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CONSIDERATION OF IONIC ATMOSPHERE IN THERMODYNAMIC STUDY OF LIQUID ALKALI METALS

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The thermodynamic behaviour of a metal, i.e., an assembly of ions and electrons having an ionic atmosphere about each ion are studied from the point of view of the Debye-Huckel theory of ionic solutions. To avoid an inconsistency between a partly microscopic and partly macroscopic approach, the value of the dielectric constant, D, for the medium in the Poisson equation is taken to be unity, i.e., the solvent is absent. The contribution due to the ionic atmosphere in the expression for the free energy is calculated and then added to the kinetic energy and internal energy of the assembly to obtain the total free energy. For experimental verification the free energies "based on H^0_{298}" are calculated for the liquid alkali metals for the range of temperatures from 298 K to 800 K from the expression for free energy obtained here. Also the values of entropy at the melting points are calculated for liquid metals and then subtracted from the accepted values of entropy for solid metals at the melting points to obtain entropy changes. It is striking to note that the agreement between calculated and standard values in both cases are fairly good.

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1. *Introduction*

In the Debye-Huckel [1] theory of ionic solutions, ions are distributed according to the Boltzmann distribution formula and the effect of the Coulomb interaction (assumed to be of an electrostatic nature) is taken into account through the Poisson equation. In this theory the notion of ionic atmosphere is important. It is characterized by a certain regularity in the distribution of ions. This notion of ionic atmosphere is also introduced in other theories of assembly of charged particles like plasmas etc.

It is easy to see that in the Debye-Huckel theory and its modifications, the effects of the Coulomb interaction is considered for solute ions but the effect of the solvent is considered through the introduction of the dielectric constant in the Poisson equation. In these theories the molecular (microscopic) structure of the solute is used but at the

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same time a macroscopic picture is taken for the solvent through the dielectric constant, D. While the ionic picture of the solute is introduced, to take the effect of the solvent into account through the introduction of the dielectric constant, the solvent is continuum, appears to be a very gross approximation. Thus there is a logical inconsistency in the theory. So in the present work, the value of the dielectric constant is taken to be unity to avoid an inconsistency between a partly microscopic and partly macroscopic approach. This means that the solvent is absent or equivalently, the substances are in the pure state. Here, as the metals are taken in pure state, there is no solvent medium, i.e., $D = 1$. In this connection, it is to be mentioned that the present model is logically more consistent as the model is fully microscopic.

With this objective in view, in the recent papers of Pal and Chakrabarti [2, 3], free energies of the alkali halides in the solid phase were investigated for a range of temperatures from 298 K to 800 K by the technique of the Debye-Huckel theory, after replacing the Boltzmann distribution formula by that of Dutta-Bagchi [4] and Dutta [5] respectively. In another paper of Pal and Chakrabarti [6], the free energies of alkali metals were investigated by the use of the distribution formula of Dutta [5]. There in all the papers [2, 3, 6], in the Poisson equation, the dielectric constant, D, for the medium was taken to be unity and excellent agreement was obtained between the calculated and accepted values. In the present paper essentially the same idea is considered and the free energies of the liquid alkali metals at different temperatures are calculated by the standard technique of the Debye-Huckel theory. Also the entropy changes at the melting points for the liquid alkali metals are calculated. The effect of the Coulombian interaction between the positively charged ions and the negatively charged electron gas is taken into account through the Poisson equation. Of course, the values of the dielectric constant, D, is taken to be unity, i.e., the solvent is absent. Here, agreement of the calculated values with the accepted values, given in the standard tables, are satisfactory.

2. *Calculations*

Assuming that the Boltzmann law of the distribution of particles in a field of varying potential energy is applicable to ions, the time average numbers of positive ions (dn_+) and of electrons (dn_-) present in the volume element dV are given by

$$dn_\pm = n_\pm \exp(\mp Z_\pm \varepsilon \psi / kT) dV, \tag{1}$$

where $n_\pm$ is the number of positive ions or electrons in a unit volume and ψ is the time-average of the electrical potential in the volume element dV. ε, k and T have their usual significance.

