Lecture 27: Diffusion of Ions: *Part 2: coupled diffusion of cations and anions as described by Nernst-Planck Equation*

Today's topics

- Continue to understand the fundamental kinetics parameters of diffusion of ions within an electrically neutral system (liquid or solid), including diffusion coefficient, diffusion flux, and compare these parameters with those we previously developed for the neutral systems of atoms or molecules, aiming to see how the electrostatic potential established with the ions affect the diffusion kinetics.
- Further understanding of the harmony diffusion of A-ions and the counter ions (B-ions) for a neutral system of A_aB_b: how to deduce the Nernst-Planck equation, and understand the coupled (in harmony) diffusion coefficient, $D_{A_aB_b}$.

- Local internal electrical field, as defined as E=dΦ/dx, can be built up if the diffusion coefficient of A and B ions are different, that is $D_A \neq D_B$.

In last lecture:

We learned how to deduce the diffusion flux for ions, specifically the A-ions and B-ions for a neutral system A_aB_b, which can be, for example, a salt like $CaCl_2$ (a=1, b=2) dissolved in a medium (e.g., water), where it dissociates into free ions: one cation Ca^{2+}, and two anion Cl^-, diffusing in the aqueous medium.

The process of dissociation of A_aB_b is usually referred as ionization, as written as

$$A_aB_b \rightleftharpoons aA^{Z_c} + bB^{Z_a}$$
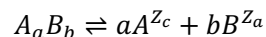
where Z_c and Z_a are the valences of A-ion (cation) and B-ion (anion) respectively.

Note that Z_c>0 but Z_a<0, and $\dfrac{Z_c}{Z_a} = -\dfrac{b}{a}$.

The potential around an individual ion is now consisted of both the regular 'chemical potential' (as marked as μ) and the 'electrical potential' (as marked as Φ) built up by the electrical charge; and this combined potential is usually referred as 'electrochemical potential' as marked as "η". Here for the A and B ions, we have:

$$\eta_A = \mu_A + Z_c e\Phi \quad \text{and} \quad \eta_B = \mu_B + Z_a e\Phi$$

Diffusion of A_aB_b (*actually A and B ions*) in the medium is regarded as a *coupled diffusion* of A_aB_b wherein 'a' number of cations move in harmony with 'b' number of anions, so as to maintain electroneutrality within the system (in other words, no electrostatic potential created, otherwise the free energy will increase).

For the "coupled (harmony) diffusion" as assumed above, we have derived the diffusion flux for A and B ions:

$$J_A = -\frac{D_A aC}{k_B T} \cdot \frac{d\eta_A}{dx} = -\frac{D_A aC}{k_B T} \cdot [\frac{d\mu_A}{dx} + Z_c \cdot e\frac{d\Phi}{dx}]$$
$$= \frac{Z_a D_A D_B abC}{k_B T[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot [Z_c \cdot \frac{d\mu_B}{dx} - Z_a \cdot \frac{d\mu_A}{dx}] \tag{1}$$

$$J_B = -\frac{D_B aC}{k_B T} \cdot \frac{d\eta_B}{dx} = -\frac{D_B aC}{k_B T} \cdot [\frac{d\mu_B}{dx} + Z_a \cdot e\frac{d\Phi}{dx}]$$
$$= -\frac{Z_c D_A D_B abC}{k_B T[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot [Z_c \cdot \frac{d\mu_B}{dx} - Z_a \cdot \frac{d\mu_A}{dx}] \tag{2}$$

Where the D_A and D_B are the diffusion coefficient of A and B ion, respectively, and C is the concentration of the dissolved salt A_aB_b.

