

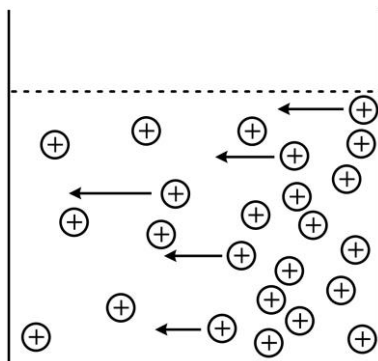
CHAPTER 8

Electrochemistry – II: Ion Transport in Solutions

❖ Ionic Movement Under the Influence of an Electric Field

In order to imagine the conduction process in electrolytic solutions at the atomic level, we can follow two approaches which are somewhat different in their initial assumptions.

The first approach includes the visualization of ionic movements governed by the diffusion phenomenon first and then studying the perturbation of this ionic movement by an externally applied electric field. Since it is a well-known fact that the diffusion of ions is simply the movement of ions from a high-numbered region to a low-numbered region. In other words, we can say the ionic diffusion is the result of a concentration-gradient in which a particular type of ions travel from a high concentration region towards a low concentration region until a homogeneity in the concentration is reached. Now, although the net movement of ions stops after the loss of concentration gradient, the individual ionic movement still happens but with zero mean displacements. In other words, we can say that in a homogeneous ionic solution, the ions can move randomly in any direction resulting in a zero net diffusion.



Diffusion of cations

Figure 1. The movement of positive ions from higher concentration to lower concentration.

Now since the ions are charged particles, the movements of these ions are strongly affected when an electric field is applied. From the laws electrostatic interactions, we can conclude that the cations will prefer to move towards the negative electrode whereas the anions will prefer to move towards the positive electrode. More specifically, the application of an electric field makes the ions to adopt a single direction in space, which is a direction along or opposite to the direction of the applied field. Therefore, the ions drift under the applied field and stop their random walk.

The second approach to study the phenomenon of electrolytic conduction at the atomic level includes the framing of the drift of only one ion under the externally applied field. The electric field would make the ion to accelerate as per Newton's second law. Now if the ion is in the vacuum, it would show an acceleration until it strikes with the respective electrode. However, it will not happen since a large number of other ions also present in the same electrolytic solution along with the solvent as well. Consequently, the ion is almost bound to collide with other ions or solvent particles in its journey. The ion will stop for some time and then will start to accelerate again. This stop-start phenomenon will impart a discontinuity in the speed and direction of this moving ion. It means that ionic movement is not very much smooth but actually a resistance is offered by the surrounding medium. Therefore, we can say that the application of an external electric field will make the ion move towards the oppositely charged electrode but in a stops-starts and zigzag fashion.

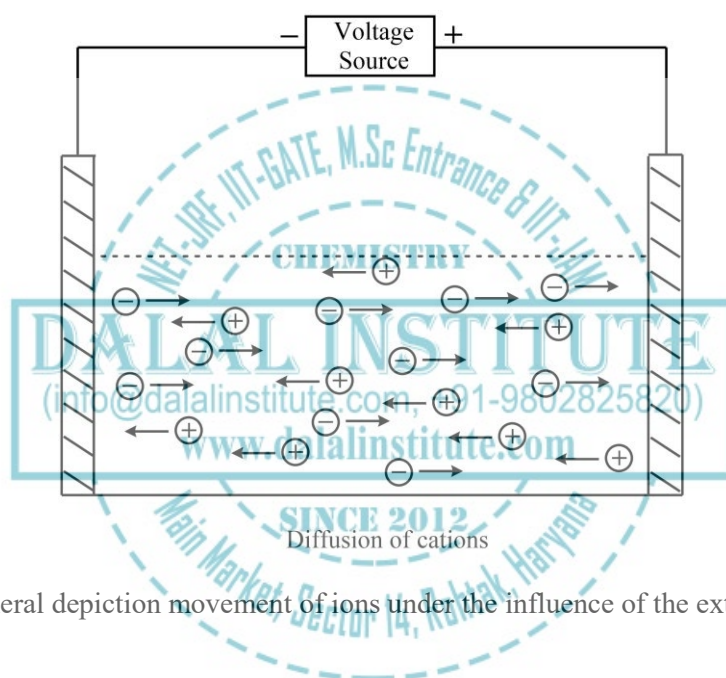


Figure 2. The general depiction movement of ions under the influence of the external electric field.

