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FREE ENERGIES BASED ON H^0_{298} OF THE ALKALI METALS IN CONDENSED PHASE

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Free energies of five alkali metals in the condensed phase have been calculated with due consideration for Coulombian and hard core repulsive interactions using the distribution formula of Dutta. The method applied here is similar to that of the Debye-Huckel theory for strong electrolytes in solution. The only difference is that the value of the dielectric constant, D, for the medium is taken to be one, i.e., the solvent is absent. The free energy thus calculated is added to the contribution of kinetic energy to obtain the total free energy. For experimental verification the free energy "based on H^0_{298}" was calculated for a range of temperatures from 298 K to 1000 K.

1. *Introduction*

The calculation of the free energy of any substance, particularly in crystalline form lattice vibration, was fully developed by Einstein [1], Debye [2], Born [3] and others. According to experimental evidences, the substances like alkali metals exist as free ions and therefore the notion of ionic atmosphere is important. So for studying the thermodynamic properties of substances like alkali metals, with due consideration for the Coulombian and short range forces, the Debye-Huckel theory [4] with the necessary modifications [5–11] should be duly considered.

The notion of an ion atmosphere is important in the theory of Debye-Huckel which is practically accepted as satisfactory in the limiting case of extremely dilute solutions. Although this theory has given a valuable insight into the nature of ionic solutions, there

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remains some unsolved questions of its validity when considering the mocroscopic picture for solute ions together with the macroscopic picture for the solvent through the dielectric constant, and secondly when the short-range forces between the ions, etc., are considered.

It is evident that in the pure state the short-range interaction particularly hard core repulsive type should be taken into account. To take into account the short-range forces of the hard core repulsive type, instead of using the Boltzmann distribution formula, the distribution formula of Dutta-Bagchi [12] was used in the paper of Pal and Chakrabarti [13]. The distribution formula of Dutta-Bagchi [12] really corresponds to the state where binary encounters are very important. In the state where higher order encounters are significant, this formula requires modification. In 1966, Dutta [14] modified it [12] from the consideration of close packing. This formula [14] was used in the papers of Pal [15] and Pal and Chakrabarti [16, 17].

In all the above theories concerning the molecular (microscopic) structure of solutions, the dielectric constant has been used for the solvent which is a macroscopic property of the system. Thus, there is a logical inconsistency when considering the microscopic and macroscopic picture together. This difficulty can be avoided if the dielectric constant, D, for the medium is taken to be one. This means that the solvent is absent or, equivalently, the substances are in pure state. With this objective in view the free energies for alkali halides in the solid phase for a range of temperatures from 298 K to 800 K were recently investigated [13, 16]. An excellent agreement was obtained between the calculated and accepted values. In this paper this is done for alkali metals in the condensed phase using the distribution formula of Dutta [14].

In this connection the following points should be noted. The force of interactions between the atoms in a metal are electrostatic in nature and depend on the distribution of outer electrons in space. The attractive force increases as the distance between the atoms decreases until a limit is reached, when a short range repulsive force between the like charges of nuclei comes into play. The metal atoms part with their valence electrons which move through the volume of the crystal like an electron gas or electron fluid. It is the attraction between the positively charged metal ions and the negatively charged electron gas that binds the configuration of the system. Drude [18] and Lorentz [19] 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.

2. *Calculations*

The complete derivation of the distribution formula of Dutta [14] was given following a method developed by Dutta [20] in connection with the statistical investigations of real gases. He also introduced a modified technique in which notion of coursegraining was employed for taking into account the hard core potential in addition to other potentials. The above method of taking into account the hard core potential has a wider acceptance in the literature of Statistical Physics [21].

In this distribution formula, as assembly under consideration consists of N_+ and N_- particles with charges Z_+ and Z_-, respectively. The forces are of regular type, so that the configurational space is divided into potential layers of potential $-\psi_1, -\psi_2, \ldots -\psi_n \ldots$ so that the potential energies in the n-th layer of particles of the first and second type are $Z_+\varepsilon\psi_n$ and $Z_-\varepsilon\psi_n$ respectively. These layers are again devided into cells of volume b. If b_+ and b_- denote the exclusion volume of the first and second types for particles of the same types and $b_{+-}(= b_{-+})$ denote the same for particles of different types and if we write

$$p_+ = \left[\frac{b}{b_+}\right], \quad p_- = \left[\frac{b}{b_-}\right], \quad p_{j+} = \left[\frac{b-jb_{+-}}{b_+}\right], \quad p_{l-} = \left[\frac{b-lb_{+-}}{b_-}\right]$$

then a cell may remain vacant or may be occupied utmost by p_+ particles only of the first type, or utmost by p_- particles only of the second type, or utmost by p_{j+} particles of the first type when it is already occupied by j particles of the second type or utmost p_{l-} particles of the second type when it is already occupied by l particles of the first type.

