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The Nernst-Planck Type Equation in Nonequilibrium Thermodynamics

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Synopsis. A single-term expression of the Nernst-Planck type equation conformable with nonequilibrium thermodynamics has been presented. The equation may be applicable to treat the electric properties of the multi-ionic system, although the individual ion flux is unobservable.

It is well known that the Nernst-Planck equation is a single-term expression and has been regarded as applicable to multi-ionic systems in classical transport theory.

On the other hand, in nonequilibrium thermodynamics, an isothermal ion flux in a multi-ionic system is expressed by a linear combination of the negative electrochemical potential gradients with the phenomenological coefficients, or the sum of Nernst-Planck type equations.[1] However, it is formidable to treat a multi-ionic system due to many phenomenological coefficients which must be experimentally determined, although nonequilibrium thermodynamics is known to be theoretically rigorous.

Thus, it is advantageous to determine the conditions for utilizing Nernst-Planck type equations in a way so as not to contradict nonequilibrium thermodynamics. This will greatly simplify the treatment of the transport process.

It has been shown in a preceding paper[2] that a Nernst-Planck type equation with a diffusion coefficient can express only ionic movements without an electric current in a binary electrolyte solution. It will be shown in the present paper that a Nernst-Planck type equation with a conductive absolute mobility is applicable to the transport process of a multi-ionic system, although the ion flux is unobservable.

Theory

The isothermal flux of an ion α, j_α, in a multi-ionic electrolyte solution may be written on the basis of nonequilibrium thermodynamics[1]

$$j_\alpha = -\sum_\beta l_{\alpha\beta} \nabla \bar{\mu}_\beta \tag{1}$$

where the subscript β refers to ion β; $l_{\alpha\beta}$ denotes the phenomenological coefficient, and $\nabla \bar{\mu}_\beta$ is the gradient of the electrochemical potential of ion β, $\bar{\mu}_\beta$.

For the sake of simplicity, it is assumed that the system is in a steady-state condition in which the fluxes, the concentration and the potential profiles are functions only of the coordinate and are independent of time.

Equation 1 leads to an equation for the electric current I as follows;

$$I = \sum_\alpha Z_\alpha F j_\alpha = -\sum_\alpha Z_\alpha F u_\alpha C_\alpha \nabla \bar{\mu}_\alpha \tag{2}$$

where Z_α denotes the charge, F the Faraday constant and C_α the concentration. u_α, the conductive absolute mobility, is related to $l_{\alpha\beta}$ by[1]

$$u_\alpha = \sum_\beta Z_\beta l_{\beta\alpha} / Z_\alpha C_\alpha . \tag{3}$$

Putting

$$j_\alpha{}^* = -u_\alpha C_\alpha \nabla \bar{\mu}_\alpha \tag{4}$$

and comparing Eq. 2 with Eqs. 1, 3 and 4, we find

$$I = \sum_\alpha Z_\alpha F j_\alpha = \sum_\alpha Z_\alpha F j_\alpha{}^* . \tag{5}$$

In Eq. 5, $Z_\alpha F j_\alpha{}^*$ denotes the part of the electrical ion current that is driven by the electrochemical potential gradient of ion α. Equation 4 is the same form as the Nernst-Planck equation with an absolute mobility. However, it should be noted that $j_\alpha{}^*$ is an unobservable flux and differs from the observable flux j_α as can be seen by comparing Eq. 1 with Eqs. 3 and 4. Nevertheless, Eq. 4 can be used to obtain an equation for the electric current, as can be seen from Eq. 5. When the system is in a steady state, $j_\alpha{}^*$ may also be regarded as a constant.

