❖ Total Driving Force for Ionic Transport: Nernst-Planck Flux Equation

The rate perspective of the conduction process has already been discussed in the previous sections of this chapter. During the whole of the discussion, we assumed that the composition of the electrolyte was uniform throughout. However, the case will become somewhat different if we assume a concentration gradient w.r.t. tracer ions (cations in this case). Let the concentration of tracer cations is $(c_+)_x$ at a distance x on the left of the barrier-maximum whereas the concentration $(c_+)_{x+l}$ on the right of the barrier maximum. Now, if we assume that $(c_+)_{x+l} > (c_+)_x$, we can say that

$$(c_+)_{x+l} = (c_+)_x + \frac{d(c_+)_x}{dx} \times l \tag{126}$$

Owing to the decreasing concentration gradient of tracer ions from right to left, we cannot use the simple expression for current density.

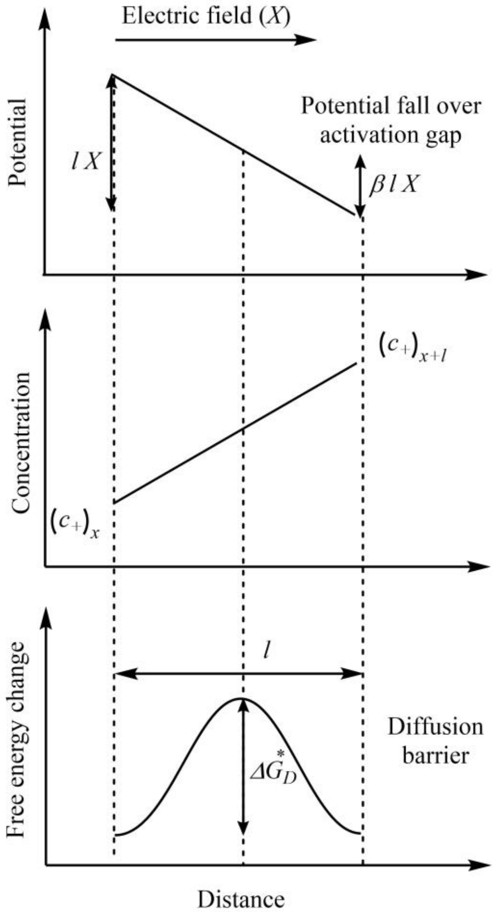

Figure 8. The general depiction of the ionic movement from right to left due to diffusion facing activation barrier under the influence of the external electric field.

Therefore, the fundamental relation between the ionic drift velocity (v_d) and current density (J) for cation must be recalled first i.e.

$$J = z_+ cFv_d \tag{127}$$

Where z is the charge number and c is the concentration of the ions. The symbol F represents the Faraday constant. Also, the drift velocity can be assumed as the resultant velocity of the velocity of ions in the direction of the force field ($\vec{v}$) and the velocity of ions in the opposite direction ($\overleftarrow{v}$). Mathematically, we can say as given below.

$$v_d = \vec{v} - \overleftarrow{v} \tag{128}$$

Using the above result in equation (127), we get

$$J = z_+ cF(\vec{v} - \overleftarrow{v}) \tag{129}$$

$$J = z_+ cF\vec{v} - z_+ cF\overleftarrow{v}$$

Since concentration for left and on right are $(c_+)_x$ and $(c_+)_{x+l}$; the above equation can also be written as

$$J = z_+ (c_+)_x F\vec{v} - z_+ (c_+)_{x+l} F\overleftarrow{v} \tag{130}$$

Using the value of $(c_+)_{x+l}$ from equation (126) in equation (130), we get

$$J = z_+ (c_+)_x F\vec{v} - z_+ \left((c_+)_x + \frac{d(c_+)_x}{dx} \times l\right) F\overleftarrow{v} \tag{131}$$

For simplicity, the label $(c_+)_x$ with c_+ i.e.

$$J = z_+ c_+ F\vec{v} - z_+ \left(c_+ + \frac{dc_+}{dx} l\right) F\overleftarrow{v} \tag{132}$$

Recalling the values of $\vec{v}$ and $\overleftarrow{v}$ i.e.

$$\vec{v} = l\, k_D e^{pX} \tag{133}$$

$$\overleftarrow{v} = l\, k_D\, e^{-pX} \tag{134}$$

Where k_D is the jumping frequency for diffusion and X is simply the electric field. The expression for symbol $p = z_+ Fl/2RT$. When the field strength is very low, $pX \ll 1$; and therefore, equations (133, 134) can be expended as given below.