Since an ion starts moving towards the positively charged electrode only after the application of the electric field; the initial velocity before that can simply be neglected because it arises from random collisions, which can be in any random direction. However, after applying the electric field, the ion feels a force that makes it move in the same direction, i.e., the direction of the electrostatic force. In other words, the electric field will create an additional velocity component on the ion under consideration that drifts the ion to the oppositely charged electrode. Now, let \vec{F} be the force vector that imparts a drift velocity v_d ; and then using Newton's second law of motion states that this force divided by the particle's mass is simply equal to the acceleration. From the general expressions for acceleration, we have

$$a = \frac{dv}{dt} \quad (1)$$

And

$$a = \frac{\vec{F}}{m} \quad (2)$$

From equation (1) and equation (2), we have

$$\frac{\vec{F}}{m} = \frac{dv}{dt} \quad (3)$$

Now although the time between two collisions may vary significantly, we can use a mean time τ for simplicity which can be formulated as (if N collisions take place in 't' time) given below.

$$\tau = \frac{t}{N} \quad (4)$$

Now because the drift velocity is imparted to the ion by the external force, its value must be equal to the product of meantime and the acceleration due to force, i.e.,

$$v_d = \frac{dv}{dt} \tau \quad (5)$$

Using the value of dv/dt from equation (3) in equation (5), we get

$$v_d = \frac{\vec{F}}{m} \tau \quad (6)$$

It is obvious from the above relation that the meantime is related to the drift velocity showing that the jumps between collisions affect ionic movement. Besides, it is also clear that the drift velocity is directly proportional to the driving force of the applied electric field. The ionic flux can be formulated in terms of drift velocity as given below.

$$\text{Flux} = \text{Ionic concentration} \times \text{Drift velocity} \quad (7)$$

Hence, since the drift velocity is directly proportional to the electric force simulating conduction, the flux must also be proportional to the magnitude of the electric field, i.e.,

$$\text{Flux} \propto \text{Electric field} \quad (8)$$

The nature of equation (6) also unveils the situation where the flux or the drift velocity no longer holds the direct proportionality with the applied electric field. For equation (6), it is very important to assume that during the collision, the velocity component imparted to the ion by applied electric field vanishes completely and the ion starts as a full-fresher each time. If this is not satisfied, these leftover velocity components would add up after every collision and the real velocity, in that case, would be much greater than the calculation given by equation (6). In other words, equation (6) will no longer be valid. Therefore, we can conclude that for a reasonable guess for drift velocity, the magnitude of the applied electric field must be very small.

❖ Mobility of Ions

It has already been discussed in the previous section that the ions in a homogeneous electrolytic solution move randomly with zero net displacements, and the situation changes when the external electric field is applied. The applied field imparts a directive velocity component to the ion under consideration and makes it move towards the oppositely charged electrode. This ion collides with other ions and drifts towards the oppositely charged electrode with a stop-start and zig-zag fashion. The drift velocity (v_d) of such ion is given by the following relation.

$$v_d = \frac{\tau}{m} \vec{F} \quad (9)$$

Where \vec{F} is the force exerted upon the ion by applied field and m is the mass of the ion. The symbol τ represents the mean lifetime between to collisions during the ionic drift.

It is obvious from the equation (9) that drift velocity is proportional to forces exerted by the electric field and τ/m is the constant of proportionality. The physical significance of the proportionality constant lies in the fact that it becomes equal to the drift velocity when the force is unity, and therefore, represents the “mobility nature” of the ion considered. In other words, we can say that the proportionality constant in equation (9) represents the absolute mobility (\bar{u}_{abs}) of the ion i.e.

$$\bar{u}_{abs} = \frac{\tau}{m} = \frac{v_d}{\vec{F}} \quad (10)$$

The units of absolute mobility are $\text{cm s}^{-1} \text{ dyne}^{-1}$. Now, since the functional electric force is equal to the electric force per unit charge; or the electric field (X) multiplied with the charge on the ion ($z_i e_0$) i.e.

$$\vec{F} = z_i e_0 X \quad (11)$$

After using the value of \vec{F} from equation (11) in equation (10), we get

$$\bar{u}_{abs} = \frac{v_d}{z_i e_0 X} \quad (12)$$

$$v_d = \bar{u}_{abs} z_i e_0 X \quad (13)$$

When, $X = 1 \text{ volt}$, the above equation takes the form

$$(v_d)_{1\text{volt cm}^{-1}} = \bar{u}_{abs} z_i e_0 = \bar{u}_{conv} \quad (14)$$

Where \bar{u}_{conv} represents the conventional mobility of the ion with units $\text{cm}^2 \text{ Volt}^{-1} \text{ s}^{-1}$. Now although the expressions of both types of mobilities are quite similar, it is worthy to note that the “absolute mobility” has a broader domain of application because any force that governs the drift velocity can be used. On the other hand, the conventional mobility is pretty much limited to the electric force only.

