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Diffusion of electrolytes in solution under gravitational forces

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Abstract

An equation was mathematically derived using the theory of irreversible thermodynamics for the diffusion of electrolytes in solution in the presence of an external gravitational force. It was demonstrated that diffusion coefficients of electrolyte species are dependent on the difference of radii and densities of anion and cation ionized from the electrolyte in solution. For a special case that radii and densities of the anion and cation are the same, the diffusion coefficient is independent of the external gravitational force. Entropy production was also estimated for the system under consideration. It was found that the rate of entropy production is proportional to the sum of the gravitational forces induced to all electrolyte species.
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1. Introduction

The general equation for fluid flow can be expressed by Navier–Stokes and continuity equations:

$$\frac{d\vec{v}}{dt} + \vec{v}\nabla\vec{v} = -\frac{\vec{\nabla}P}{\rho} + v\nabla^2\vec{v} + \vec{F}_i, \tag{1a}$$

$$\vec{\nabla} \cdot \vec{v} = 0, \tag{1b}$$

where ρ is density, v fluid velocity, p pressure, μ dynamic viscosity, and F_i an external force acting on the fluid. This equation describes the movement of fluid element (1 cm³) expressed in Cartesian coordinates. Indeed, this expresses Newton's second law for an incompressible fluid element. The left-hand side of the equation gives the effect of the mass of this element on its acceleration and the other side specifies the forces acting on it.

The effects of different external forces on fluid flow in both electrochemical and non-electrochemical systems have been extensively investigated [1–3]. Although, gravitational force is an important example of

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such external forces on fluid dynamics and its effect has been widely studied in the context of fluid mechanics, no attention has been made to this important force on convective–diffusion processes in electrochemical systems. This can be attributed to the fact that the effect of gravitational force on electrochemical processes has not been considered in electrochemistry, due to the lack of appropriate apparatus to perform experimental investigations. More recently, we have widely studied the effect of gravitational forces induced by centrifugal fields on different electrochemical systems from applied research point of view [4–9]. Indeed, gravitational forces (centrifugal forces) have been employed to enhance electrochemical processes for specified applications. For example, gravitational forces have been used to improve magnetic properties of soft magnetic films for the fabrications of head recording devices (e.g., for the construction of hard disk drive, HDD) [6,7], to enhance metallization of silicon surfaces for microelectronic applications [8], to increase electrical conductivity of semiconducting materials such as conductive polymers [9], etc.

In fact, due to recent developments of 'electrochemistry under centrifugal forces' [4–12], it is desirable to achieve some generalization of diffusion of electroactive species under gravitational forces. Here, we would like to communicate some theoretical aspects in this context. To this aim, the theory of irreversible thermodynamics is employed. Due to the vast investigations and progress of thermodynamics of irreversible processes or nonequilibrium thermodynamics in mid-twentieth century, it has been introduced as a powerful theory for the investigations of complex systems by means of thermodynamics. The theoretical considerations were generally made for a gravitational force. Assuming that the gravitational force induced by an applied centrifugal force is completely perpendicular to the cell, the results can be considered for an external centrifugal force induced to an electrochemical system. Appropriate apparatus and visual illustration of the gravitational force induced to an electrochemical system as a result of the applied centrifugal force have been reported in our previous experimental papers [6,7].

2. General theory derived based on irreversible thermodynamics

In the present Letter, we attempt to investigate the diffusion of electrolyte species in solution as a result of simple electrolytic ionization. For a simple electrolyte dissociation into two charged species, as it can be assumed that the system is isothermal and no chemical reaction occurs and there is no external applied potential field, the dissipation function ϕ_0 corresponding to the simultaneous diffusion of the dissociated charged species (cations and anions) is expressed by [13]

$$\phi_0 = \sum_i \mathbf{J}_i \cdot \mathrm{grad}(-\mu_i), \tag{2}$$

where $\mathbf{J}_i$ is the flux of the component i and μ_i the chemical potential. In the presence of an external force, i.e., gravitational force in the system under consideration, the total dissipation function ϕ_t should be expressed containing two dissipation functions involved

$$\phi_t = \phi_0 + \phi_G, \tag{3}$$

where ϕ_G is the dissipation function representing the effect of an external gravitational force $\mathbf{G}$ on the simultaneous diffusion of electrolyte species:

$$\phi_G = \sum_k \mathbf{J}_k \cdot \mathbf{G}_k, \tag{4}$$

and thus the total dissipation of the system can be re-written as

$$\phi_t = -\sum_i \mathbf{J}_i \cdot \mathrm{grad}\,\mu_i + \sum_i \mathbf{J}_i \cdot \mathbf{G}_i. \tag{5}$$