Equation 1 may also be written as[3]

$$j_\alpha = -\sum_\beta Z_\beta F l_{\alpha\beta} \nabla (\psi - \psi_\beta) \tag{6}$$

where ψ denotes the electric potential and ψ_β the equilibrium potential for ion β. Similarly, Eq. 4 leads to

$$j_\alpha{}^* = -Z_\alpha F C_\alpha u_\alpha \nabla (\psi - \psi_\alpha) . \tag{7}$$

Equations 6 and 7 hold even in the absence of an electric current, where j_α, $j_\alpha{}^*$, and ψ become j_α^0, j_α^{*0}, and ψ^0, respectively. When the electric current is small, it may be assumed that changes in the concentration profiles and phenomenological coefficients caused by an electric current can be ignored. This corresponds to an assumption of constant ψ_α's. In this case, we have from Eqs. 3, 6, and 7

$$j_\alpha - j_\alpha^0 = j_\alpha^* - j_\alpha^{*0} = -Z_\alpha F C_\alpha u_\alpha \nabla (\psi - \psi^0) , \tag{8}$$

which is conformable with Eq. 5. It is evident from Eq. 8 that

$$j_\alpha = j_\alpha^* = -Z_\alpha F C_\alpha u_\alpha \nabla \psi , \tag{9}$$

when there is no concentration gradient.

For a membrane-aqueous electrolyte system with an isotropic membrane, the equations for isothermal fluxes relative to the membrane can be expressed by[4]

$$j_\alpha = -\sum_\beta l_{\alpha\beta} \nabla \tilde{\mu}_\beta - l_{\alpha w} \nabla \tilde{\mu}_w , \tag{10}$$

$$j_w = -\sum_\beta l_{w\beta} \nabla \tilde{\mu}_\beta - l_{ww} \nabla \tilde{\mu}_w , \tag{11}$$

where α and β refer to ions α and β, respectively, and w, water. The hydrodynamic electrochemical potential is given by

$$\tilde{\mu}_\gamma = \bar{\mu}_\gamma + P \bar{v}_\gamma , \quad (\gamma = \alpha, \beta, w) \tag{12}$$

where P denotes the pressure and $\bar{v}_\gamma$ the partial molar volume of species γ. For this system, the membrane current is given by

$$I=\sum_{\alpha} Z_\alpha F j_\alpha=\sum_{\alpha} Z_\alpha F j_\alpha^{*}+F j_w^{*}, \tag{13}$$

where

$$j_\gamma{}^{*}=-u_\gamma C_\gamma \nabla \tilde{\mu}_\gamma, \quad (\gamma=\alpha, \beta, w). \tag{14}$$

The conductive absolute mobility u_α for ion α is given by Eq. 3. Similarly, the equation for the electroosmotic water mobility is expressed by

$$u_w=\sum_{\alpha} Z_\alpha l_{\alpha w}/C_w. \tag{15}$$

Regarding flux, Eq. 8 also holds for all ionic species. For the observable flux of water, the equation for the electroosmotic water flow is

$$j_w-j_w^{0}=-F C_w u_w \nabla(\psi-\psi^{0}). \tag{16}$$

For an unobservable flux,

$$j_w^{*}=j_w^{*0} \tag{17}$$

since there is no potential term in $\tilde{\mu}_w$.

Discussion

According to Eqs. 8 and 16, $C_\gamma u_\gamma$ ($\gamma=\alpha$, β, w) can be determined by measuring the fluxes and the potentials; hence, the electrical properties of the system, such as ion and electroosmotic conductances, the membrane conductance and the transport number can be evaluated from the $C_\gamma u_\gamma$'s. In addition, the unobservable fluxes ($j_\gamma{}^{*}$ and $j_\gamma{}^{*0}$) can also be evaluated using Eq. 14. Thus, j_α can be calculated according to Eq. 8, provided j_α^{0} is known. However, all the phenomenological coefficients should be determined in order to predict the diffusional flux j_α^{0}. Unfortunately, it seems to be hopeless to predict j_α^{0} in a multi-ionic system having more than three kinds of ionic species. This is because there are too many phenomenological coefficients which must be experimentally determined.