❖ Ionic Drift Velocity and Its Relation with Current Density

In this section, we will try to explain how the ionic movement is quantitatively related to current density flowing through an electrolytic solution under the influence of an applied electric field. To do so, we need to understand the ionic drift velocity and then its relationship with current density.

➤ Ionic Drift Velocity

When an ion in the electrolytic solution is placed under the externally applied electric field, the electric field will make the ion to accelerate as per Newton's second law. Now if the ion is in the vacuum, it would show an acceleration until it strikes with the respective electrode. However, it will not happen since a large number of other ions also present in the same electrolytic solution along with the solvent as well. Consequently, the ion is almost bound to collide with other ions or solvent particles in its journey. The ion will stop for some time and then will start to accelerate again. This stop-start phenomenon will impart a discontinuity in the speed and direction of this moving ion. It means that ionic movement is not very much smooth but actually a resistance is offered by the surrounding medium. Therefore, we can say that the application of the external electric field will make the ion move towards the oppositely charged electrode but in a stops-starts and zigzag fashion. An ion starts moving towards the positively-charged electrode only after the application of the electric field. The initial velocity before that can simply be neglected because it arises from random collisions which can be in any random direction. However, after applying the electric field, the ion feels a force that makes the ion move in the same direction, i.e., the direction of the electrostatic force. Now let F be the force vector that imparts drift velocity v_d , then from Newton's second law of motion states that this force divided by the particle's mass is simply equal to the acceleration.

$$\frac{\vec{F}}{m} = \frac{dv}{dt} \quad (15)$$

Now although the time between two collisions may vary significantly, we can use a mean time τ for simplicity which can be formulated as (if N collisions take place in ' t ' time) given below.

$$\tau = \frac{t}{N} \quad (16)$$

Now because the drift velocity is imparted to the ion by the external force, its value must be equal to product meantime and the acceleration due to this force i.e.

$$v_d = \frac{dv}{dt} \tau \quad (17)$$

Using the value of dv/dt from equation (15) in equation (17), we get

$$v_d = \frac{\vec{F}}{m} \tau \quad (18)$$

It is obvious that the drift velocity is directly proportional to the driving force of the applied electric field.

➤ **The Relationship between Ionic Drift Velocity and Current Density**

It is obvious from the equation (18) that drift velocity is proportional to forces exerted by the electric field and τ/m is the constant of proportionality. The physical significance of the proportionality constant lies in the fact that it becomes equal to the drift velocity when the force is unity, and therefore, represents the “mobility nature” of the ion considered. In other words, we can say that the proportionality constant in equation (18) represents the absolute mobility (\bar{u}_{abs}) of the ion, i.e.,

$$\bar{u}_{abs} = \frac{\tau}{m} = \frac{v_d}{\vec{F}} \quad (19)$$

The units of absolute mobility are $\text{cm s}^{-1} \text{ dyne}^{-1}$. Now, since the functional electric force is equal to the electric force per unit charge; or the electric field (X) multiplied with the charge on the ion ($z_i e_0$), i.e.,

$$\vec{F} = z_i e_0 X \quad (20)$$

After using the value of \vec{F} from equation (20) in equation (19), we get

$$\bar{u}_{abs} = \frac{v_d}{z_i e_0 X} \quad (21)$$

$$v_d = \bar{u}_{abs} z_i e_0 X \quad (22)$$

When, $X = 1 \text{ volt}$, the above equation takes the form

$$(v_d)_{1 \text{ volt cm}^{-1}} = \bar{u}_{abs} z_i e_0 = \bar{u}_{conv} \quad (23)$$

Where \bar{u}_{conv} represents the conventional mobility of the ion with units $\text{cm}^2 \text{ Volt}^{-1} \text{ s}^{-1}$. Now although the expressions of both types of mobilities are quite similar, it is worthy to note that the “absolute mobility” has a broader domain of application because any force that governs the drift velocity can be used. On the other hand, the conventional mobility is pretty much limited to the electric force only.

Now consider a plane with unit area perpendicular to the direction of ionic movement under the influence of the externally applied field. Now although the cations and anions move in opposite directions, both types of ions will pass through this transit. If v_+ is the drift velocity of cation, then all the cations present within v_+ cm of this transit plane will pass through it. Let j_+ be the cationic flux that represents the total number of mole of ions passing through this area in every second. Therefore, the cationic flux must be equal to the multiplication of the corresponding volume ($1 \text{ cm}^2 \times v_+ \text{ cm}$) and the concentration of cations (c_+) in moles cm^{-3} . Mathematically, we can say that

$$j_+ = c_+ v_+ \quad (24)$$

The current density (J_+) or the charge flowing through this transit plane per second due to this cationic flux can simply be obtained by multiplying the cationic flux by the charge carried by 1 mole of ions ($z_+ F$), i.e.,

$$J_+ = c_+ v_+ z_+ F \quad (25)$$

Similarly, If v_- is the drift velocity of anion and c_- the concentration of anions in moles cm^{-3} , the anionic current density may simply be written as

$$J_- = c_- v_- z_- F \quad (26)$$

Where z_- is the charge number of the anion and F is Faraday constant. In general, we can write for the i^{th} species as

$$J_i = c_i v_i z_i F \quad (27)$$

Where z_i and c_i are the charge number and concentration in moles cm^{-3} of the i^{th} type of ion.