In 1966, Dutta deduced a distribution formula by considering the above mentioned description of the assembly and from the simple properties of ions by a method developed by Dutta [20].

In the case of an assembly of charged particles if it is assumed that the average minimum approach of oppositely charged particles is very small compared to that of the particles of like charges, i.e., $b_{+-} \ll b_+$ and b_- then the distribution formula of Dutta [14] is given by

$$n_\pm = \frac{1}{b}\left[\frac{1}{\exp(v_\pm \pm Z_\pm\varepsilon\psi/kT)-1} - \frac{(p_\pm+1)}{\exp\{(p_\pm+1)(v_\pm \pm Z_\pm\varepsilon\psi/kT)\}-1}\right]. \tag{1}$$

Here $n_\pm$ is the number densities of positive ions and electrons at a point where the electrostatic potential is ψ. $b = \frac{4}{3}\pi(2r)^3$ is the volume of a cell so that a cell may be either vacant or occupied by $p_\pm$ particles only, r being the radii of positive ions. $v_\pm$ are parameters of the distribution, Z_+ is the valency of positive ions, Z_- is the number of valency electrons, ε, k, T have their usual significances.

Taking $p_\pm = 2$

$$n_\pm = \frac{1}{b}\left[\frac{1}{\exp(v_\pm \pm Z_\pm\varepsilon\psi/kT)-1} - \frac{3}{\exp\{3(v_\pm \pm Z_\pm\varepsilon\psi/kT)\}-1}\right]. \tag{2}$$

As sometimes assumed in the theory, when $\psi \to 0$, the distribution is, on average, uniform, i.e.,

$$n_\pm^0 = \frac{1}{b}\left[\frac{1}{\exp(v_\pm)-1} - \frac{3}{\exp 3(v_\pm)-1}\right]. \tag{3}$$

The charge density, ϱ, at any point in the assembly is given by

$$\varrho = \varepsilon(n_+Z_+ - n_-Z_-), \tag{4}$$

where ε is the charge of an electron. Thus, for small values of ψ we have when

$$\frac{\varepsilon\psi}{kT} \ll 1, \qquad \varrho_{\psi\to 0} = -\frac{\varepsilon^2}{bkT}\sum A_i Z_i^2 \psi, \tag{5}$$

where

$$A_i = 3B_i + \frac{2}{C_i - 1}(B_i - 1) - B_i^2, \tag{6}$$

$$B_i = n_i^0 b, \tag{7}$$

and C satisfies

$$\sum_{p=0}^{2} C_i^p B_i = \sum_{p=1}^{2} p C_i^{2-p}. \tag{8}$$

The Poisson equation

$$\nabla^2 \psi = -\frac{4\pi\varrho}{D}, \tag{9}$$

satisfied by the potential for the interionic field, then reduces to

$$\frac{1}{\xi}\frac{d}{d\xi}\left(\xi^2 \frac{d\lambda}{d\xi}\right) = \lambda, \tag{10}$$

where

$$\lambda = \frac{\varepsilon\psi}{kT}, \qquad \xi = \chi r,$$

and

$$\chi^2 = \frac{4\pi\varepsilon^2}{DkT}\left[\frac{\sum A_i Z_i^2}{b}\right]. \tag{11}$$

The solution of the Poisson equation, subject to the boundary conditions

$$\psi \to 0 \quad \text{as} \quad r \to \alpha, \tag{12}$$

and

$$\int \frac{d\psi}{dr}\, ds = -\frac{4\pi\varepsilon}{D} \quad \text{(Gauss' theorem)}, \tag{13}$$

as given by Pal [15] and Pal-Chakrabarti [16] is

$$\lambda = \frac{Z_{+}\varepsilon^2\chi}{DkT}\,\frac{e^{\xi_a}}{1+\xi_a}\,\frac{e^{-\xi}}{\xi}, \tag{14}$$

where

$$\xi_a = \chi a.$$

The available electric work using the charging process [22] as given by Pal [15] and Pal-Chakrabarti [15, 17] is

$$w = -\frac{(Z_{+}\varepsilon)^2\chi}{D(\chi a)^3}\left[\ln(1+\chi a)-\chi a+\frac{(\chi a)^2}{2}\right], \tag{15}$$

where a is the radius of a sphere whose volume is equal to the volume per conduction electron given by

$$\frac{V}{N} = \frac{1}{n^0} = \frac{4\pi a^3}{3} \quad \text{or} \quad a = \left(\frac{3}{4\pi n^0}\right)^{1/3}. \tag{16}$$

