❖ The Rate-Process Approach to Ionic Migration

In order to understand the rate-process approach to ionic migration, recall the fundamental relation between the ionic drift velocity (v_d) and current density (J) i.e.

$$J = zcFv_d \tag{90}$$

Where z is the charge number and c is the concentration of the ions. The symbol F represents the Faraday constant. The drift velocity (v_d) is related to the macroscopic force

$$v_d = \frac{\tau}{m}\vec{F} \tag{91}$$

Where m is the mass of the ion. The symbol τ represents the mean lifetime between to collisions during the ionic drift. The symbol $\vec{F}$ is the viscose or electric force that can be formulated as

$$\vec{F} = 6\pi r\eta v \qquad or \qquad \vec{F} = ze_0X \tag{92}$$

Where η is the coefficient of viscosity and r is the radius of the cation. In the right-hand relation, z is the charge number of the ion under consideration, e_0 is the electronic charge and X is the applied electric field.

Furthermore, the drift velocity can also 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.

$$v_d = \vec{v} - \overleftarrow{v} \tag{93}$$

Now, since the velocity is also the ratio of average jump distance (l) to the average time between two successive jumps (τ), we can also write as

$$\vec{v} = \frac{l}{\tau} \tag{94}$$

Furthermore, the jump frequency i.e. number of jumps per unit of time ($k = 1/\tau$) is simply the reciprocal of the mean time between successive jumps. Therefore, the velocities can also be written as

$$\vec{v} = l\,\vec{k} \tag{95}$$

or

$$\overleftarrow{v} = l\,\overleftarrow{k} \tag{96}$$

Now in case of diffusion, the jumps of ions can be considered as a rate phenomenon for which the participating ion must possess a minimum amount of free energy to activation to do so. It was found that

$$\vec{k} = \frac{kT}{h}e^{-\Delta G^*/RT} \tag{97}$$

For the diffusion only (from right to left), the above equation can be relabelled with subscript *D* i.e.

$$\overleftarrow{k}_D = \frac{kT}{h} e^{-\Delta G_D^*/RT} \tag{98}$$

However, when the electric field is applied, the diffusion of ions from right to left will be opposed. Therefore, the work-done (w) in moving the ion from the equilibrium state to the barrier-maximum will be equal to the product of the ionic charge (z_+e_0), and the potential difference between the activated state and equilibrium position. Now assume that this potential difference is simply a fraction β of the overall active potential (Xl).

$$w = z_+e_0\beta Xl \tag{99}$$

Where X is the electric field and l is the distance between the two equilibrium states. For one mole of ions, the equation (99) takes the form

$$W = N_A z_+e_0\beta Xl \tag{100}$$

or

$$W = z_+F\beta Xl \tag{101}$$

The overall depiction of the rate-process approach to the ionic migration phenomenon under the influence of an external electric field is shown below.

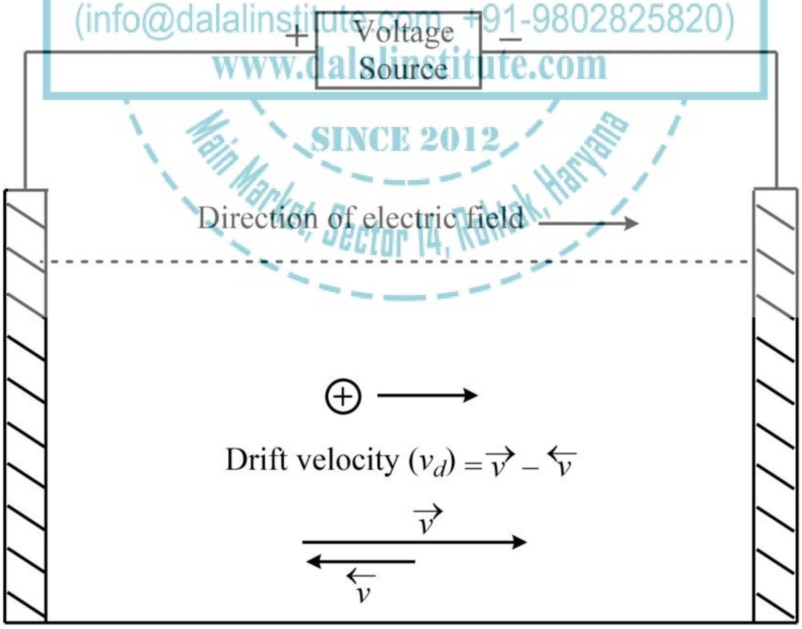

Figure 5. The general depiction of the rate-process approach to ionic migration under the influence of an external electric field.