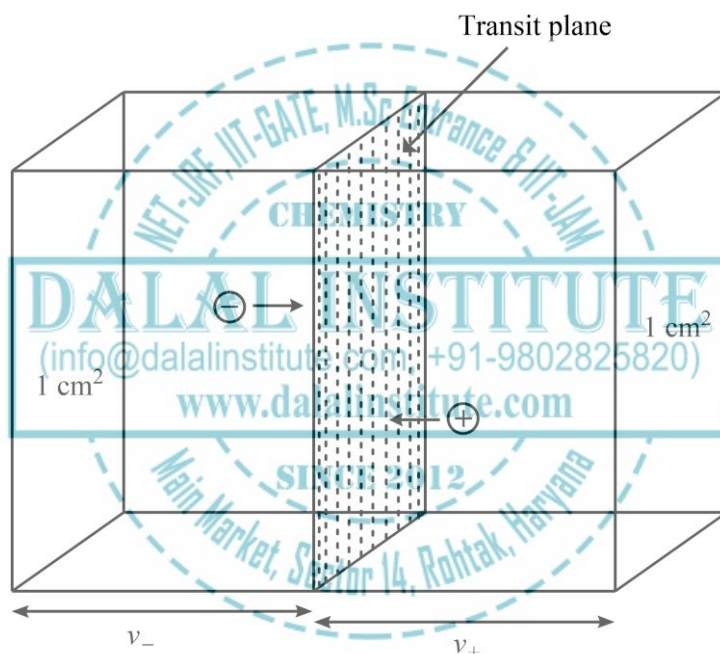


Figure 3. The general depiction ionic movement through transit plane under applied field.

Hence, the total current density from all the ionic species must be the summation of their individual current densities, i.e.,

$$J = \sum_i J_i = \sum_i c_i v_i z_i F \quad (28)$$

For univalent electrolytes like NaCl, we have $z_+ = z_- = z$ and $c_+ = c_- = c$; therefore, we can write

$$J = zcF(v_+ + v_-) \quad (29)$$

Now we can start to relate the ionic drift velocity with more generally measurable quantities in the phenomenon of electrolytic conductance like molar conductivity, equivalent conductivity or simply the conductance. To do so, use the fundamental expression for the ionic drift velocity from equation (23) in equation (28), i.e.,

$$J = \sum_i z_i F c_i (u_{conv})_i X \quad (30)$$

Now since the J/X is equal to specific conductivity (σ), the above equation takes the form

$$\sigma = \frac{J}{X} = \sum_i z_i F c_i (u_{conv})_i \quad (31)$$

Therefore, for univalent electrolytes, we have

$$\sigma = \frac{J}{X} = z F c [(u_{conv})_+ + (u_{conv})_-] \quad (32)$$

It is clear from the above expression that the specific conductivity is directly proportional to the concentration of the electrolytic solution, which can be explained in terms of the fact that the number of ions per unit volume changes with dilution.

Now, in order to connect the ionic drift velocities with molar conductivity (Λ_m) for monovalent electrolytes, recalling the expression for molar conductivity here, i.e.,

$$\Lambda_m = \frac{\sigma}{c} \quad (33)$$

After putting the value of specific conductivity from equation (32), the above equation takes the form

$$\Lambda_m = \frac{z F c [(u_{conv})_+ + (u_{conv})_-]}{c} \quad (34)$$

$$\Lambda_m = z F [(u_{conv})_+ + (u_{conv})_-] \quad (35)$$

For equivalent conductivity (Λ_{eq}) of monovalent electrolytes, recall its correlation with molar conductivity i.e.

$$\Lambda_{eq} = \frac{\Lambda_m}{z} \quad (36)$$

Substituting the value of molar conductivity from equation (35) in equation (36), we get

$$\Lambda_{eq} = \frac{z F [(u_{conv})_+ + (u_{conv})_-]}{z} \quad (37)$$

$$\Lambda_{eq} = F [(u_{conv})_+ + (u_{conv})_-] \quad (38)$$

Hence, Λ_{eq} will be independent of concentration only if the ionic mobility doesn't vary with concentration.