In this paper we have taken say

$$n_{+}^{0} = n_{-}^{0} = n^0, \qquad D = 1, \qquad Z_{+} = Z_{-} = 1,$$

so that

$$A_{+} = A_{-} = A^0(\text{say}), \tag{17}$$

$$\chi^2 = \frac{4\pi\varepsilon^2}{kT}\left(\frac{2A^0}{b}\right), \tag{18}$$

and

$$w = -\frac{\varepsilon^2\chi}{(\chi a)^3}\left[\ln(1+\chi a)-\chi a+\frac{(\chi a)^2}{2}\right]. \tag{19}$$

For one gm. mole the total work required in charging all the ions is

$$F = -\frac{N\varepsilon^2\chi}{(\chi a)^3}\left[\ln(1+\chi a)-\chi a+\frac{(\chi a)^2}{2}\right], \tag{20}$$

where N is the Avogadro number.

On adding the contribution made to the free energy by the translational motion of the elements and internal energy due to internal motion we obtain an expression for the free energy of elements in a pure state as

$$A = NkT\ln\left[\frac{Nh^3}{\left(2\pi\frac{M}{N}kT\right)^{3/2}Ve}\right]-\frac{N\varepsilon^2\chi}{(\chi a)^3}\left[\ln(1+\chi a)-\chi a+\frac{(\chi a)^2}{2}\right]+\tfrac{3}{2}NkT. \tag{21}$$

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

$$F_T^0 = H_T^0-TS = H_T^0+T\left(\frac{\partial A}{\partial T}\right)_V. \tag{22}$$

$$-\frac{F_T^0-H_{298}^0}{T} = -\tfrac{5}{2}Nk-Nk\ln\left[\frac{Nh^3}{2\pi\left(\frac{M}{N}\right)kT^{3/2}Ve}\right]$$

$$-\left[\frac{NW}{T}+\frac{N\varepsilon^2\chi}{2T(1+\chi a)}\right]+\tfrac{5}{2}Nk\times\frac{298}{T}. \tag{23}$$

3. *Results*

From formula (23) the numerical values of free energies “based on H^0_{298}” were calculated from 298 K to 1000 K. The density, ϱ_t, of alkali metals at different temperatures, t°C, were taken from Weast [23]. The ionic radii were taken from Kittle [24]. A table of both the calculated and accepted values of $-(F^0_T-H^0_{298})/T$ is given in Table I. A comparison between the calculated and accepted values [23] clearly reveal that an excellent agreement is obtained. The accepted values (in parenthesis) were taken from Pitzer and Brewer [25].

TABLE I

Free energies “based on H^0_{298}” of the alkali metals in condensed phase
$-(F^0_T-H^0_{298})/T$ (calories per degree mole)

	298 K	400 K	500 K	600 K	700 K	800 K	900 K	1000 K	r_+[Å]
Calculated	6.70	7.50	8.24	8.89	9.48	10.00	10.48		
Li	(6.73)		(7.60)						0.94
Accepted	7.02	7.26	7.72	8.27	8.87	9.47	10.08		
Calculated	12.27	13.01	13.70	14.32	14.87	15.39	15.82	16.28	
Na	(12.24)		(13.49)					(16.96)	1.24
Accepted	12.31	12.57	13.09	13.68	14.29	14.90	15.50	16.06	
Calculated	15.65	16.33	17.00	17.61	18.14	18.65	18.75	19.56	
K	(15.34)		(16.74)					(20.20)	1.54
Accepted	15.20	15.51	16.14	16.99	17.81	18.73	19.68	20.65	
Calculated	18.52	19.20	19.86	20.47	21.02	21.53	22.00	22.44	
Rb	(18.10)		(19.60)						1.68
Accepted	16.64	16.93	17.54	18.27	19.09	19.87	20.70	21.52	
Calculated	20.43	21.09	21.74	22.33	22.88	23.39	23.85	24.28	
Cs	(20.16)		(21.70)					(25.23)	1.83
Accepted	19.79	20.07	20.62	21.23	21.85	22.44	23.01	23.55	

4. *Conclusion*

In this paper the free energy was calculated by a method similar to that of Debye-Huckel. However the main difference is that instead of the electrostatic force between the ions, the force is between the positive ion and electron. Here also short-range forces of the hard core repulsive type in addition to the Coulombian interactions are considered. Also when taking $D = 1$, the unsatisfactory feature of considering both the microscopic and macroscopic picture together was avoided. Appart from the well known standard works mentioned here [1–3], attempt has been made by others [26] to explain some thermodynamic properties of metals based on local model potential. In this local model, different types of potential are taken into account but the effect of the short-range interaction of the repulsive type is neglected. The good agreement with experimental values provides stronger support for our theory.

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