❖ The Basic Equation for the Diffusion

The basic equation for the diffusion potential can be obtained by using the Onsager phenomenological equations very easily. To do so, imagine an electrolytic solution with M^{z+} type cations, A^{z-} type anions and water as the solvent with j_+, j_- and j_0 fluxes, respectively. Now if the solvent is assumed to be non-moving, its flux can simply be put equal to zero i.e. $j_0 = 0$. Such a solution will only have two types of ionic fluxes which can be formulated as given below.

$$j_+ = L_{++}\,\vec{F}_+ + L_{+-}\,\vec{F}_- \tag{175}$$

$$j_- = L_{--}\,\vec{F}_- + L_{-+}\,\vec{F}_+ \tag{176}$$

Where L_{++} and L_{--} are coefficients for mutually independent flow, whereas L_{+-} and L_{-+} are for the mutually coupled flow.

Now, under steady-state approximation, the magnitude of positive charge flowing through the unit volume must be equal to the amount of the negative charge flowing through the same element but in the opposite direction. Mathematically, we can say that

$$z_+Fj_+ = -(z_-Fj_-) \tag{177}$$

Where F is Faraday constant. The minus sign is for the mutually opposite directions.

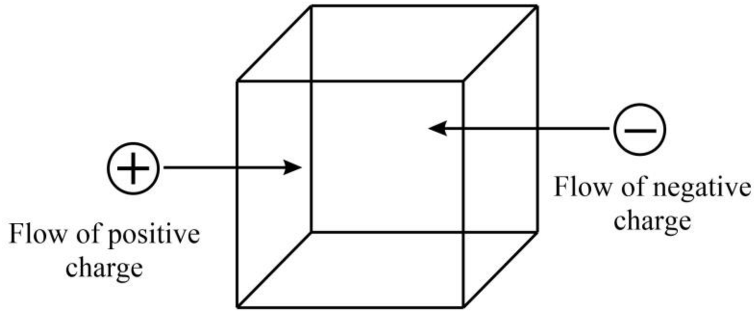

Figure 11. The flow of charge under steady-state approximation.

Rearranging equation (177) and then using values of j_+ and j_- form equation (175-176), we get

$$z_+F(L_{++}\vec{F}_+ + L_{+-}\vec{F}_-) + z_-F(L_{--}\vec{F}_- + L_{-+}\vec{F}_+) = 0 \tag{178}$$

Putting $z_+F = q_+$ and $z_-F = q_-$ for simplicity, we have

$$q_+(L_{++}\vec{F}_+ + L_{+-}\vec{F}_-) + q_-(L_{--}\vec{F}_- + L_{-+}\vec{F}_+) = 0 \tag{179}$$

$$q_+L_{++}\vec{F}_+ + q_+L_{+-}\vec{F}_- + q_-L_{--}\vec{F}_- + q_-L_{-+}\vec{F}_+ = 0 \tag{180}$$

$$\vec{F}_+(q_+L_{++} + q_-L_{-+}) + \vec{F}_-(q_+L_{+-} + q_-L_{--}) = 0 \tag{181}$$

Using short symbols $p_+ = q_+L_{++} + q_-L_{-+}$ and $p_- = q_+L_{+-} + q_-L_{--}$, we have

$$p_+\vec{F}_+ + p_-\vec{F}_- = 0 \tag{182}$$

Now recalling the expressions for driving forces i.e.

$$\vec{F}_+ = q_+\frac{d\psi}{dx} + \frac{d\mu_+}{dx} \tag{183}$$

$$\vec{F}_- = q_-\frac{d\psi}{dx} + \frac{d\mu_-}{dx} \tag{184}$$

Where $d\mu_+/dx$ and $q_+d\psi/dx$ are the driving forces for pure diffusion and pure conduction phenomena for the cations; whereas, $d\mu_-/dx$ and $q_-d\psi/dx$ are the driving forces for pure diffusion and pure conduction phenomena for the anions. Using equation (183, 184) in equation (182), we get

$$p_+q_+\frac{d\psi}{dx} + p_+\frac{d\mu_+}{dx} + p_-q_-\frac{d\psi}{dx} + p_-\frac{d\mu_-}{dx} = 0 \tag{185}$$

or

$$-p_+q_+\frac{d\psi}{dx}-p_-q_-\frac{d\psi}{dx}=p_+\frac{d\mu_+}{dx}+p_-\frac{d\mu_-}{dx} \tag{186}$$

$$-\frac{d\psi}{dx}(p_+q_++p_-q_-)=p_+\frac{d\mu_+}{dx}+p_-\frac{d\mu_-}{dx} \tag{187}$$

$$-\frac{d\psi}{dx}=\frac{p_+}{p_+q_++p_-q_-}\frac{d\mu_+}{dx}+\frac{p_-}{p_+q_++p_-q_-}\frac{d\mu_-}{dx} \tag{188}$$

Since we know that

$$\frac{p_+}{p_+q_++p_-q_-}=\frac{t_+}{z_+F} \tag{189}$$

or

$$\frac{p_-}{p_+q_++p_-q_-}=\frac{t_-}{z_-F} \tag{190}$$

Where t_+ and t_- are transport numbers of cation and anion, respectively. Using equation (189, 190) in equation (188), we get

$$-\frac{d\psi}{dx}=\frac{t_+}{z_+F}\frac{d\mu_+}{dx}+\frac{t_-}{z_-F}\frac{d\mu_-}{dx} \tag{191}$$

Or in general, we can conclude as

$$-\frac{d\psi}{dx}=\sum\frac{t_i}{z_iF}\frac{d\mu_i}{dx} \tag{192}$$

The minus sign of the electric field is because it is in the opposite direction to the chemical potential gradients of ionic diffusion. Furthermore, equation (192) can also be written as

$$-\frac{d\psi}{dx}=\frac{1}{F}\sum\frac{t_i}{z_i}\frac{d\mu_i}{dx} \tag{193}$$

or

$$-d\psi=\frac{1}{F}\sum\frac{t_i}{z_i}d\mu_i \tag{193}$$

In terms of activity (a_i), the above equation can be written as

$$-d\psi=\frac{RT}{F}\sum\frac{t_i}{z_i}d\ln\, a_i \tag{194}$$

Which is the basic equation of diffusion potential.

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