

Lecture 26: Diffusion of Ions: Part 1: basic understanding and the derivation of diffusion flux

Today's topics

- Understanding of the fundamental differences between a solution (solid or liquid) consisting of only neutral species (atoms, molecules) and the one containing ions (i.e., electrically charged atoms or molecules).
- The local potential around an individual ion is now consisted of both the regular 'chemical potential' and the electrical potential built up by the electrical charge; and this combined potential is usually referred as 'electrochemical potential'.
- The diffusion kinetics, in terms of diffusion coefficient and diffusion flux, now have to be deduced (using the Fick's first law) from the "electrochemical potential", rather than the regular 'chemical potential', using the same protocol as we went through in Lecture 5.

Brief introduction:

All the diffusion processes and kinetics we have considered so far are for electrically neutral species, e.g., atoms (carbon, iron, gold, copper, etc.) or molecules (water, alcohol, iron oxides, etc.). however, when a solution contains or consists of electrically charged species (typically ions, cations or anions), electric field will be generated around each of the ions, and such electric fields will affect the migration of other ions in proximity --- a cation attracts anions, but repulses other cations; and reversely also true for an anion. The electric fields may be externally imposed, or internally created, or both. Internal electric fields are often created during diffusion and can exist over a small distance – a few Å or nm. These are electric fields developed to maintain electroneutrality. In all physical processes, electroneutrality is almost always assumed. *How to integrate the effect of electrical fields into the diffusion kinetics is the topic of today's and next lecture.*

Electrochemical potential:

For an ion 'i' with charge = $Z_i e$ (where Z_i is the valence; positive for cations (e.g., +1 for Na^+ , +2 for Ca^{2+} , +3 for Fe^{3+} , etc.), negative for anions (e.g., -1 for Cl^- , -2 for SO_4^{2-} , -3 for PO_4^{3-} , etc.), 'e' is the charge of one electron (= $1.60217646 \times 10^{-19}$ coulombs). The potential of the ion 'i', now called electrochemical potential, η_i , is consisted of both the chemical potential and electrical potential, as given by

$$\eta_i = \mu_i + Z_i e \Phi \quad (\text{per ion})$$

where Φ = local electrostatic potential.

The above definition is on a per ion basis. On a per mole basis, it becomes:

$$\eta_i = \mu_i + Z_i F \Phi \quad (\text{per mole})$$

where F = Faraday constant (96,487 coulombs/mole).

Diffusion of ions:

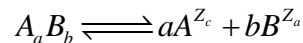
As we learned in Lecture 5, according Fick's first Law, the diffusion flux of neutral species like atoms can be expressed as:

$$J = -D \cdot \frac{dC}{dx} = -D \cdot \frac{C}{k_B T} \cdot \frac{d\mu}{dx}$$

Now, replace the "chemical potential, μ " with "electrochemical potential, η_i ", we will have the diffusion flux expressed for an ion "i".

$$J_i = -\frac{D_i C_i}{k_B T} \cdot \frac{d\eta_i}{dx} \quad (\text{in unit of \#/cm}^2 \cdot \text{sec})$$

Now let us consider a salt $A_a B_b$ (for example 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^- . This process usually referred as ionization, can be written as



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

$$\frac{a}{b} = -\frac{Z_a}{Z_c}.$$

Diffusion of $A_a B_b$ (actually A and B ions) in the medium may be regarded as *molecular diffusion* of $A_a B_b$, or a *coupled diffusion* of $A_a B_b$ wherein 'a' number of cations move in harmony with 'b' number of anions. The later description is more accurate when the salt is dissolved (dissociated) and ionized. The flux of cations and anions **must be coupled**, because *large charge separation will create local electrostatic potential and thus increase the free energy of the system*. For this reason, the condition of electroneutrality is assumed. In the dissociated state, the fluxes of A and B ions are given by:

$$J_A = -\frac{D_A C_A}{k_B T} \cdot \frac{d\eta_A}{dx}; \quad J_B = -\frac{D_B C_B}{k_B T} \cdot \frac{d\eta_B}{dx}$$

Where D_A and D_B are the diffusion coefficient of A and B ion, respectively, and C_A and C_B are the concentrations of A and B ion respectively.