For a binary electrolyte solution, the diffusional ion flux at zero electric current j_α^{0} is given by a single-term expression[2]

$$j_\alpha^{0}=-D_\alpha C_\alpha \nabla \bar{\mu}_\alpha/RT=-\omega_\alpha C_\alpha \nabla \bar{\mu}_\alpha, \tag{18}$$

where D_α denotes the diffusion coefficient, ω_α $(=D_\alpha/\boldsymbol{R}T)$ the diffusional absolute mobility, $\boldsymbol{R}$ the gas constant, and T the absolute temperature. D_α and ω_α are related to the phenomenological coefficients as follows[2];

$$D_\alpha C_\alpha/\boldsymbol{R}T=\omega_\alpha C_\alpha=Z_\beta(l_{\alpha\alpha}l_{\beta\beta}-l_{\alpha\beta}{}^{2})/(Z_\alpha l_{\alpha\beta}+Z_\beta l_{\beta\beta}). \tag{19}$$

Comparing Eq. 18 with Eq. 4,

$$\frac{j_\alpha^{0}}{j_\alpha^{*0}}=\frac{\omega_\alpha}{u_\alpha}=1-\lambda_{\alpha\beta}\left(\frac{1}{\lambda_\alpha}+\frac{1}{\lambda_\beta}\right)=F(\lambda_{\alpha\beta}), \tag{20}$$

where λ_α and λ_β are the equivalent conductances of ions α and β, respectively. $\lambda_{\alpha\beta}$ is an element of the equivalent ion conductance matrix, given by the relation[2]

$$\lambda_{\alpha\beta}=Z_\alpha Z_\beta F^{2} l_{\alpha\beta}/|Z_\alpha|C_\alpha. \tag{21}$$

Since the phenomenological coefficients or the elements of the conductance matrix for a binary electrolyte solution can be determined experimentally[1], j_α^{0} can be evaluated according to Eq. 18. Hence, from Eqs. 8 and 20,

$$j_\alpha=j_\alpha^{*}-j_\alpha^{*0}+j_\alpha^{0}=j_\alpha^{*}-j_\alpha^{*0}[1-F(\lambda_{\alpha\beta})] \tag{22}$$

enabling us to evaluate j_α from j_α^{*}, j_α^{*0}, and $F(\lambda_{\alpha\beta})$.

Concerning $F(\lambda_{\alpha\beta})$, it has been shown in the preceding paper[2]

$$F(\lambda_{\alpha\beta})=|Z_\alpha|F^{2}D_\alpha/\boldsymbol{R}T\lambda_\alpha \tag{23}$$

$$F(\lambda_{\alpha\beta})=\nu_\alpha|Z_\alpha|D_s/(\nu_\alpha+\nu_\beta)\lambda t_\alpha t_\beta(1+d\ln\gamma_s/d\ln C_s), \tag{24}$$

where the subscript s refers to salt. ν_α and ν_β denote the stoichiometric coefficients, D_s the diffusion coefficient, λ the equivalent conductance of salt, t_α and t_β the transport numbers, γ_s the activity coefficient and C_s, the salt concentration. The value of $F(\lambda_{\alpha\beta})$ decreases with a decrease in the electrolyte concentration and tends to unity as the concentration approaches zero[2] where $u_\alpha=\omega_\alpha$. This indicates that interionic interactions vanish at an infinite dilution and there is no distinction between Eqs. 1 and 4. When $F(\lambda_{\alpha\beta})$ is unity, Eqs. 23 and 24 lead to the Nernst–Einstein and Nernst–Hartley equations, respectively. These are derived on the basis of the Nernst–Planck equation. Thus, it may be said that the original Nernst–Planck equation is valid only at an infinite dilution where Eqs. 4 and 18 are identical.

Eqations 4 and 18 differ from each other at finite electrolyte concentrations (where $F(\lambda_{\alpha\beta})$ differs from unity) and should be used with the precautions described in the present paper. From this point of view, u_α and ω_α should be distinguished from each other and can be called the conductive absolute mobility and the diffusional absolute mobility, respectively. This is due to the process by which they are defined. Nevertheless, these equations are still being used in current papers without distinction. However, the Nernst–Planck type equations (4, 14, and 18) are single-term expressions and enable us to use the results from classical membrane theories based on the Nernst–Planck equation if those theories were formulated under reasonable assumptions and the proposed precautions are taken into account.

Thus, the use of single-term expressions is advantageous for an easier treatment of the transport process using nonequilibrium thermodynamics. Hence, these equations can be regarded as revised Nernst–Planck equations. A determination of all phenomenological coefficients is required in order to completely describe and characterize the transport process in a multi-ionic system. At present this process seems to be hopeless in systems having more than four components. Further study is required in order to solve this problem.

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