If we restrict our investigation to a simple two-component system including a cation and an anion, the equation can be written as

$$\phi_t = \mathbf{J}_1 \cdot [\mathbf{G}_1 - \operatorname{grad}\mu_1] + \mathbf{J}_2 \cdot [\mathbf{G}_2 - \operatorname{grad}\mu_2]. \tag{6}$$

According to the principles of the irreversible thermodynamics, fluxes $\mathbf{J}_1$ and $\mathbf{J}_2$ can be expressed as two interacting diffusion flows representing ion flow relative to solvent:

$$\mathbf{J}_1 = L_{11}[\mathbf{G}_1 - \operatorname{grad}\mu_1] + L_{12}[\mathbf{G}_2 - \operatorname{grad}\mu_2], \tag{7a}$$

$$\mathbf{J}_2 = L_{21}[\mathbf{G}_1 - \operatorname{grad}\mu_1] + L_{22}[\mathbf{G}_2 - \operatorname{grad}\mu_2], \tag{7b}$$

where L_{ij}s are Onsager's phenomenological coefficients. The importance of phenomenological coefficient for electrochemical systems has also been recently reported [14,15]. Assuming that there is no electric current in the system, according to the conservation laws:

$$\mathbf{J}_1 + \mathbf{J}_2 = 0. \tag{8}$$

Therefore,

$$L_{11}[\mathbf{G}_1 - \operatorname{grad}\mu_1] + L_{12}[\mathbf{G}_2 - \operatorname{grad}\mu_2] + L_{21}[\mathbf{G}_1 - \operatorname{grad}\mu_1] + L_{22}[\mathbf{G}_2 - \operatorname{grad}\mu_2] = 0. \tag{9}$$

On the other hand, the chemical potential of the electrolyte (salt) μ_s is the sum of the separate chemical potentials of the ions:

$$\operatorname{grad}\mu_s = v_1 \operatorname{grad}\mu_1 + v_2 \operatorname{grad}\mu_2, \tag{10}$$

where v_1 and v_2 are the corresponding valencies. Thus, the chemical potentials of the electrolyte species can be expressed as

$$\operatorname{grad}\mu_1 = \frac{\operatorname{grad}\mu_s(-L_{12} - L_{22}) + v_2\mathbf{G}_1 \cdot (L_{11} + L_{21}) + v_2\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}, \tag{11a}$$

$$\operatorname{grad}\mu_2 = \frac{\operatorname{grad}\mu_s(L_{11} + L_{21}) - v_1\mathbf{G}_1 \cdot (L_{11} + L_{21}) - v_1\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}. \tag{11b}$$

Consequently, the fluxes $\mathbf{J}_1$ and $\mathbf{J}_2$ can be expressed in terms of $\operatorname{grad}\mu_s$:

$$\mathbf{J}_1 = L_{11}\left[\mathbf{G}_1 + \frac{\operatorname{grad}\mu_s(L_{12} + L_{22}) - v_2\mathbf{G}_1 \cdot (L_{11} + L_{21}) - v_2\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}\right]$$
$$+ L_{12}\left[\mathbf{G}_2 - \frac{\operatorname{grad}\mu_s(L_{11} + L_{21}) - v_1\mathbf{G}_1 \cdot (L_{11} + L_{21}) - v\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}\right], \tag{12a}$$

$$\mathbf{J}_2 = L_{21}\left[\mathbf{G}_1 + \frac{\operatorname{grad}\mu_s(L_{12} + L_{22}) - v_2\mathbf{G}_1 \cdot (L_{11} + L_{21}) + v_2\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}\right]$$
$$+ L_{22}\left[\mathbf{G}_2 - \frac{\operatorname{grad}\mu_s(L_{11} + L_{21}) - v_1\mathbf{G}_1 \cdot (L_{11} + L_{21}) - v\mathbf{G}_2 \cdot (L_{12} + L_{22})}{v_2(L_{11} + L_{21}) - v_1(L_{12} + L_{22})}\right]. \tag{12b}$$

The flow of the electrolyte (salt) is

$$\mathbf{J}_s = \frac{\mathbf{J}_1}{v_1} = \frac{\mathbf{J}_2}{v_2}. \tag{13}$$

Thus, the flow of an electrolyte (salt) in the solution in the presence of an applied gravitational field can be expressed (derived from Eq. (12a)) by

$$\mathbf{J}_s = \frac{L_{11}}{v_1}\left[\mathbf{G}_1 - \frac{v_2\mathbf{G}_1\cdot(L_{11}+L_{12}) + v_2\mathbf{G}_2\cdot(L_{12}+L_{22})}{v_2(L_{11}+L_{21}) - v_1(L_{12}+L_{22})}\right]$$
$$+ \frac{L_{12}}{v_1}\left[\mathbf{G}_2 + \frac{v_1\mathbf{G}_1\cdot(L_{11}+L_{21}) + v_1\mathbf{G}_2\cdot(L_{12}+L_{22})}{v_2(L_{11}+L_{21}) - v_1(L_{12}+L_{22})}\right]$$
$$+ \operatorname{grad}\mu_s\left[\left(\frac{L_{11}}{v_1}\right)\frac{L_{11}+L_{21}}{v_2(L_{11}+L_{21}) - v_1(L_{12}+L_{22})} - \left(\frac{L_{12}}{v_1}\right)\frac{L_{12}+L_{22}}{v_2(L_{11}+L_{21}) - v_1(L_{12}+L_{22})}\right]. \quad (14)$$