The charge density in a medium of dielectric constant, D, is given by

$$\varrho = (Z_+ dn_+ - Z_- dn_-)/dV = -(\varepsilon^2 \psi \sum_i n_i Z_i^2)/kT. \tag{2}$$

The most direct method of evaluating ψ is by solving Poisson's equation

$$\nabla^2 \psi = -(4\pi\varrho)/D. \tag{3}$$

The solution of Poisson's equation is given by Debye-Huckel [1] as

$$\psi_i(r) = -\frac{Z\varepsilon}{D}\,\frac{\exp(\chi a)}{1+\chi a}\,\frac{\exp(-\chi r)}{r}, \tag{4}$$

where

$$\chi = \left(\frac{4\pi\varepsilon^2}{DkT}\sum_i n_i Z_i^2\right)^{1/2}. \tag{5}$$

The potential energy of an ion with respect to its ionic atmosphere is therefore

$$u_i = \int_a^{\alpha} \frac{Z_i\varepsilon}{Dr}\,4\pi r^2 \varrho\, dr = -(Z_i^2\varepsilon^2\chi)/D(1+\chi a). \tag{6}$$

From equation (6) the following is obtained for the potential at an ion with the charge $Z_i\varepsilon$

$$\psi_i = -(Z_i\varepsilon\chi)/D(1+\chi a). \tag{7}$$

The free excess energy from the potential at the point occupied by the ion using the charging process is

$$w = \sum_{i=1}^{s-1} N_i \int_0^{\alpha} \psi_i(\lambda) Z_i \varepsilon\, d\lambda \tag{8}$$

$$= -V \sum_{i=1}^{s-1} [(n_i Z_i^2 \varepsilon^2)/D] \int_0^1 (\lambda^2 d\lambda)/(1+\lambda\chi a), \tag{9}$$

where $\psi_i(\lambda)$ is the potential corresponding to a system with the charges λZ_i and $\chi(\lambda) = \lambda\chi$.

Thus the work required in charging a single positive ion is given as

$$W = \left(\frac{(Z_+\varepsilon)^2\chi}{D(\chi a)^3}\right)[\chi a - (\chi a)^2/2 - \ln(1+\chi a)]. \tag{10}$$

In this paper

$$n_+ = n_- = n, \quad D = 1, \quad Z_+ = Z_- = 1,$$

a is the radius of a sphere whose volume is equal to the volume per conduction electron, given by [8]

$$V/N = 1/n = (4\pi a^3)/3 \quad \text{or} \quad a = (3/4\pi n)^{1/3} \tag{11}$$

and $n = (0.6025 \times 10^{24} \times \varrho_{\mathrm{m}})/M$ so that

$$\chi^2 = (8\pi\varepsilon^2 n)/kT \tag{12}$$

$$W = \varepsilon^2\chi[\chi a - (\chi a)^2/2 - \ln(1+\chi a)]/(\chi a)^3. \tag{13}$$

For one gm mole ($n_+ = n_- = N$ = Avogadro number), the total work required in charging all the positive ions is

$$F = N\varepsilon^2\chi[\chi a-(\chi a)^2/2-\ln(1+\chi a)]/(\chi a)^3. \tag{14}$$

On adding the contribution made to the free energy by the translational motion of the ions and contribution due to internal motions we obtain, as an expression for the free energy of metals in vacuum,

$$A = NkT\ln\left[\frac{Nh^3}{(2\pi MkT/N)^{3/2}Ve}\right]+\frac{N\varepsilon^2\chi}{(\chi a)^3}\left[\chi a-\frac{(\chi a)^2}{2}-\ln(1+\chi a)\right]+\tfrac{3}{2}NkT, \tag{15}$$

where M is the atomic weight of metals, V is the volume of metals in c.c., e is the base of natural logarithm.