$$\vec{v} = l\, k_D (1 + pX) \tag{135}$$

$$\overleftarrow{v} = l\, k_D\, (1 - pX) \tag{136}$$

Now, after rearranging equation (132) and then using equations (135, 136), we have

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$$J = z_+c_+F\vec{v} - c_+z_+F\overleftarrow{v} - \frac{dc_+}{dx}lz_+F\overleftarrow{v} \tag{137}$$

$$J = z_+c_+Fl\,k_D(1+pX) - c_+z_+Fl\,k_D\,(1-pX) - \frac{dc_+}{dx}lz_+Fl\,k_D\,(1-pX) \tag{138}$$

$$J = 2z_+c_+Fl\,k_DpX - z_+Fl^2\,k_D\,(1-pX)\frac{dc_+}{dx} \tag{139}$$

Neglecting pX in comparison to one for low-field approximation, we have

$$J = 2z_+c_+Fl\,k_DpX - z_+Fl^2\,k_D\,\frac{dc_+}{dx} \tag{140}$$

Since $p = z_+Fl/2RT$, the equation (140) can be transformed to

$$J = 2z_+c_+Fl\,k_D\frac{z_+Fl}{2RT}X - z_+Fl^2\,k_D\,\frac{dc_+}{dx} \tag{141}$$

$$J = z_+^2c_+F^2\frac{l^2k_D}{RT}X - z_+Fl^2\,k_D\,\frac{dc_+}{dx} \tag{142}$$

Since $l^2k_D = D_+$, the equation (142) takes the form

$$J = z_+^2c_+F^2\frac{D_+}{RT}X - z_+FD_+\frac{dc_+}{dx} \tag{143}$$

Now recalling the correlation between current density (J_+) and flux (j_+) of positive ions i.e.

$$j_+ = \frac{J_+}{z_+F} \tag{144}$$

Now because the current density given by equation (143) is only from cations, the corresponding flux can be obtained putting value of J_+ from equation (143) in equation (144), we get

$$j_+ = \frac{z_+^2c_+F^2D_+X}{z_+FRT} - \frac{z_+FD_+}{z_+F}\frac{dc_+}{dx} \tag{145}$$

$$j_+ = \frac{c_+D_+}{RT}z_+FX - D_+\frac{dc_+}{dx} \tag{146}$$

After multiplying and dividing the second term by c_+RT, we have

$$j_+ = \frac{c_+D_+}{RT}z_+FX - \frac{D_+c_+}{RT}\frac{RT}{c_+}\frac{dc_+}{dx} \tag{147}$$

$$j_+ = \frac{c_+D_+}{RT}z_+FX - \frac{D_+c_+}{RT}\frac{d(RT\ln c_+)}{dx} \tag{148}$$

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$$j_+ = \frac{c_+D_+}{RT}z_+FX - \frac{D_+c_+}{RT}\frac{d(\mu_+^0 + RT\ln c_+)}{dx} \tag{149}$$

$$j_+ = \frac{c_+D_+}{RT}z_+FX - \frac{D_+c_+}{RT}\frac{d(\mu_+^0 + RT\ln c_+)}{dx} \tag{150}$$

Since $\mu_+^0 + RT\ln c_+ = \mu_+$, the above equation becomes

$$j_+ = \frac{c_+D_+}{RT}z_+FX - \frac{D_+c_+}{RT}\frac{d\mu_+}{dx} \tag{151}$$

It is a well-known fact in electrochemical theory that the electric field is simply equal to negative of the gradient of electrostatic potential i.e. $X = -d\psi/dx$. Therefore, the equation (151) takes the form

$$j_+ = \frac{c_+D_+}{RT}z_+F\left(-\frac{d\psi}{dx}\right) - \frac{D_+c_+}{RT}\frac{d\mu_+}{dx} \tag{152}$$

or

$$j_+ = -\frac{c_+D_+}{RT}\left(z_+F\frac{d\psi}{dx} + \frac{d\mu_+}{dx}\right) \tag{153}$$

Since the $-d\mu_+/dx$ and $-z_+F\,d\psi/dx$ are the driving forces for pure diffusion and pure conduction phenomena, respectively; the total driving force for ionic transport must be equal to the negative gradient of chemical potential and electrostatic potential. The sum of the two potentials is called as electrostatic-chemical potential ($\bar{\mu}_+$), and is defined by

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$$\bar{\mu}_+ = z_+F\psi + \mu_+ \tag{154}$$

Taking negative both sides and then differentiating w.r.t. x, we have

$$-\frac{d\bar{\mu}_+}{dx} = -\left(z_+F\frac{d\psi}{dx} + \frac{d\mu_+}{dx}\right) \tag{155}$$