From the two equations above, we have

$$\frac{J_A}{J_B} = -\frac{Z_a}{Z_c},$$

or $Z_c J_A + Z_a J_B = 0$, *as indeed consistent with the 'coupled' diffusion flux of A and B ions as discussed above, where the diffusion of A is in harmony with (or neutralized by) the diffusion of B.*

also considering the electroneutrality of A_aB_b, we have $\dfrac{Z_c}{Z_a} = -\dfrac{b}{a}$, where $Z_c > 0$, $Z_a < 0$

then we have, $\dfrac{J_A}{a} = \dfrac{J_B}{b}$

defining $\dfrac{J_A}{a} = \dfrac{J_B}{b} = J_{A_aB_b}$

This implies that *when 'a' A-ions and 'b' B-ions move in harmony, it is as if one A_aB_b molecule moves.* <u>Now let's understand this harmony through the following treatment.</u>

Recalling the assumption we made for the ionization equilibrium, which remains during the diffusion:
$$A_aB_b \rightleftharpoons aA^{Z_c} + bB^{Z_a}$$
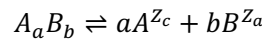
That means, $a\mu_A + b\mu_B = \mu_{A_aB_b}$

Where $\mu_{A_aB_b}$ is the chemical potential of A_aB_b. Note that A_aB_b is electrically neutral.

Differentiating the above equation, $\quad a\dfrac{d\mu_A}{dx} + b\dfrac{d\mu_B}{dx} = \dfrac{d\mu_{A_aB_b}}{dx} \tag{3}$

Again, considering $\dfrac{Z_c}{Z_a} = -\dfrac{b}{a}$

We can have $Z_c = b \cdot \alpha$ and $Z_a = -a \cdot \alpha$, where α is a positive integer.

For example: for salts like KCl, CaCl$_2$, $\alpha = 1$; for salts like MgSO$_4$, $\alpha = 2$. Thus, timing the both side of Eq. (3) with α, we have

$$\alpha a \cdot \frac{d\mu_A}{dx} + \alpha b \cdot \frac{d\mu_B}{dx} = \alpha \cdot \frac{d\mu_{A_a B_b}}{dx}$$

Or, $\quad -Z_a \cdot \dfrac{d\mu_A}{dx} + Z_c \cdot \dfrac{d\mu_B}{dx} = \alpha \cdot \dfrac{d\mu_{A_a B_b}}{dx}$ \hfill (4)

The left-hand side is the term in parenthesis [] in equations (1) and (2).

Substituting Eq. (4) into Eqs. (1) and (2), we have

$$J_A = \frac{Z_a D_A D_B abC}{k_B T [Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \alpha \cdot \frac{d\mu_{A_a B_b}}{dx}$$

Or,

$$J_A = -\frac{Z_a C}{k_B T} \cdot \frac{D_A D_B ab\alpha}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left[-\frac{d\mu_{A_a B_b}}{dx} \right] \tag{5}$$

The same way, we have,

$$J_B = \frac{Z_c C}{k_B T} \cdot \frac{D_A D_B ab\alpha}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left[-\frac{d\mu_{A_a B_b}}{dx} \right] \tag{6}$$

now

$$\frac{J_A}{a} = -\frac{Z_a}{a} \frac{C}{k_B T} \cdot \frac{D_A D_B ab\alpha}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left\{ -\frac{d\mu_{A_a B_b}}{dx} \right\}$$

With $\dfrac{Z_a}{a} = -\alpha$

Then, $\quad \dfrac{J_A}{a} = \dfrac{C}{k_B T} \cdot \dfrac{D_A D_B ab\alpha^2}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left\{ -\dfrac{d\mu_{A_a B_b}}{dx} \right\}$ \hfill (7)

The same way,

$$\frac{J_B}{b} = \frac{C}{K_B T} \cdot \frac{D_A D_B ab\alpha^2}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left\{ -\frac{d\mu_{A_a B_b}}{dx} \right\} \tag{8}$$

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Now, from Eqs. (7) and (8), we have indeed seen that

$$\frac{J_A}{a} = \frac{J_B}{b} = J_{A_a B_b}$$

--- again, **when 'a' A-ions and 'b' B-ions move in harmony, it is as if one $A_a B_b$ molecule moves.**

so, $\quad J_{A_a B_b} = C \frac{1}{K_B T} \cdot \frac{D_A D_B a b \alpha^2}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \{-\frac{d\mu_{A_a B_b}}{dx}\}$ $\qquad$ (9)