Entropy

$$S = -\left(\frac{dA}{dT}\right)_V = -Nk\ln\left[\frac{Nh^3}{(2\pi MkT/N)^{3/2}Ve}\right]-\left[\frac{NW}{T}+\frac{N\varepsilon^2\chi}{2T(1+\chi a)}\right] \tag{16}$$

and

$$S_{\mathrm{m}} = S_{\mathrm{liquid}}-S_{\mathrm{solid}} \tag{17}$$

$$F_T^0 = H_T^0-TS = H_T^0+T\left(\frac{dA}{dT}\right)_V \therefore -(F_T^0-H_{298}^0)/T = -(H_T^0-H_{298}^0)/T-\left(\frac{dA}{dT}\right)_V. \tag{18}$$

3. *Results*

From formula (18) the numerical values of free energies "based on H_{298}^0" are calculated from 298 K to 800 K. The radii of the free electron spheres are slightly adjusted from that of the exact values as in equation (11), only at room temperatures, i.e., at 298 K and then these adjusted values are kept unaltered at other temperatures. In the previous three papers [2, 3, 6] we have considered the temperature variation of "a". In the present paper we neglect it as it contributes nothing significant to the results. The density, ϱ_T, of the liquid alkali metals at different temperatures, T, are taken from Weast [9]. The values of $H_T^0-H_{298}^0$ of the liquid alkali metals are taken from Stull and Prophet [7]. A table of both calculated and accepted (standard) values of $-(F_T^0-H_{298}^0)/T$ is given (Table I). Also from formula (16) the numerical values of the entropy of the liquid metals at the melting points are calculated. The values of entropy thus calculated are subtracted from the accepted values [7, 10] of the entropy of solid metals to obtain entropy changes. In Table II calculated and accepted values of the entropy changes are given. A comparison between the calculated and accepted values [7] in all the cases clearly reveal that fairly good agreement is obtained.

TABLE I

Free energies based on H^0_{298} for liquid alkali metals

Metal		$-(F^0_T - H^0_{298})/T$ in calories per degree mole					
		298 K	400 K	500 K	600 K	700 K	800 K	a(Å)
Li	accepted	8.113	8.405	8.951	9.557	10.158	10.734	1.81
	calculated	8.115	8.594	9.103	9.590	10.043	10.462	
Na	accepted	13.827	14.130	14.693	15.314	15.928	16.514	2.3
	calculated	13.838	14.210	14.653	15.091	15.508	15.894	
K	accepted	17.078	17.381	17.944	18.566	19.182	19.772	2.8
	calculated	17.115	17.422	17.826	18.459	18.642	19.023	
Cs	accepted	22.005	22.306	22.869	23.494	24.117	24.718	3.3
	calculated	22.118	22.357	22.716	23.100	23.480	23.848	

TABLE II

Entropy changes of melting

Metal	T_m (K)	S_{solid}(acc) e.u.	S_{liquid}(calc) e.u.	S_m(acc) e.u.	S_m(calc) e.u.	a(Å)
Li	453.7	9.10	10.57	1.50	1.47	1.81
Na	371.0	13.35	15.07	1.70	1.71	2.30
K	336.4	16.15	17.77	1.70	1.62	2.80
Rb	312.6	18.35	20.02	1.68	1.67	2.90
Cs	301.5	20.40	22.18	1.65	1.78	3.30

4. Conclusion

In this paper the free energies and the entropy changes are calculated by the standard technique of the Debye-Huckel theory of ionic solutions. However, the main difference is that instead of the electrostatic force between the ions the force is between the positive ion and electron. Also when taking $D = 1$, the unsatisfactory feature of considering both microscopic and macroscopic picture together was avoided and the substances are in the pure state. The good agreement provides stronger support for our new model.

In this connection the following points may be noted. A liquid metal is a severe test for any liquid theory. Since the conducting (nonlocalized) electrons of a metal are spread out over the positive ions, rather than the metal atoms, it is the metal ions which become displaced from their lattice positions or fluidized. The force of interactions between the atoms in a metal is electrostatic in nature and depends on the distribution of outer electrons in space. It is the attraction between the positively charged metal ions and the negatively charged electron gas that binds the configuration of the system. Drude [11] and Lorentz [12] assumed that the free electrons in metals could be treated as an ideal gas of free particles when in thermal equilibrium, and obey Maxwell-Boltzmann statistics.

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