Utilizing the above result in equation (153), we get

$$j_+ = -\frac{c_+D_+}{RT}\frac{d\bar{\mu}_+}{dx} \tag{156}$$

Since the Einstein relation is $D_+ = (\bar{u}_{abs})_+kT$, the above equation becomes

$$j_+ = -\frac{c_+(\bar{u}_{abs})_+kT}{RT}\frac{d\bar{\mu}_+}{dx} \tag{157}$$

Moreover, the relationship between conventional $(\bar{u}_{conv})_+$ and absolute mobilities $(\bar{u}_{abs})_+$ is

$$(\bar{u}_{conv})_+ = (\bar{u}_{abs})_+\, z_+e_0 \tag{158}$$

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Therefore, the use of equation (158) in equation (157) gives

$$j_{+} = -\frac{c_{+}(\bar{u}_{conv})_{+}k}{z_{+}e_{0}R}\frac{d\bar{\mu}_{+}}{dx} \tag{159}$$

Since $R = N_A k$, the above equation becomes

$$j_{+} = -\frac{c_{+}(\bar{u}_{conv})_{+}}{z_{+}e_{0}N_{A}}\frac{d\bar{\mu}_{+}}{dx} \tag{160}$$

Putting $e_0 N_A = F$, we have

$$j_{+} = -\frac{(\bar{u}_{conv})_{+}}{z_{+}F}c_{+}\frac{d\bar{\mu}_{+}}{dx} \tag{161}$$

Which is the famous Nernst-Planck flux equation that relates the total driving force for the ionic transport with the overall flux.

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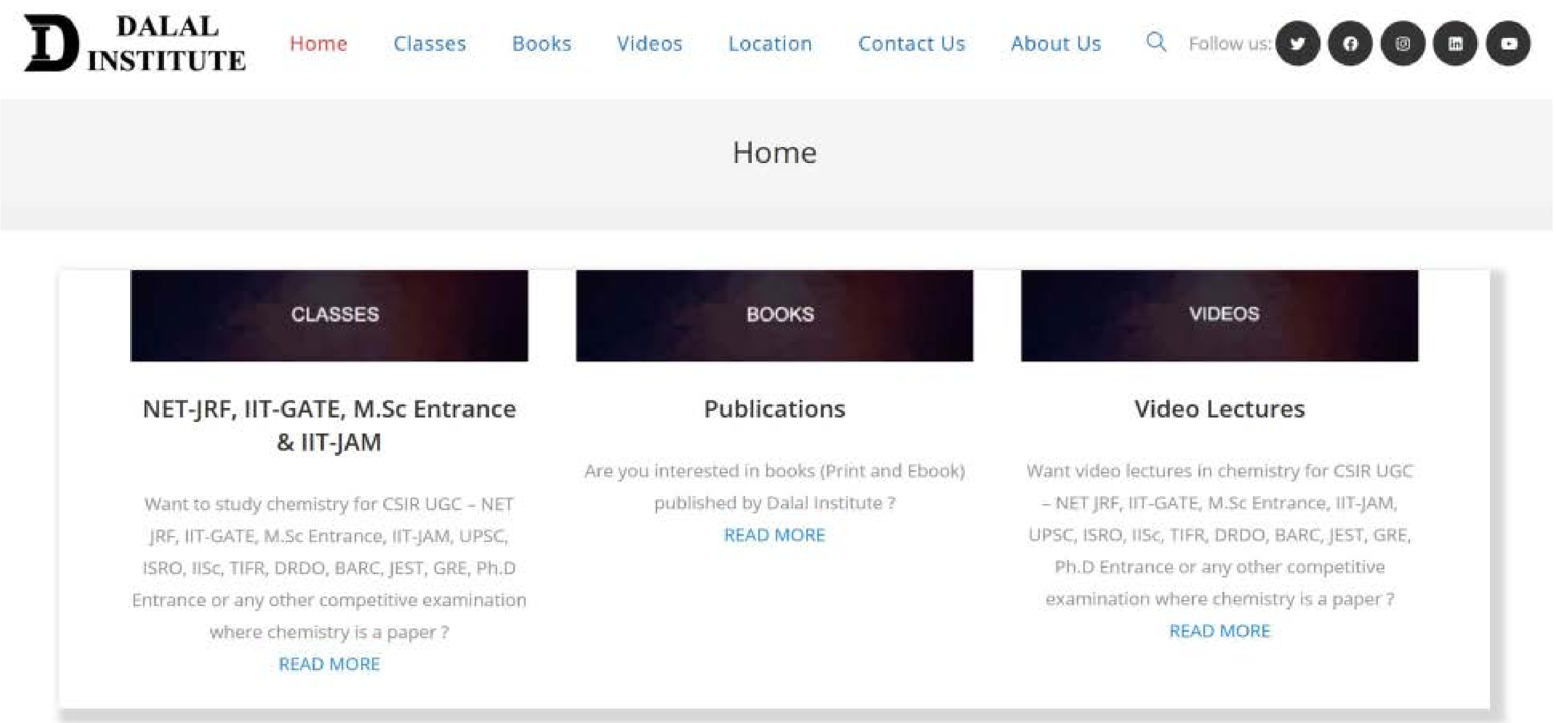