❖ Einstein Relation Between the Absolute Mobility and Diffusion Coefficient

Since it is a well-known fact that the diffusion of ions is simply the zig-zag walking of ions from a high-numbered region to a low-numbered region. In other words, we can say the ionic diffusion is the result of a concentration gradient in which a particular type of ions travel from a high concentration region towards a low concentration region until a homogeneity in concentration is reached. On the other hand, the conduction or the ionic migration is a result of the drift velocity component imparted to the ions by the electric force. However, it is important here to recall the fact that this velocity component does not stop the zig-zag walk of diffusion but actually gets superimposed on it. Albert Einstein understood this and formulated a relation between ionic mobility (\bar{u}_{abs}) and diffusion coefficient (D).

Now, since the conduction, as well as the diffusion, are irreversible processes, they cannot be treated by equilibrium statistical mechanics or by the equilibrium thermodynamics. However, the situation can be considered as a pseudo-equilibrium if the conduction and diffusion take place in the opposite direction but with same rates. To do so, consider an electrolytic solution of salt MX in which some of the cations are radioactive in nature. Now assume that M^+ ions are present in higher concentrations in one region and in lower concentration in some other region. In other words, the tracer ions are present with a concentration gradient. According to Fick's law of diffusion, the overall diffusion flux (J_D) must be

$$j_D = -D \frac{dc}{dx} \quad (39)$$

After applying the electric field, the tracer ions will feel the field and will start to move towards the opposite electrode. The drift velocity can be given as

$$v_d = \bar{u}_{abs} \vec{F} \quad (40)$$

The current density produced by this drift velocity is

$$J = z_+ c F v_d \quad (41)$$

The conduction flux can be obtained by dividing the current density by charge carried by one mole of ions i.e.

$$j_c = \frac{z_+ c F v_d}{z_+ F} \quad (42)$$

or

$$j_c = c v_d \quad (43)$$

After using the expression of drift velocity from equation (40) in the above expression, we get

$$j_c = c \bar{u}_{abs} \vec{F} \quad (44)$$

The strength of the applied electric field is varied in such a way that the conduction flux and diffusion flux are equal and opposite. Mathematically, it should be like

$$j_c = -j_D \quad (45)$$

$$j_c + j_D = 0 \quad (46)$$

After using values of j_D and j_c from equations (39, 44) in the above expression, we get

$$c \bar{u}_{abs} \vec{F} - D \frac{dc}{dx} = 0 \quad (47)$$

or

$$\frac{dc}{dx} = \frac{c \bar{u}_{abs} \vec{F}}{D} \quad (48)$$

Since there is no net flow of ions, and therefore, this pseudo-equilibrium can be studied by Boltzmann law.

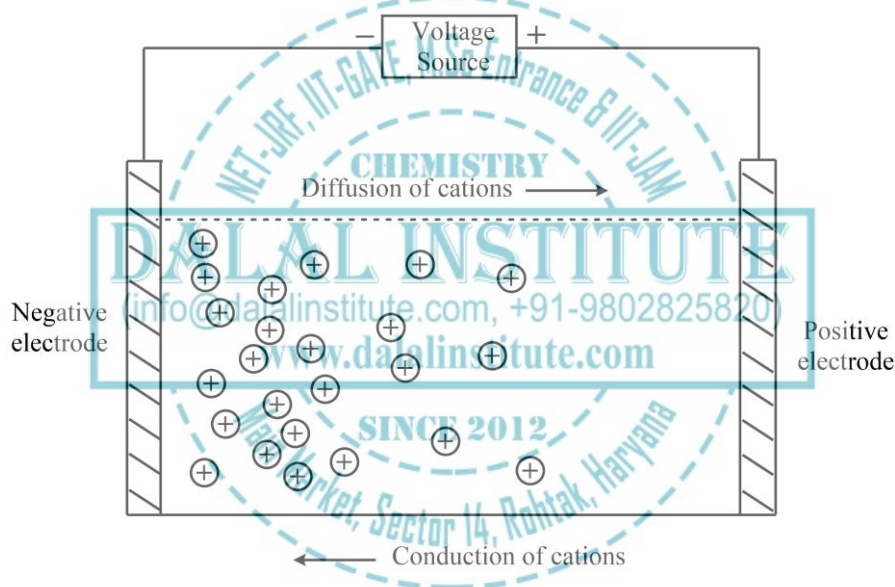


Figure 4. The pseudo-equilibrium when diffusion flux and conduction flux are equal and opposite.

