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Dimensional Relations in the Theory of Electrolytes. A Correction

Recent analyses by Onsager[1] and by Halpern[2] throw considerable light on the foundations of the theory of electrolytes. Much of the previous work is superseded or stands in need of revision. Halpern[2] has called attention to an inconsistency in our treatment of dimensional relations.[3] It can be corrected as follows: From Eq. (10) of our paper and from the relation

$$\partial W/\partial \epsilon_i = \psi_i \tag{1.1}$$

we obtain two values of the second derivative $\partial^2 W/\partial V \cdot \partial \epsilon_i$, which when equated give

$$\psi_i = -\sum_{j=1}^{j=N} \epsilon_j \cdot \frac{\partial \psi_i}{\partial \epsilon_j} - 6V \cdot \frac{\partial \psi_i}{\partial V} \tag{2.1}$$

instead of (14).

In the same way Eqs. (21) and (1.1) lead to

$$\psi_i\left[1 - \frac{T}{D}\cdot\frac{dD}{dT}\right] = \left[1 + \frac{T}{D}\cdot\frac{dD}{dT}\right]\cdot\sum_{j=1}^{j=N} \epsilon_j \cdot \frac{\partial \psi_i}{\partial \epsilon_j} + 2T\cdot\frac{\partial \psi_i}{\partial T} \tag{3.1}$$

instead of (25).

Integrating we obtain:

$$\psi_i = V^{-1/6}\cdot f_1(\epsilon_j/V^{1/6}), \tag{4.1}$$

f_1 being a function of the N arguments $\epsilon_j/V^{1/6}$ and

$$\psi_i = T^{1/2}\cdot D^{-1/2}\cdot f_2(\epsilon_j/T^{1/2}D^{1/2}), \tag{5.1}$$

f_2 being a function of the N arguments $\epsilon_j/T^{1/2}D^{1/2}$.

(4.1) and (5.1) when combined give:

$$\psi_i = V^{-1/6}T^{1/2}D^{-1/2}\cdot f_3(\epsilon_j/V^{1/6}T^{1/2}D^{1/2}). \tag{6.1}$$

Assuming, as is implied in the Debye-Hückel procedure[1] that

$$\psi_1/\epsilon_1 = \psi_2/\epsilon_2 = \cdots = \psi_i/\epsilon_i = \cdots \tag{7.1}$$

and introducing the Boltzmann constant k, (6.1) becomes

$$\psi_i = (\epsilon_i/V^{1/3}D)\cdot f_4(\epsilon_j/(DkT)^{1/2}V^{1/6}). \tag{8.1}$$

It will easily be seen that the Debye-Hückel expression for ψ_i verifies this dimensional relation. Considerations concerning the dependence of ψ_i on the numbers N_j, the ionic strength, etc., could be developed in a manner similar to Halpern's treatment.

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April 26, 1934.

[1] L. Onsager, Chem. Rev. **13**, 73 (1933).
[2] O. Halpern, J. Chem. Phys. **2**, 85 (1934).
[3] P. Van Rysselberghe, J. Chem. Phys. **1**, 205 (1933).