This is the general equation for the electrolyte flux of a simple two-component system derived mathematically by assuming that the applied gravitational has no significant effect on the physical properties of the solution such as electrical conductance. Indeed, it is the common assumption in studies of so-called Newtonian fluids. For a simple two-component system, such electrolyte solution of KCl, the electrolyte species (cation and anion) are K^+ and Cl^-. To keep the electro-neutrality of the solution, it is needed that

$$v_1z_1 + v_2z_2 = 0, \quad (15)$$

where z is the charge of the electrolyte species. As for this system, we have

$$z_1 = -z_2 = 1; \quad v_1 = v_2 = 1, \quad (16)$$

where Eq. (14) can be significantly reduced. On the other hand, according to the Onsager formalism known as Onsager reciprocity relation, $L_{12} = L_{21}$. Therefore, the flux electrolyte for the system under investigation can be re-written as

$$\mathbf{J}_s = \frac{(L_{11}L_{22} - L_{12}^2)}{(L_{11} - 2L_{12} + L_{22})}(\mathbf{G}_1 - \mathbf{G}_2 - \operatorname{grad}\mu_s) = X(\mathbf{G}_1 - \mathbf{G}_2 - \operatorname{grad}\mu_s), \quad (17)$$

where

$$X = \frac{L_{11}L_{22} - L_{12}^2}{L_{11} - 2L_{12} + L_{22}}. \quad (18)$$

Recalling that

$$\operatorname{grad}\mu_s = \mu_{ss}\operatorname{grad}c_s, \quad (19)$$

where $\mu_{ss} = \partial\mu_s/\partial c_s$, the flux equation can be re-written as

$$\mathbf{J}_s = X(\mathbf{G}_1 - \mathbf{G}_2 - \mu_{ss}\operatorname{grad}c_s). \quad (20)$$

In the absence of an external gravitational force, the electrolyte flux is

$$\mathbf{J}_s^0 = -X\mu_{ss}\operatorname{grad}c_s. \quad (21)$$

This equation is comparable with the Fick's second law

$$\mathbf{J}_s^0 = -D^0\operatorname{grad}c_s. \quad (22)$$

Similarly, the electrolyte flux induced by the applied gravitational force can be expressed in accordance with the Fick's law

$$J_s^G = -D^G\operatorname{grad}c_s, \quad (23)$$

where D^G represents an experimentally obtained diffusion coefficient for the diffusing electrolyte species in a solution subjected to an externally applied gravitational force. By dividing Eq. (23) by Eq. (22), the ratio between fluxes $\mathbf{J}_s^H$ and $\mathbf{J}_s^0$ can be expressed as the ratio between the experimentally obtainable diffusion coefficients

$$\frac{\mathbf{J}_s^G}{\mathbf{J}_s^0} = \frac{D^H}{D^0}. \tag{24}$$

And by dividing Eq. (20) by Eq. (21), one obtains

$$\frac{\mathbf{J}_s^G}{\mathbf{J}_s^0} = 1 + \frac{\mathbf{G}_1 - \mathbf{G}_2}{\mu_{ss}\,\mathrm{grad}\,c_s}. \tag{25}$$

Comparing two latter equations obtained and solving for D^H leads to

$$D^H = D^0\left[1 + \frac{\mathbf{G}_1 - \mathbf{G}_2}{\mu_{ss}\,\mathrm{grad}\,c_s}\right]. \tag{26}$$

This equation simply shows the relationship of the two experimentally obtainable diffusion coefficients D^G and D^0 of an electrolyte in solution. In the absence of an external gravitational force, where $\mathbf{G}_1 = \mathbf{G}_2 = 0$, there is no difference between these two diffusion coefficients. Indeed, this is the conventional case where no external gravitational force is induced to the diffusing species and both diffusion coefficients estimated for both diffusing species are just related to natural diffusion processes. Note that natural gravitation is not included in the mentioned external gravitational force and should be considered as a condition of conventional diffusion. It should also be emphasized that natural gravitation should not essentially be included in conventional diffusion, but it is assumed since all conventional experiments are performed on the Earth's surface and subject to natural gravitation. Of course, the error made by this assumption is negligible, since the external gravitation force employed is significantly higher than the natural gravitation (note that, for instance, inducing external gravitational force to a diffusing system is just possible for the experiments performed under sufficiently high centrifugal forces, which make an opportunity to consider them as one-dimensional gravitational forces. Interestingly, even in the presence of an external gravitational force, but when $\mathbf{G}_1 = \mathbf{G}_2 \neq 0$, the two diffusion coefficients are still equal. This means that the difference of the gravitational forces induced to different diffusing species can affect the diffusion process, not the strength of the gravitational force.