Owing to the x -dependent variation, recall the ionic concentration at distance x , i.e.,

$$c = c_0 e^{-U/kT} \quad (49)$$

Where c_0 is the ionic concentration in the zero potential region while U is the potential energy of the ion under consideration in the externally applied electric field. Differentiating the above equation w.r.t. x , we have

$$\frac{dc}{dx} = -c_0 e^{-U/kT} \frac{1}{kT} \frac{dU}{dx} \quad (50)$$

Replacing $c_0 e^{-U/kT}$ by c i.e. using equation (49), we get

$$\frac{dc}{dx} = -\frac{c}{kT} \frac{dU}{dx} \quad (51)$$

Since the force is $F = -dU/dx$, the above equation takes the form

$$\frac{dc}{dx} = \frac{c}{kT} F \quad (52)$$

From equation (48) and equation (52), we get

$$\frac{c\bar{u}_{abs}\vec{F}}{D} = \frac{c}{kT}\vec{F} \quad (53)$$

$$\frac{\bar{u}_{abs}}{D} = \frac{1}{kT} \quad (54)$$

or

$$D = \bar{u}_{abs}kT \quad (54)$$

Which is the famous Einstein relation between the absolute mobility and diffusion coefficient.

Furthermore, from the phenomenological treatment of the diffusion coefficient, it is also a quite well-known correlation that

$$D = BRT \quad (55)$$

Where B represents the undetermined phenomenological coefficient and R is the gas constant. Now, comparing equation (54) and equation (55), we have

$$\bar{u}_{abs}kT = BRT \quad (56)$$

or

$$B = \frac{\bar{u}_{abs}kT}{RT} = \frac{\bar{u}_{abs}k}{R} \quad (57)$$

Since $N = R/k$, the above equation can also be written as

$$B = \frac{\bar{u}_{abs}}{N} \quad (58)$$

It is obvious from the above equation that the phenomenological coefficient B can simply be defined as the ratio of absolute mobility to the Avogadro number. Furthermore, The Einstein relation also connects the phenomena of diffusion with force arising from viscous drag and force of electric field on the ion during its drifting movement. Therefore, the formulation also forms the basis of Stokes-Einstein (viscosity and diffusion) and Nernst–Einstein relation (equivalent conductivity and diffusion).

❖ The Stokes-Einstein Relation

Albert Einstein realized that an ion moving in an electrolytic solution is somewhat analogous to a macroscopic sphere moving in a liquid medium. A macroscopic sphere can travel very fast if it is outside of water or any other liquid; however, its velocity will definitely be affected if it is put in some liquid. The reduced velocity of the sphere in liquid can be attributed to an opposing force exerted upon it by the diameter of the sphere (d), viscosity of the medium (η), density of the medium (ρ) and the speed of the ion itself (v). All these factors are correlated mathematically to give “Reynolds number (R_e)” as

$$R_e = vd \frac{\rho}{\eta} \quad (59)$$

If the hydrodynamics has a profile that makes the $R_e \ll 1$, Stokes proved that the dragging force (F) on the sphere can be formulated by the following relation.

$$F = 6\pi r\eta v \quad (60)$$

Which is the famous Stokes’ law.

Now although the equation (60) is very useful in case of a macroscopic sphere moving in water or in any other liquid, the applicability of the same to microscopic ions requires some testing first. One condition that must be satisfied for the practicality of Stokes law to ion in solution is the very small value of Reynolds number i.e. $R_e \ll 1$. After using the ionic diameter and typical drift velocity of ion, it is found that Reynolds number is very small in comparison to unity, and therefore, suggests that Stokes law can be applied to ionic movement. However, equation (60) would show deviations from experimental results if the ions tagged are not completely spherical, and therefore, should be modified for such particles. It has been shown that for cylindrical particles, the factor 6π must be replaced by 4π to get reasonable results. It is also worthy to note that the Stokes law fails to explain the viscous drag on extremely small ions, justifying the need for some other advanced models. Furthermore, besides the viscous drag, the presence of other ions also creates collisions and stop-start zig-zag movement which makes it very difficult to apply Stokes’ law.

Albert Einstein developed a modified approach to correlate the viscosity with the diffusion coefficient by suggesting that a driving force ($-d\mu/dx$) operates on the particles during diffusion which can be formulated as given below.

$$-\frac{d\mu}{dx} = 6\pi r\eta v_d \quad (61)$$

Where v_d is the steady-state velocity of the ion under consideration. The right-hand side of the above equation means that the driving force we assumed must be opposed by an equal and opposite resistive force given by Stokes’ law.