Let's write

$$D_{A_a B_b} = \frac{D_A D_B a b \alpha^2}{[Z_c^2 D_A a + Z_a^2 D_B b]} \qquad (10)$$

The above is known as the Nernst-Planck equation. $D_{A_a B_b}$ is the diffusion coefficient of $A_a B_b$ in the medium under consideration. It is apparently related to the individual ionic diffusion coefficients, *can thus be regarded as a parameter reflecting the 'coupled' diffusion of A and B ions.*

Taking $D_{A_a B_b}$ as defined in Eq. (10), the diffusion flux for $A_a B_b$ in general can be given by

$$J_{A_a B_b} = C_{A_a B_b} \cdot \frac{D_{A_a B_b} \cdot}{k_B T} \cdot \{-\frac{d\mu_{A_a B_b}}{dx}\} \qquad (11)$$

$$\underset{\text{concentration}}{\nearrow} \quad \underset{\text{mobility}}{\uparrow} \quad \underset{\text{force}}{\uparrow}$$

Where $\quad C_{A_a B_b} = C$, $\quad D_{A_a B_b} = \frac{D_A D_B a b \alpha^2}{[Z_c^2 D_A a + Z_a^2 D_B b]}$, $\quad \mu_{A_a B_b} = a\mu_A + b\mu_B$, as defined above, respectively.

Considering two extreme conditions:

- if $\quad D_A \gg D_B$, $\quad D_{A_a B_b} = \frac{D_B a b \alpha^2}{Z_c^2 a} = \frac{D_B}{b}$

- if $\quad D_B \gg D_A$, $\quad D_{A_a B_b} = \frac{D_A a b \alpha^2}{Z_a^2 b} = \frac{D_A}{a}$

Let us now return to the equation for the potential gradient $\frac{d\Phi}{dx}$ given by the equation we developed in last lecture,

$$\frac{d\Phi}{dx} = -\frac{[Z_c D_A a \cdot \frac{d\mu_A}{dx} + Z_a D_B b \frac{d\mu_B}{dx}]}{e[Z_c^2 D_A a + Z_a^2 D_B b]} \qquad (12)$$

For dilute solution of $A_a B_b$ as assumed above, we have

$$\mu_A = \mu_A^0 + k_B T \ln C_A = \mu_A^0 + k_B T \ln[aC]$$

$$\mu_B = \mu_B^0 + k_B T \ln C_B = \mu_B^0 + k_B T \ln[bC]$$

The above assumption is not completely true, even for dilute solutions. However, we will use it for simplicity.

Then,

$$\frac{d\mu_A}{dx} = \frac{k_B T}{C} \cdot \frac{dc}{dx}$$

$$\frac{d\mu_B}{dx} = \frac{k_B T}{C} \cdot \frac{dc}{dx}$$

So,   Eq. (12) can be re-written as

$$\frac{d\Phi}{dx} = -\frac{[Z_c D_A a \cdot \frac{d\mu_A}{dx} + Z_a D_B b \frac{d\mu_B}{dx}]}{e[Z_c^2 D_A a + Z_a^2 D_B b]}$$

$$= -\frac{(Z_c D_A a + Z_a D_B b)}{e[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \frac{k_B T}{C} \cdot \frac{dc}{dx}$$

Remember $Z_a = -\alpha a$, $Z_c = \alpha b$,   so, $Z_c a = \alpha a b$, $Z_a b = -\alpha a b$

Substituting both $Z_c a$ and $Z_a b$ into the above equation, we have

$$\frac{d\Phi}{dx} = -\frac{\alpha a b (D_A - D_B)}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \frac{k_B T}{e} \cdot \frac{1}{C} \cdot \frac{dc}{dx}$$

The local electrical field (E) is given by

$$E = -\frac{d\Phi}{dx} = \frac{\alpha a b (D_A - D_B)}{[Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \frac{k_B T}{e} \cdot \frac{1}{C} \cdot \frac{dc}{dx}$$

This is a local internal field, not measurable.   *If $D_A = D_B$, there is no internal electrical field.*