

ENTROPIES OF THE ALKALI METALS IN THE LIQUID PHASE FROM THE CONSIDERATION OF THE IONIC ATMOSPHERE

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Free energies of five alkali metals in the liquid phase have been calculated by the technique of the Debye-Hückel theory for strong electrolytes in solutions. The distribution formula of Dutta-Bagchi is used here and also the value of the relative permittivity for the medium in the Poisson equation is taken to be unity. The free energy thus calculated is added to the additional contribution made to the free energy by the translational motion of the alkali metals to obtain the total free energy. For experimental verification, the numerical values of entropy in the liquid phase and also entropy changes at the melting points for the alkali metals are calculated. The agreement between the calculated and the experimental values in both cases are fairly good.

ЭНТРОПИИ ШЕЛОЧНЫХ МЕТАЛЛОВ В ЖИДКОЙ ФАЗЕ С ТОЧКИ ЗРЕНИЯ ИОННОЙ АТМОСФЕРЫ

В работе на основе теории электролитической проводимости Дебая-Хюккеля для сильных электролитов в растворах рассчитаны свободные энергии пяти щелочных металлов в жидкой фазе. При этом использовалась формула распределения Дутта-Багчи, и значение относительной диэлектрической проницаемости для среды в уравнении Пуассона равно единице. Полученная таким образом свободная энергия добавлена к добавке, представляющей собой свободную энергию поступательного движения щелочных металлов, и таким образом получена полная свободная энергия. С целью экспериментальной проверки полученных результатов рассчитаны численные значения энтропии в жидкой фазе, а также изменения энтропии в точках плавления щелочных металлов. В обоих случаях обнаружено довольно хорошее согласие данных расчета с экспериментальными значениями.

I. INTRODUCTION

In the Debye-Hückel [1] theory of ionic solutions, ions are distributed according to the Boltzmann distribution formula and the effect of the coulombian

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interactions only (neglecting interactions of the Van der Waals type) is taken into account through the Poisson equation. In this theory the notion of the ionic atmosphere is introduced, which plays an important role. This notion of the ionic atmosphere is also introduced in other theories of the assembly of charged particles like plasma etc. According to experimental evidence, substances like alkali metals exist as free ions and therefore the notion of the ionic atmosphere is important. Hence for studying the thermodynamic properties of alkali metals with due consideration for the coulombian and short-range forces, the Debye-Hückel theory of ionic solutions with necessary modifications [2-9] should be used.

It is easy to see that in the Debye-Hückel theory, the effect of the coulombian interactions and in the modified versions [2-9] hard core repulsive terms in addition to the coulombian interactions are considered for solute ions and the effect of the solvent is considered through the introduction of the relative permittivity in the Poisson equation. In these theories the molecular (microscopic) structure of the solute is used but at the same time a macroscopic picture is taken for the solvent through the relative permittivity. Thus the Debye-Hückel theory of ionic solutions in its many variant forms suffers from the inconsistency that while it considers a microscopic structure for the solute ions, a macroscopic picture for the solvent is assumed through the introduction of the relative permittivity. It has been pointed out earlier by Chakrabarti [10, 11] and Pal-Chakrabarti [12, 13, 14] that the inconsistency between the partly macroscopic approach does not arise if the value of the relative permittivity is taken to be one as in the case of pure metals existing in crystalline form. To put the relative permittivity equal to 1 towards the fact that for the metals such choice is natural, moreover it is the case of a pure metal and naturally without any solvent. This is the main difference with the Debye-Hückel theory, which is used for solutions with a permittivity much greater than 1, where for the uses of solvent relative permittivity has universally proved true. Earlier works [10-14] regarding this problem use the original Debye-Hückel theory and after replacing further the Boltzmann distribution formula by that of Dutta [7] have been particularly successful. In the present paper essentially the same idea is considered and the contribution of the ionic atmosphere in the expression of the free energy for an assembly of charged particles like ions and electrons is calculated with due consideration for the coulombian and hard core repulsive interactions using the distribution formula of Dutta-Bagchi [3]. The free energy thus calculated is added to the contribution made to the free energy by the translational motion of the alkali metals to obtain the total free energy. From this free energy numerical values of entropy of the liquid alkali metals at different temperatures above the melting points up to 1000 K are calculated. Also values of entropy at the melting points are calculated for liquid metals and then subtracted from the experimental values of entropy for solid metals at the melting points to obtain entropy changes.

The entire motivation of this work is to examine how far the simple model obtained from that of the Debye-Hückel theory with the necessary modification mentioned above succeeds in explaining thermodynamic behaviours of the alkali metals in the liquid phase. It is clearly revealed that the comparisons between the calculated and the experimental values in all the cases are fairly good. This may be looked upon as evidence of the suitability of models with the notion of the ion atmosphere.

