CALCULATION OF THERMODYNAMIC CONDUCTANCE COEFFICIENTS USING A RELATIONSHIP INCLUDING IONIC MOBILITIES

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Received January 11, 1989
Presented by Prof. Dr. J. Nagy

Abstract

Relationships have been derived to describe the thermodynamic conductance coefficients by combining the thermodynamic equation and the Debye–Hückel–Onsager description of the ionic mobilities.

The relationships can be used for calculating the thermodynamic conductance coefficients L_{kk}, L_{aa} and L_{ka}.

Transport processes taking place in electrolyte solutions can be well described in terms of irreversible thermodynamics. For example the electrical conductivity of binary electrolytes can be described by three thermodynamic conductance coefficients which depend on concentration. Using these coefficients the diffusion coefficients and transference numbers of the ions can also be calculated [1–5].

These data — the electrical conductance diffusion coefficients and transference numbers can be calculated using relationships derived based on the Debye– Hückel–Onsager theory [6–8].

The idea has arisen earlier [9] that thermodynamic conductance coefficients could be calculated directly in terms of the Debye–Hückel–Onsager theory. However, the relationships derived for the conductance, diffusion coefficients and transference numbers include neglections [6–8, 10]. In the present work it has been attempted to calculate thermodynamic conductance coefficients using a relationship derived for the ionic mobilities from the Debye–Hückel– Onsager theory, which can be used in a fairly wide concentration range.

Let us consider a strong electrolyte consisting of one kind of cation and one kind of anion dissolved in a solvent of uncharged molecules (e.g. water), in which there is no convection. Let the temperature be identical at each point of the solution. The concentration of the electrolyte and the electrical potential may change from point to point. Under these conditions the ions may diffuse and electrical conduction may occur in the solution. Due to the non-uniform

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composition a diffusion potential may establish in the solution. These phenomena can be described in terms of irreversible thermodynamics by the following equations:

$$J_k = L_{kk} X_k + L_{ka} X_a \tag{1}$$

$$J_a = L_{ka} X_k + L_{aa} X_a \tag{2}$$

where J_k and J_a and X_k and X_a mean the fluxes of the ions and the thermodynamic forces felt by the ions, L_{kk}, L_{ka} and L_{aa} are the so called conductance coefficients which depend on the composition and temperature of the solution but are independent of the thermodynamic forces. In formulating the equations the Onsager relation has been taken into account [11]. J_k and J_a, the diffusion fluxes mean the number of moles of the respective ions passing through unit area (1 cm^2) perpendicular to the direction of flow in unit time (1 s).

According to thermodynamic consideration X_k and X_a for a cation of z_k and an anion of $-z_a$ charge can be given as:

$$X_k = -\text{grad}\, \tilde{\mu}_k = -(\text{grad}\, \mu_k + z_k F\, \text{grad}\, \varphi) \tag{3}$$

$$X_a = -\text{grad}\, \tilde{\mu}_a = -(\text{grad}\, \mu_a - z_a F\, \text{grad}\, \varphi) \tag{4}$$

where F is the Faraday, μ and $\tilde{\mu}$ are the chemical and electrochemical potential of the ion, and φ is the electrical potential.

The sum of the products of thermodynamic forces and fluxes is equal to the product of temperature and the local entropy produced.

$$T\sigma = J_k X_k + J_a X_a \tag{5}$$

where σ is the entropy produced by the material in unit volume, due to the diffusion of ions. Thermodynamic forces are calculated so that they, when multiplied by the fluxes, yield the product of the local entropy with temperature.

It is also usual to define thermodynamic forces in a way that the product of thermodynamic forces with fluxes yield the entropy

$$\sigma = J_k X'_k + J_a X'_a \tag{6}$$

In this case the thermodynamic forces are smaller by a factor of T. In the following discussion the definition given by equation 5 will be used.

Electrical conduction in electrolyte solutions

Electrical conductance is usually given for homogeneous (grad $c = 0$) and isothermal (grad $T = 0$) solutions.

