

Direct Correlation between Diffusion Coefficient and Transport Numbers in Dilute Electrolyte Solutions

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For dilute solutions of a strong electrolyte containing two kinds of ions, there is a direct correlation between the diffusion coefficient and the transport numbers. This follows from the Onsager and Onsager-Fuoss equations by elimination of the electrophoretic term.

We consider diffusion (interdiffusion) and electromigration in a dilute solution of a single strong electrolyte containing two kinds of ions, i. e. cations of (positive) charge number z_+ and anions of (negative) charge number z_- , in a neutral solvent. As independent state variables, we choose the thermodynamic temperature T , the pressure P , and the molality m of the electrolyte. We denote the gas constant by R and the Faraday constant by F .

The thermodynamic properties of the solution can be expressed in terms of the conventional (stoichiometric mean ionic molal) activity coefficient γ which depends on T , P , and m . For dilute solutions γ coincides with all the other mean activity coefficients.

The relevant transport coefficients are the diffusion coefficient (interdiffusion coefficient) D and the cationic and anionic conductivities λ_+ and λ_- (or the mobilities $u_+ = \lambda_+/F$ and $u_- = \lambda_-/F$). The ionic conductivities can be derived from measured values of the equivalent conductivity Λ of the solution and of the transport numbers t_+ and t_- of the cations and anions. The quantities λ_i and t_i are defined in the Hittorf reference system (reference substance: solvent) while Λ is independent of the reference system. For the type of solution considered here, we have the interrelations

$$\lambda_+ = t_+ \Lambda, \quad \lambda_- = t_- \Lambda, \\ \lambda_+ + \lambda_- = \Lambda, \quad t_+ + t_- = 1. \quad (1)$$

All the transport coefficients are functions of T , P , and m . The limiting values for infinite dilution ($m \rightarrow 0$) of D , Λ , λ_i , and t_i are denoted by D^0 , Λ^0 , λ_i^0 , and t_i^0 , respectively. They only depend on T and P .

We restrict the discussion to solutions so dilute that $\ln \gamma$ and the composition-dependent parts of the transport coefficients are proportional to $m^{\frac{1}{2}}$. Then the following relations hold:

$$\ln \gamma = -b_1 m^{\frac{1}{2}} \text{ (Debye-Hückel limiting law)}, \quad (2)$$

$$\Lambda^0(t_+^0 - t_-^0) = (z_+ t_-^0 + z_- t_+^0) b_2 m^{\frac{1}{2}} \quad \text{(Onsager limiting law)}, \quad (3)$$

$$D = (D^0 + \Delta)(1 + \Gamma) \quad \text{(Onsager-Fuoss limiting law)} \quad (4)$$

where

$$D^0 = \frac{RT}{F^2} \left(\frac{1}{z_+} - \frac{1}{z_-} \right) t_+^0 t_-^0 \Lambda^0 = \\ \frac{RT}{F^2} \left(\frac{1}{z_+} - \frac{1}{z_-} \right) \frac{\lambda_+^0 \lambda_-^0}{\lambda_+^0 + \lambda_-^0}, \quad (5)$$

$$\Delta = \frac{RT}{F^2} \frac{1}{z_+ z_-} (z_+ t_-^0 + z_- t_+^0)^2 b_2 m^{\frac{1}{2}}, \quad (6)$$

$$\Gamma = m \left(\frac{\partial \ln \gamma}{\partial m} \right)_{T, P}, \quad (7)$$

b_1 and b_2 being positive functions of T and P given by

$$b_1 = -z_+ z_- [\frac{1}{2} (z_+^2 \nu_+ + z_-^2 \nu_-)]^{\frac{1}{2}} B, \\ 3 z_+ z_- \eta b_2 = -4 RT \varepsilon b_1.$$

In this, ν_+ and ν_- denote the dissociation numbers of the cations and anions, B the Debye-Hückel constant (in the molality scale), η the viscosity of the solvent, and ε the (absolute) dielectric constant (rationalized permittivity) of the solvent.

The fact that the same function $b_2 m^{\frac{1}{2}}$ (describing the first-order electrophoretic effect) occurs in (3) and (6) is not immediately obvious from the formulas in the literature. After some elementary calculations, however, one soon realizes the fact indicated.

Equations (3) and (4) are due to Onsager¹ and Onsager and Fuoss², respectively. The relations for λ_i and Λ , corresponding to (3) and also given by Onsager¹, will not be considered here since they involve the relaxation effect, too.

Equation (5) is equivalent to a formula derived by Noyes (1908) which becomes the well-known equation of Nernst (1888) in the case of uni-univalent electrolytes ($z_+ = -z_- = 1$). The relation of Hartley (1931) follows from (4) and (5) with $\Delta = 0$ (no electrophoretic effect).

We obtain the explicit expression for Γ from (2) and (7):

$$\Gamma = -\frac{1}{2} b_1 m^{\frac{1}{2}}. \quad (8)$$

Since, in view of (6) and (8), the product $\Gamma \Delta$ is proportional to m and thus lies outside the $m^{\frac{1}{2}}$ -range, we rewrite (4) as follows:

$$D = D^0(1 + \Gamma) + \Delta. \quad (9)$$

This equation is consistent with (2) and (3).

Eliminating $b_2 m^{\frac{1}{2}}$ between (3) and (6), we derive from (1), (8), and (9):

$$D = D^0 (1 - \frac{1}{2} b_1 m^{\frac{1}{2}}) + \frac{RT}{F^2} \left(\frac{\lambda_+^0}{z_+} + \frac{\lambda_-^0}{z_-} \right) (t_+^0 - t_+). \quad (10)$$

This is a direct correlation between the diffusion coefficient D and the transport number t_+ (or $t_- = 1 - t_+$), valid for the $m^{\frac{1}{2}}$ -range. According to (1)

and (5) the limiting values D^0 and t_+^0 can be calculated from λ_-^0 and λ_+^0 . The composition dependence of D is seen to be due to both the Debye-Hückel term and the term containing $t_+^0 - t_+$ ($= t_- - t_-^0$).

Though the derivation given here is straightforward, the correlation (10) has never been established in the literature, as far as the author is aware.

¹ L. Onsager, Physik Z. **27**, 388 [1926]; **28**, 277 [1927].

² L. Onsager and R. M. Fuoss, J. Phys. Chem. **36**, 2689 [1932].