II. CALCULATIONS

In the present treatment the assembly of ions and electrons is considered and calculations are made in an ionic atmosphere in which charged particles are distributed according to the Dutta-Bagchi [3] distribution formula. The complete derivation of the Dutta-Bagchi [3] distribution formula has been given following a method developed by Dutta [15] in connection with the statistical investigations of real gases. Since in the present work we are studying the monovalent metals, the Dutta-Bagchi [3] distribution formula is given by

$$n_{\pm}^{\pm} = \frac{1/b_{\pm}}{\exp(v_{\pm} \pm e\psi_r/kT) + 1} \quad (1)$$

Here n_{\pm}^{\pm} are the number densities of positive ions or electrons at a point where the electrostatic potential is ψ_r .

$b_{\pm} = \frac{4}{3}\pi(2r_{\pm})^3$ are the exclusion volumes of the mutual close approach between two like ions or two electrons, r_{\pm} being the radii of positive ions or electrons. v_{\pm} are parameters of distribution, e , k and T have their usual significance. As some times assumed in the theory, when $\psi_r \rightarrow 0$, the distribution is, on average, uniform, i.e.,

$$n_{\pm}^{\pm} = \frac{1/b_{\pm}}{\exp(v_{\pm}) + 1} \quad (2)$$

As in the Debye-Hückel theory, the analysis has been carried out only for the system in which the average electrostatic potential ψ_r would be small so that

$$e\psi_r \ll kT \text{ or } (e\psi_r)/kT \ll 1. \quad (3)$$

Based on this assumption, the $\exp(e\psi_r/kT)$ of equation (1) is expanded and all terms except the first two terms are neglected. Thus in equation (1)

$$n_{\pm}^{\pm} = \frac{1}{b_{\pm} [\exp(v_{\pm}) \exp(\pm e\psi_r/kT) + 1]} = n_{\pm}^{\pm} [1 \mp (1 - n_{\pm}^{\pm} b_{\pm}) (e\psi_r/kT)]. \quad (4)$$

The charge density q , at the point in the atmosphere of the ion, where the potential is ψ , will be given by

$$q = e [n^+ - n^-]. \quad (5)$$

Substituting (4) into (5), applying the condition of neutrality and simplifying we get,

$$q = -\frac{e^2 \psi'}{kT} [n^+ + n^-] - \{(n^+)^2 b_+ + (n^-)^2 b_-\}. \quad (6)$$

Now as in the theory of Debye-Hückel, the potential for the interionic field satisfies the Poisson equation

$$\nabla^2 \psi = -\frac{q}{\epsilon} \quad (7)$$

or

$$\nabla^2 \psi = \frac{e^2}{\epsilon kT} [(n^+ + n^-) - \{(n^+)^2 b_+ + (n^-)^2 b_-\}]. \quad (8)$$

The use of higher degree terms in q , in (5) will make equation (8) non linear. In that case we shall face the difficulty regarding the consistency of equation (8) itself [16, 17]. In this paper we have taken $n^+ = n^- = n$

$$\epsilon_r = \text{the relative permittivity} = \frac{\epsilon}{\epsilon_0} = 1, \quad (9)$$

where $\epsilon_0 = 8.85418 \times 10^{-12}$ F/m is the permittivity of free space, so that

$$\nabla^2 \psi = \chi^2 \psi, \quad (10)$$

where

$$\chi^2 = \frac{e^2}{\epsilon_0 kT} n [2 - n(b_+ + b_-)]. \quad (11)$$

It is more convenient to introduce a dimensionless variable and we shall take

$$\lambda = \frac{e \psi'}{kT}. \quad (12)$$

The Poisson equation reduces to

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{d\lambda}{d\xi} \right) = \lambda \quad (13)$$

with

$$\xi = \chi r. \quad (14)$$

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

$$\psi' \rightarrow 0 \text{ as } r \rightarrow \infty \quad (15)$$

and

$$\oint \frac{d\psi'}{dr} ds = -\frac{q}{\epsilon_0} \quad (\text{Gauss' theorem}) \quad (16)$$

is

$$\lambda = \frac{e^2 \chi}{4\pi kT \epsilon_0} \left(\frac{e \xi_a}{1 + \xi_a} \right) \frac{e^{-\xi}}{\xi} \quad (17)$$

where

$$\xi_a = \chi a \quad (18)$$

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

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi a^3}{3} \quad \text{or} \quad a = \left(\frac{3}{4\pi n} \right)^{1/3}. \quad (19)$$

Then using the usual process of charging, the expression for the available electric work is given by [7]

$$W = -\frac{e^2 \chi}{4\pi \epsilon_0 (\chi a)^3} \left[\ln(1 + \chi a) - a + \frac{(\chi a)^2}{2} \right]. \quad (20)$$

For one mole $n^+ = n^- = n = N = N_A$ Avogadro number, the total work required in charging all the ions is

$$NW = -\frac{Ne^2 \chi}{4\pi \epsilon_0 (\chi a)^3} \left[\ln(1 + \chi a) - \chi a + \frac{(\chi a)^2}{2} \right]. \quad (21)$$

On adding the contribution made to the free energy by the translational motion [18, 19] of the ions we obtain an expression for the free energy of the alkali metals in the pure state as

$$A = NkT \ln \left[\frac{N h^3}{2\pi \left(\frac{M}{N} \right) kT} \right]^{3/2} \frac{M}{Q_T} e^A - \frac{Ne^2 \chi}{4\pi \epsilon_0 (\chi a)^3} \left[\ln(1 + \chi a) - \chi a + \frac{(\chi a)^2}{2} \right], \quad (22)$$

where M is the molar mass of metals, Q_T is the density of metals at temperature T , e^A is the base of the logarithm and h is the Planck's constant.