The rate of migration of ions at unit field strength is called the absolute ionic mobility and is designated by u_k and u_a for a cation and an anion, respectively. In practice the terms $l_k = Fu_k$ and $l_a = Fu_a$ are used instead of u_k and u_a.

The ionic mobility can be given as follows:

$$l_k = \frac{F^2}{c_e}(L_{kk}z_k^2 - L_{ka}z_k z_a) \tag{7}$$

$$l_a = \frac{F^2}{c_e}(L_{aa}z_a^2 - L_{ka}z_k z_a) \tag{8}$$

where $c_e = c_k \cdot z_k = c_a \cdot z_a$, the so called equivalent concentration. It should be emphasized that three conductance coefficients cannot be calculated from experimental mobilities (l_k and l_a) since two equations are not enough to calculate three unknowns (L_{kk}, L_{aa} and L_{ka}). However, for solutions of infinite dilution according to the Kohlrausch rule stating the independent migration of ions, the mobility of an ion is independent of the nature of the counter ion. This means that L_{ka} tends to zero as the concentration tends to zero. Hence the conductance coefficients can be calculated for solutions of infinite dilution from ionic mobilities extrapolated to infinite dilution.

Since $L_{ka}^0 = 0$

$$l_k^0 = \frac{F^2 L_{kk}^0 z_k^2}{c_e} \tag{9}$$

$$l_a^0 = \frac{F^2 L_{aa}^0 z_a^2}{c_e} \tag{10}$$

The index 0 refers to zero concentration. For more concentrated solutions $L_{ka} \neq 0$ and L_{kk} and L_{aa} will be different from the values determined for infinite dilution.

In irreversible thermodynamics there is relationship for the calculation of the diffusion coefficients of electrolytes which also includes the three thermodynamic conductance coefficients L_{kk}, L_{aa} and L_{ka}.

To the calculation of the three conductance coefficients for a given solution three independent data are needed, which may be for example the mobilities of two ions and the diffusion coefficient, i.e. the conductance coefficients can be calculated from l_k, l_a and the diffusion coefficient D [9, 11].

Also the Debye–Hückel–Onsager theory provides a relationship for the calculation of ionic mobilities. In the following treatment the relationship given in refs [6–8] will be used as follows:

$$l_k = l_k^0 - (A_1 l_k^0 + A_2)\frac{\sqrt{c_e}}{1 + B\mathring{a}\sqrt{c_e}} \tag{11}$$

$$l_a = l_a^0 - (A_1 l_a^0 + A_2)\frac{\sqrt{c_e}}{1 + B\mathring{a}\sqrt{c_e}} \tag{12}$$

By comparing Eqs 11 and 12 with Eqs 7 and 8, it is clear that both contain a term which is the same for the anion and the cation, namely

$$\frac{F^2}{c_e}\cdot L_{ka}z_k z_a, \quad \text{and} \quad \frac{A_2\sqrt{c_e}}{1+B\mathring{a}\sqrt{c_e}}$$

Hence, they must be equal

$$\frac{F^2}{c_e}L_{ka}z_k z_a=\frac{A_2\sqrt{c_e}}{1+B\mathring{a}\sqrt{c_e}} \tag{13}$$

In the thermodynamic equations 7 and 8, and in the Debye–Hückel–Onsager equations 11 and 12 there are terms which are different for the cation and anion. E.g. for the cation $\frac{F^2}{c_e}\cdot L_{kk}z_k^2$ and $l_k^0-\frac{A_1 l_k^0 c_e}{1+B\mathring{a}\sqrt{c_e}}$.

Obviously, they are equal:

$$\frac{F^2}{c_e}\cdot L_{kk}z_k^2=l_k^0-\frac{A_1 l_k^0\sqrt{c_e}}{1+B\mathring{a}\sqrt{c_e}} \tag{14}$$

Similarly, for the anions:

$$\frac{F^2}{c_e}L_{aa}z_a^2=l_a^0-\frac{A_1 l_a^0\sqrt{c_e}}{1+B\mathring{a}\sqrt{c_e}} \tag{15}$$

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