respectively; in Case 1, only one kind of flow units acts in the deformation, and in Case 2, two kinds flow units act, and stress is expressed by $f = X_1 f_1 + X_2 f_2$ where f_1 and f_2 are the stresses acting on the flow units of kind 1 and 2, respectively, and X_1, X_2 are the fractions of the surface area occupied by the two kinds of flow units; $f_j = (1/\alpha_j) \sinh^{-1} \beta_j \dot{s}$ ($j = 1$ or 2), where $1/\alpha_j$ and β_j are proportional to the shear modulus and relaxation time, respectively. (4) We found that grain-boundary flow units only act in the deformation of Fe and Ti alloys whereas dislocation flow units do not show any appreciable contribution. (5) The deformations of Fe and Ti alloys belong generally to pattern A (Case 1) and B(Case 2), respectively. (6) By applying the equations, $f = (1/\alpha_{g1}) \sinh^{-1} (\beta_{g1} \dot{s})$ and $f = (X_{g1}/\alpha_{g1}) \sinh^{-1} (\beta_{g1} \dot{s}) + (X_{g2}/\alpha_{g2}) \sinh^{-1} (\beta_{g2} \dot{s})$ to the flow data of Fe and Ti alloys, the parametric values of x_{gj}/α_{gj} and β_{gj} ($j = 1$ or 2) were determined, here the subscript g signifies a grain-boundary flow unit. (7) From the values of $(\beta_{gj})^{-1}$ at different temperatures, the activation enthalpy $\Delta H_{gj}^{\neq}$ of deformation due to flow unit gj was determined, $(\beta_{gj})^{-1}$ being proportional to k_{gj}, the jumping frequency (the rate constant) of flow unit gj. The $\Delta H_{gj}^{\neq}$ agreed very well with $\Delta H_j^{\neq}$ (self-diff) of the element j whose diffusion in the sample is a critical step for the deformation as proposed by Kim-Ree's theory (Refer to Tables 3 and 4). (8) The fact, $\Delta H_{gj}^{\neq} = \Delta H_j^{\neq}$ (self-diff), justifies the Kim-Ree theory and their method for determining activation enthalpies for deformation. (9) A linear relation between β^{-1} and carbon content $[C]$ in hot-rolled steel was observed, *i.e.*, $\ln \beta^{-1} = -50.2 [C] - 40.3$. This equation explains very well the experimental facts observed with regard to the deformation of hot-rolled steel.

1. Introduction

It may be said that the Nabarro-Herring theory[1] of lattice diffusion and Coble's grain boundary diffusion theory[2] are the representatives among many theories of plastic deformation in the literature. The Raj and Ashby equation[3] is an equation which was developed from Nabarro-Herring theory. But, all these theories are applicable in a limited stress region only. Thus, in order to describe plastic deformation in a wide range of stress, a phenomenological equation was proposed.[4] However, it includes many parameters which are lack of physical meanings.

In this study, the Kim-Ree generalized theory of plastic deformation[5-8] is applied to Fe and Ti alloys. This theory is an extension of the Ree-Eyring theory of viscous flow,[9,10] and has an advantage to describe plastic deformation in a wide range of stress, in addition, the physical meanings of the parameter in the equations are clear.

The activation enthalpies $\Delta H^{\neq}$ for the plastic deformation have been calculated from Kim-Ree's theory, and they have been compared with the activation enthalpies of self-diffusion $\Delta H^{\neq}_{\text{self-diff}}$ of the elements in the alloys. It has been found

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