The process of activation can be described by the diagram given below.

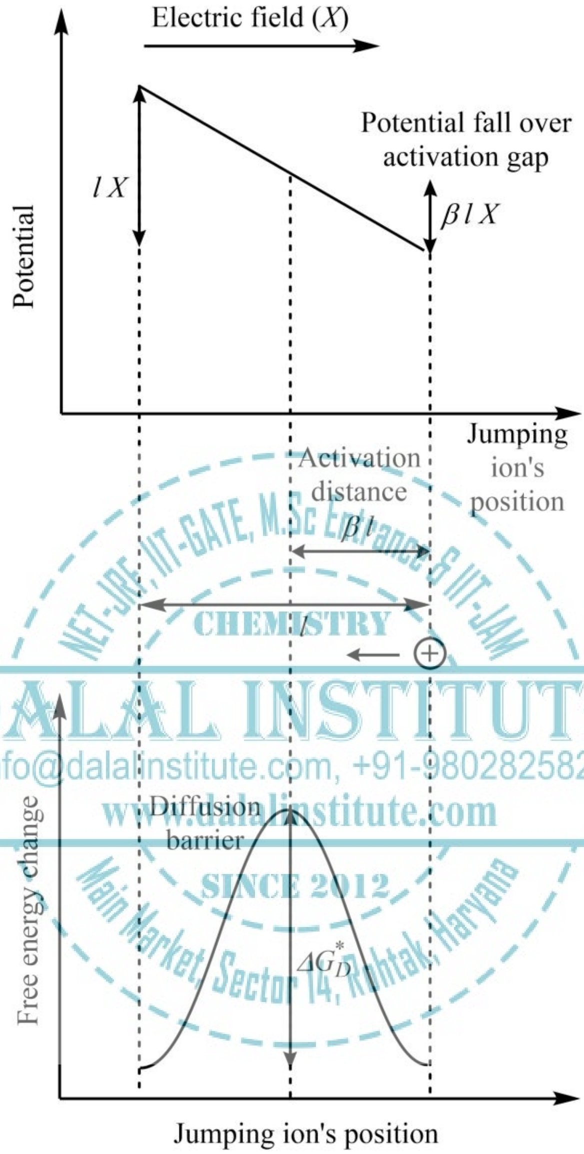

Figure 6. The general depiction ionic movement from the right to left facing the activation barrier under the influence of an external electric field.

The work done obtained in the abovementioned route will induce a free-energy change (ΔG_e^*) that will contribute to the free energy of activation, i.e.,

$$\Delta G_{total}^* = \Delta G_D^* + \Delta G_e^* \tag{102}$$

or

$$\Delta G^*_{total} = \Delta G^*_D + z_+ F\beta X l \tag{103}$$

After using ΔG^*_{total} from equation (103), the equation (97) for "right to left" jumps in the presence of applied electric field take the form

$$\overleftarrow{k} = \frac{kT}{h} e^{-(\Delta G^*_D + z_+ F\beta X l)/RT} \tag{104}$$

or

$$\overleftarrow{k} = \frac{kT}{h} e^{-\Delta G^*_D/RT}\; e^{-z_+ F\beta X l/RT} \tag{105}$$

Recalling expression for $\overleftarrow{k}_D$ from equation (98), the equation (105) can also be written as

$$\overleftarrow{k} = k_D\, e^{-z_+ F\beta X l/RT} \tag{106}$$

Similarly, the jump frequency for the "left to right" movement may be found. However, since the cations are moving along the field (left to right) in case, their movement is favored. The fraction of the barrier these ions need to climb will be $(1-\beta)$. Finally, it is very important to note that the electrical work of activation should be negative in "left to right" because field supports the ion. Therefore, the jump frequency for left to right movement should look like

$$\overrightarrow{k} = k_D e^{z_+ F(1-\beta)X l/RT} \tag{107}$$

Now if $\beta = 1/2$, then $1-\beta$ will also be equal to $1/2$. This transforms equation (106, 107) as

$$\overleftarrow{k} = k_D e^{-pX} \tag{108}$$

and

$$\overrightarrow{k} = k_D\, e^{pX} \tag{109}$$

Where $p = z_+ F l/2RT$. From equation (108), it is very obvious that $\overleftarrow{k} < k_D$ whereas equation (109) implies that $\overrightarrow{k} > k_D$. Hence $\overrightarrow{k} > \overleftarrow{k}$.