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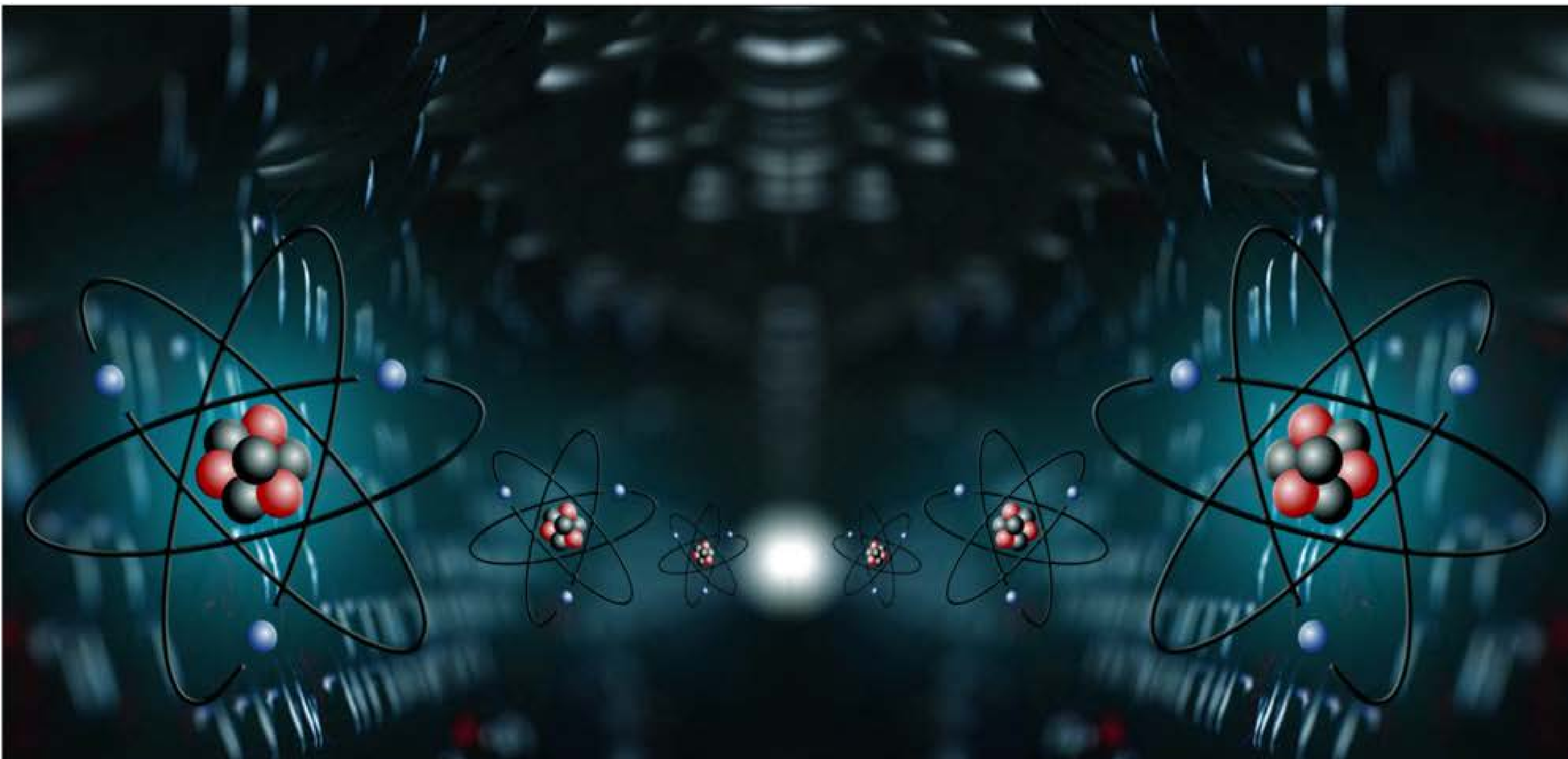

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