

Dimensional Relations in the Theory of Electrolytes. A Correction

Pierre Van Rysseberghe

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Dimensional Relations in the Theory of Electrolytes. A Correction

Recent analyses by Onsager¹ and by Halpern² throw considerable light on the foundations of the theory of electrolytes. Much of the previous work is superseded or stands in need of revision. Halpern² 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

$$\partial W / \partial \epsilon_i = \psi_i \quad (1.1)$$

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

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

instead of (14).

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

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

instead of (25).

Integrating we obtain:

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

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

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

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

(4.1) and (5.1) when combined give:

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

Assuming, as is implied in the Debye-Hückel procedure⁴ that

$$\psi_1 / \epsilon_1 = \psi_2 / \epsilon_2 = \dots = \psi_i / \epsilon_i = \dots \quad (7.1)$$

and introducing the Boltzmann constant k , (6.1) becomes

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

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.

PIERRE VAN RYSSSELBERGHE

Chemistry Department,
Stanford University,
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).