Besides, when a charged particle moves in a polar solvent, solvent dipoles surround it from oppositely charged ends; and this surrounding environment is destroyed and built up again and again due to movement,

and takes time for it. In this relaxation process, a relaxation force is in operation which can be considered as an additional frictional force on the tagged ion. Therefore, the dragging force expression is modified to

$$F = 6\pi\eta vr - 6\pi\eta v \frac{s}{\epsilon} \quad (62)$$

Where $s = (4/9)(\tau/6\pi\eta)e_0^2/r^3$ whereas ϵ represents the dielectric constant of the solvent. The correction factor sometimes can be very large but will be neglected for the simplicity of the derivation Stokes-Einstein law. Now, from the definition of absolute mobility, i.e.,

$$\bar{u}_{abs} = \frac{v_d}{\vec{F}} \quad (63)$$

The drift velocity can be divided either by the diffusional driving force or by the equal and opposite viscous force given by Stokes law. Therefore, using equation (61) in equation (63), we get

$$\bar{u}_{abs} = \frac{v_d}{-d\mu/dx} = \frac{v_d}{6\pi r\eta v_d} = \frac{1}{6\pi r\eta} \quad (64)$$

At this stage, recall the famous Einstein's relation between the absolute mobility and diffusion coefficient, i.e.,

$$D = \bar{u}_{abs} kT \quad (65)$$

Substituting the value of \bar{u}_{abs} from equation (64) in the above expression, we have

$$D = \frac{kT}{6\pi r\eta} \quad (66)$$

Which is the famous Stokes-Einstein's relation between the viscosity and diffusion coefficient.

The Stokes-Einstein relation inspired the pioneering work of Perrin who studied the random walk of a colloidal particle using an ultramicroscope and found that the mean square distance ($\langle x^2 \rangle$) covered in 't' time is correlated with the diffusion coefficient as given below.

$$D = \frac{\langle x^2 \rangle}{2t} \quad (67)$$

From the knowledge of the weight of colloidal particles and corresponding density, the magnitude of radius r can be obtained, which in turn can be employed (along with medium's viscosity) to find the value of Boltzmann constant from the rearranged form of equation (66)

$$k = \frac{6\pi r\eta D}{T} \quad (68)$$

Since $k = R/N_A$, the value of the Avogadro number can be obtained from $N_A = R/k$. Furthermore, the Stokes-Einstein law can also be used to find the value of conventional ionic mobility (\bar{u}_{conv}). To do so, recall the expression for conventional mobility i.e.

$$\bar{u}_{conv} = \bar{u}_{abs} z_i e_0 \quad (69)$$

Now using the value of \bar{u}_{abs} from equation (64), we have

$$\bar{u}_{conv} = \frac{z_i e_0}{6\pi r \eta} \quad (70)$$

The mobility given is typically labeled as Stokes mobility. The physical significance of the above equation lies in the fact that it shows the correlation of conventional mobility with the charge on the ion, radius of the ion and viscosity of the solvent used. It should also be noted that the equation does not explain the concentration dependence of ion-ion interaction, and therefore, is an oversimplified approach.

❖ The Nernst-Einstein Equation

Just like the Stokes-Einstein's relation found the connection between the viscosity and the diffusion coefficient; another important equation, popularly called as Nernst-Einstein relation, correlated the diffusion coefficient with equivalent conductivity. In order to derive the Nernst-Einstein's equation, recall the expression for equivalent conductivity (Λ_{eq}) in terms of conventional mobilities for $z: z$ valent electrolyte, i.e.,

$$\Lambda_{eq} = F[(u_{conv})_+ + (u_{conv})_-] \quad (71)$$

Where F is the Faraday constant; whereas $(u_{conv})_+$ and $(u_{conv})_-$ are the conventional mobilities of cation and anion, respectively. Now, since for $z: z$ electrolyte $z_+ = z_- = z$, the conventional mobilities are

$$(u_{conv})_+ = z_+ e_0 (\bar{u}_{abs})_+ = z e_0 (\bar{u}_{abs})_+ \quad (72)$$

$$(u_{conv})_- = z_- e_0 (\bar{u}_{abs})_- = z e_0 (\bar{u}_{abs})_- \quad (73)$$

Using equation (72, 73) in equation (71), we get

$$\Lambda_{eq} = F[z e_0 (\bar{u}_{abs})_+ + z e_0 (\bar{u}_{abs})_-] \quad (74)$$

$$\Lambda_{eq} = z e_0 F[(\bar{u}_{abs})_+ + (\bar{u}_{abs})_-] \quad (75)$$

From Einstein's relation, we know that

$$(\bar{u}_{abs})_+ = \frac{D_+}{kT} \quad (76)$$

also

$$(\bar{u}_{abs})_- = \frac{D_-}{kT} \quad (77)$$

Using equation (76, 77) in equation (75), we get

$$\Lambda_{eq} = ze_0F \left[\frac{D_+}{kT} + \frac{D_-}{kT} \right] \quad (78)$$

$$\Lambda_{eq} = \frac{ze_0F}{kT} (D_+ + D_-) \quad (79)$$

Which is the popular Nernst-Einstein relation that allows us to find the value of equivalent conductivity just by knowing the diffusion coefficient of cation and anion only.