Hence, we can conclude that the jumping frequency becomes anisotropic in the presence of externally applied filed. The jumping frequency in the applied field's direction is higher than what is against. Nevertheless, in the absence of field, the value of jump frequency is equal in all directions which is a characteristic feature of the random walk. When the field is applied, this isotropy is abolished and the walk is not completely random anymore. The ions start moving along the field creating a net current density. In other words, we can say that ionic drift due to the field is the multiplication of perturbation induced by the field and the random walk in the field's absence.

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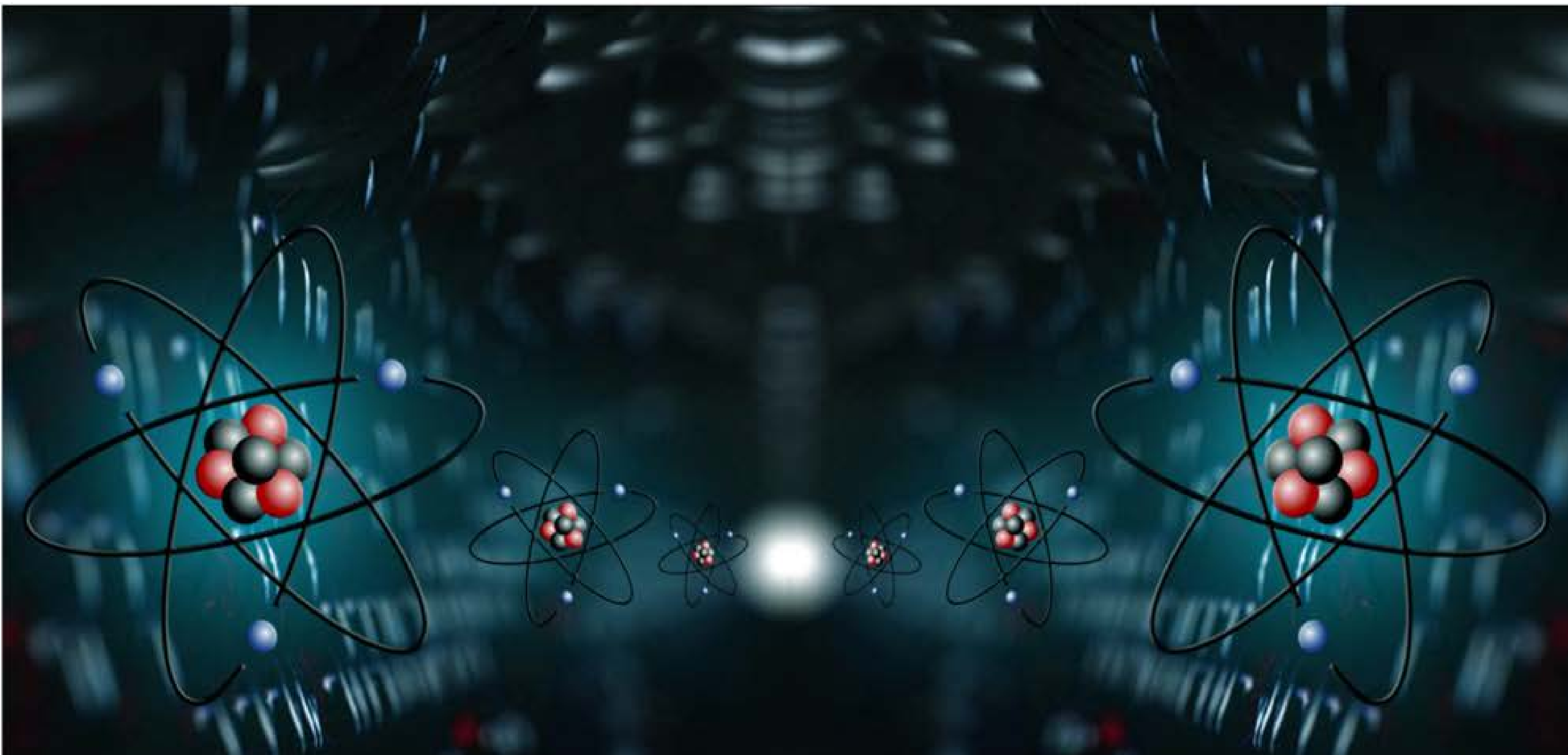

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