Let the concentration of the dissolved salt $A_a B_b$ be 'C'. Then, $C_A = aC$ and $C_B = bC$. The above flux can now be written as:

$$J_A = -\frac{D_A aC}{k_B T} \cdot \frac{d\eta_A}{dx}$$

$$J_B = -\frac{D_B b C}{k_B T} \cdot \frac{d\eta_B}{dx}$$

substituting for $\eta_A = \mu_A + Z_c e \Phi$ and $\eta_B = \mu_B + Z_a e \Phi$, then we have,

$$J_A = -\frac{D_A a C}{k_B T} \cdot \frac{d\eta_A}{dx} = -\frac{D_A a C}{k_B T} \cdot \left[\frac{d\mu_A}{dx} + Z_c \cdot e \frac{d\Phi}{dx} \right]$$

$$J_B = -\frac{D_B b C}{k_B T} \cdot \frac{d\eta_B}{dx} = -\frac{D_B b C}{k_B T} \cdot \left[\frac{d\mu_B}{dx} + Z_a \cdot e \frac{d\Phi}{dx} \right]$$

The local electrical current density due to A is

$$I_A = Z_c \cdot e \cdot J_A$$

The same way, the local electrical current density due to B is

$$I_B = Z_a \cdot e \cdot J_B$$

Since the diffusion fluxes of A and B are always coupled, the condition of electroneutrality should be maintained. That is, there should be no net current (if no external field is applied). So, $I_A + I_B = 0$

$$\text{Or, } Z_c \cdot e \cdot J_A + Z_a \cdot e \cdot J_B = 0$$

Submitting for J_A and J_B obtained above, then we have,

$$Z_c D_A a \frac{d\mu_A}{dx} + Z_c^2 D_A a e \frac{d\Phi}{dx} + Z_a D_B b \frac{d\mu_B}{dx} + Z_a^2 D_B b e \frac{d\Phi}{dx} = 0$$

The above equation can be re-written as:

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

Then,

$$\frac{d\Phi}{dx} = -\frac{(Z_c D_A a \frac{d\mu_A}{dx} + Z_a D_B b \frac{d\mu_B}{dx})}{e[Z_c^2 D_A a + Z_a^2 D_B b]} \quad (1)$$

The above equation gives the *gradient in local electrostatic potential*, which is defined as, $E = -\frac{d\Phi}{dx}$, the

local internal electrical field.

Now, let us substitute for $\frac{d\Phi}{dx}$ in the equations for J_A and J_B .

$$J_A = -\frac{D_A a C}{k_B T} \cdot \frac{d\eta_A}{dx} = -\frac{D_A a C}{k_B T} \cdot \left[\frac{d\mu_A}{dx} + Z_c \cdot e \frac{d\Phi}{dx} \right]$$

using the relationship $Z_c a = -Z_a b$ (for the electroneutrality of $A_a B_b$) as mentioned above, the above equation can be eventually derived as:

$$J_A = \frac{Z_c D_A D_B a b C}{k_B T [Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left[Z_c \cdot \frac{d\mu_B}{dx} - Z_a \cdot \frac{d\mu_A}{dx} \right] \quad (2)$$

Similarly, from $J_B = -\frac{D_B a C}{k_B T} \cdot \frac{d\eta_B}{dx} = -\frac{D_B a C}{k_B T} \cdot \left[\frac{d\mu_B}{dx} + Z_a \cdot e \frac{d\Phi}{dx} \right]$, we can have

$$J_B = -\frac{Z_c D_A D_B a b C}{k_B T [Z_c^2 D_A a + Z_a^2 D_B b]} \cdot \left[Z_c \cdot \frac{d\mu_B}{dx} - Z_a \cdot \frac{d\mu_A}{dx} \right] \quad (3)$$

From Eq. (2) and (3) above, we have

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

or $Z_c J_A + Z_a J_B = 0$, just as required by 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 $A_a B_b$, we have $\frac{Z_c}{Z_a} = -\frac{b}{a}$, where $Z_c > 0$, $Z_a < 0$

then, $\frac{J_A}{a} = \frac{J_B}{b}$

now we can define $\frac{J_A}{a} = \frac{J_B}{b} = J_{A_a B_b}$

That is, when ‘a’ A-ions and ‘b’ B-ions move in harmony, it is as if one $A_a B_b$ molecule moves. Next lecture, we will continue to discuss in detail how such a “diffusion harmony” can be reflected from the diffusion flux considered for a “neutral” $A_a B_b$ molecule --- the **Nernst-Planck equation**.