Entropy

$$S = -\left(\frac{dA}{dT} \right) \quad (23)$$

or

$$S = -Nk \ln \left[\frac{N h^3}{2\pi \left(\frac{M}{N} \right) kT} \right]^{3/2} \frac{M}{Q_T} e^A + \frac{3}{2} Nk - \left[\frac{NW}{T} + \frac{Ne^2 \chi}{4\pi \epsilon_0 2T(1 + \chi a)} \right] \quad (24)$$

Table 1

	400 K	500 K	600 K	700 K	800 K	900 K	1000 K	r_c [m]
Calculated	—	50.434	55.957	60.434	64.191	67.404	70.149	0.90×10^{-10}
Li								
Accepted	—	49.848	55.287	59.798	63.664	67.069	70.111	
(Expt.)								
Calculated	67.438	74.283	79.534	83.789	87.429	90.429	93.621	1.15×10^{-10}
Na								
Accepted	67.291	74.216	79.718	84.270	88.153	91.554	94.596	
(Expt.)								
Calculated	80.726	87.529	92.943	97.223	100.97	104.16	107.04	1.46×10^{-10}
K								
Accepted	80.885	87.822	93.365	97.985	101.96	105.47	108.64	
(Expt.)								
Calculated	101.96	108.59	113.74	117.94	121.49	124.98	128.10	1.67×10^{-10}
Cs								
Accepted	101.46	108.49	114.11	118.89	123.02	126.66	129.92	
(Expt.)								

and

$$S_f = S_l - S_s, \quad (25)$$

where S_f is the entropy change of melting (latent heat of fusion); S_l is the entropy of liquid metals at the melting point and S_s is the entropy of solid metals at the melting point. The subscripts f and i denote the saturated liquid and the saturated solid phase, respectively.

III. RESULTS

From formula (24) the numerical values of entropy are calculated at different temperatures above the melting points up to 1000K (i.e., from 500K to 1000K for lithium and from 400 K to 1000 K for sodium, potassium and cesium). The densities ρ_l of the liquid alkali metals at temperatures T are taken from West [20]. The ionic radii are taken from Tosi and Fumi [21]. Both the calculated and the experimental values [22] of S are given in Table 1. Also from formula (24) the numerical values of the entropy (S_l) of liquid metals at their melting points are calculated. The values of entropy thus calculated are subtracted from the experimental values [22, 23] of the entropy (S_l) of solid metals to obtain entropy changes (S_f) (Equ. 25). In Table 2 the calculated and the experimental values of the entropy changes are given.

Table 2

Metal	T_{melting}	$S_l(\text{expt.})$ J K ⁻¹ mol ⁻¹	$S_l(\text{calc})$ J K ⁻¹ mol ⁻¹	$S_f(\text{expt.})$ J K ⁻¹ mol ⁻¹	$S_f(\text{calc})$ J K ⁻¹ mol ⁻¹
Li	453.7	38.074	44.289	6.276	6.215
Na	371.0	55.856	62.983	7.113	7.127
K	336.4	67.572	74.696	7.113	7.124
Rb	312.6	76.776	83.807	7.029	7.031
Cs	301.5	85.354	92.361	6.904	7.007

IV. CONCLUSION

The objective of the work described here is to calculate the entropy of liquid alkali metals by considering the ionic atmosphere in which charged particles are distributed according to the distribution formula of Dutta – Bagchi. The notion of the light mobile electrons and the heavier relatively immobile positively charged particles is considered. In this connection the following points may be noted. It is well known that the metal atoms part with their valence electrons which move throughout the volume like a gas known as electron gas or electron cloud. When the isolated atoms condense to form a metal, the core electrons remain bound to the nucleus to form the metallic ion, but the valence electrons are allowed to wander far away from their parent atoms. It is the attraction between the positively charged ions and the negatively charged electron gas and the repulsive force between the same charged ions which keep the configuration of the body. The development of the present model is similar to that of the Debye – Hückel theory after replacing the Boltzmann distribution formula by that of Dutta – Bagchi with the modification that the coulombian interaction between the positively charged ions and the negatively charged electron gas in addition to the hard core repulsive interaction is considered. To avoid an inconsistency between a partly microscopic and a partly macroscopic approach, the value of the dielectric constant, D , is taken to be unity, i.e. the solvent is absent. The excellent agreement between the calculated and the accepted values indicates that the present modified model developed here favours the theory and is undoubtedly a promising attempt to account for studying the thermodynamic properties of substances in the liquid phase.

ACKNOWLEDGEMENT

The authors are grateful to Professor M. Dutta, professor-in-Charge of the S. N. Bose Institute of Physical Sciences, Calcutta University, for his guidance and

advice. We also express our heartfelt thanks to the referee for his valuable comments and suggestions.

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Received April 6th, 1981