3. Entropy production

The concept of entropy is essential for the investigation of thermodynamical systems. For a thermodynamical system, the rate of entropy production can be expressed by [16]

$$\frac{\mathrm{d}S_{int}}{\mathrm{d}t} = \frac{1}{T}\sum_i J_i X_i, \tag{27}$$

where X_i is the corresponding force. For a two-component system

$$\frac{\mathrm{d}S_{int}}{\mathrm{d}t} = \frac{1}{T}\left[L_{AA}X_A^2 + 2L_{AB}X_A X_B + L_{BB}X_B^2\right], \tag{28}$$

where $J_A = L_{AA}X_A + L_{AB}X_B$. The rate of entropy production for the system under consideration is expressed as

$$\frac{\mathrm{d}S_{int}^G}{\mathrm{d}t} = \frac{1}{T}[\mathbf{J}_1 \cdot (\mathbf{G}_1 - \mathrm{grad}\,\mu_1) + \mathbf{J}_2 \cdot (\mathbf{G}_2 - \mathrm{grad}\,\mu_2)]. \tag{29}$$

Consequently, the rate of entropy production due to the applied gravitational force is the difference of entropy production for the system in the presence and absence of the external gravitational force:

$$\frac{\mathrm{d}S_{int}^G}{\mathrm{d}t} - \frac{\mathrm{d}S_{int}^0}{\mathrm{d}t} = \frac{1}{T}[\mathbf{J}_1 \cdot (\mathbf{G}_1) + \mathbf{J}_2 \cdot (\mathbf{G}_2)]. \tag{30}$$

This indicates that the rate of entropy production due to an applied gravitational force is directly proportional to the force induced. As stated above, for the case of $\mathbf{G}_1 = \mathbf{G}_2 \neq 0$, the diffusion coefficient is the same as that of conventional case (Eq. (26)), and indeed the applied gravitational force has no effect on the diffusion coefficient. However, even in this case, the rate of entropy production increases by increasing each of gravitational forces ($\mathbf{G}_1$ or $\mathbf{G}_2$).

It can be obtained from Eq. (28) or by substituting the corresponding values in Eq. (30) that

$$\frac{\mathrm{d}S_{\mathrm{int}}^{\mathrm{G}}}{\mathrm{d}t} - \frac{\mathrm{d}S_{\mathrm{int}}^{0}}{\mathrm{d}t} = \frac{1}{T}\left(\mathbf{G}_1^2 + \mathbf{G}_2^2\right). \tag{31}$$

In fact, the latter relation indicates a strong dependence of the rate of entropy production for an electrochemical system under gravitational forces, as the rate of entropy production is proportional to the sum of square of gravitational forces induced to the electrolyte species.

4. Conclusion

Based on the theory of irreversible thermodynamics, the dependence of the flux of an electrolyte in solution on an external gravitational force was shown mathematically. A special case was introduced in which the electrolyte flux is independent of applied gravitational force when the radii and densities of the electrolyte species are the same. The results reported in Section 2 (i.e., the heart of the present Letter) suggest theoretical consideration for diffusion of electrolyte species under gravitation force. In Section 2, the gravitational force induced to each electrolyte species was briefly described. And in Section 3, the role of the applied gravitational force to increase the rate of entropy production of the system was presented. The results were indicative of the fact that although, increasing the applied gravitational force may have no significant effect on the electrolyte flux (e.g., under special case $\mathbf{G}_1 = \mathbf{G}_2 \neq 0$), however, increasing the applied gravitational force always leads to increase of the rate of entropy production of the system.

The results reported are of general importance, as they predict the influence of a known external force viz. gravitational force on various physical variables of a simple system such as an electrolyte solution. The interesting feature of this work is to show the powerfulness of the thermodynamics of irreversible processes for mathematical derivation of appropriate equations describing physical phenomena. This was based on Onsager formalism of irreversible thermodynamics. Interestingly, Onsager originally proposed this theory based on diffusion of electrolytes. In addition to the interesting results reported about influence of gravitation force on diffusion of electrolytes, the present Letter shows powerfulness of irreversible thermodynamic for theoretical consideration of various physical phenomena.

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