Another popular form of the Nernst-Einstein equation can be obtained by multiplying and dividing the right-hand side of equation (79) by Avogadro number as given below.

$$\Lambda_{eq} = \frac{ze_0FN_A}{kTN_A} (D_+ + D_-) \quad (80)$$

Since $e_0N_A = F$ and $kN_A = R$, the above equation takes the form

$$\Lambda_{eq} = \frac{zF^2}{RT} (D_+ + D_-) \quad (81)$$

It is also worthy to note that although nature is same, the equation (81) is more popular in electrochemical literature than equation (79).

❖ Walden's Rule

The Walden's rule states that the product of the equivalent conductivity and the viscosity of the solvent for a specific electrolyte at a given temperature is constant.

The Stokes-Einstein relation found the connection between the viscosity (η) and the diffusion coefficient (D); whereas the Nernst-Einstein relation correlates the equivalent conductivity (Λ) and diffusion coefficient. Therefore, a remarkable possibility is to eliminate the diffusion coefficient to correlate the viscosity of the solvent with the equivalent conductivity. In order to do so, recall the Stokes-Einstein relation first i.e.

$$D = \frac{kT}{6\pi r\eta} \quad (82)$$

Where k is the Boltzmann constant and η is the coefficient of viscosity. The symbol r represents the radius of the ion and T is the temperature of the electrolytic solution. Now, recall the Nernst-Einstein relation i.e.

$$D = \frac{\Lambda_{eq}RT}{zF^2} \quad (83)$$

Where z is the charge number and F is the Faraday constant. From equation (82) and equation (83), we get

$$\frac{kT}{6\pi r\eta} = \frac{\Lambda_{eq}RT}{zF^2} \quad (84)$$

$$\Lambda_{eq} = \frac{kTzF^2}{6\pi r\eta RT} \quad (85)$$

Since $e_0N_A = F$ and $kN_A = R$, the above equation can be written in the following form

$$\Lambda_{eq} = \frac{kTzFe_0N_A}{6\pi r\eta T k N_A} = \frac{zFe_0}{6\pi r\eta} \quad (86)$$

$$\Lambda_{eq}\eta = \frac{zFe_0}{6\pi r} \quad (87)$$

Putting $zFe_0/6\pi = \text{constant}$, the above equation can also be written as

$$\Lambda_{eq}\eta = \frac{\text{constant}}{r} \quad (88)$$

Now, if the radius of the ion the solvated ion is same in solvents of different viscosities, the equation (88) is reduced to

$$\Lambda_{eq}\eta = \text{constant} = \frac{zFe_0}{6\pi r} \quad (89)$$

Which is the empirical Walden's rule. The experimental data for potassium iodide in various solvents is given for more clear picture is given below.

Table 1. The experimental data for KI in different solvents.

Solvent used	Equivalent conductivity (Λ_{eq})	Viscosity of the solvent (η)	$\Lambda_{eq}\eta$
Acetophenone	39.8	0.01620	0.64476
Ethanol	50.9	0.01096	0.55786
Pyridine	71.4	0.00958	0.68401
Methanol	114.5	0.00545	0.62403
Propanone	185.4	0.00316	0.58586
Acetonitrile	198.3	0.00345	0.68414

It is obvious for the data listed in 'Table 1' that the product of equivalent conductivity and viscosity of the solvent is almost constant with slight deviation, which can be attributed to different solvated radii in different solvents.

❖ 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.

$$J = zcFv_d \quad (90)$$

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

$$v_d = \frac{\tau}{m} \vec{F} \quad (91)$$

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

$$\vec{F} = 6\pi r\eta v \quad \text{or} \quad \vec{F} = ze_0X \quad (92)$$

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 (\vec{v}). Mathematically, we can say as given below.

$$v_d = \vec{v} - \vec{v} \quad (93)$$

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

$$\vec{v} = \frac{l}{\tau} \quad (94)$$

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

$$\vec{v} = l \vec{k} \quad (95)$$

or

$$\vec{v} = l \vec{k} \quad (96)$$

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

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

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

$$\bar{k}_D = \frac{kT}{h} e^{-\Delta G_D^*/RT} \quad (98)$$

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).

$$w = z_+e_0\beta Xl \quad (99)$$

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

$$W = N_A z_+ e_0 \beta Xl \quad (100)$$

or

$$W = z_+ F \beta Xl \quad (101)$$

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

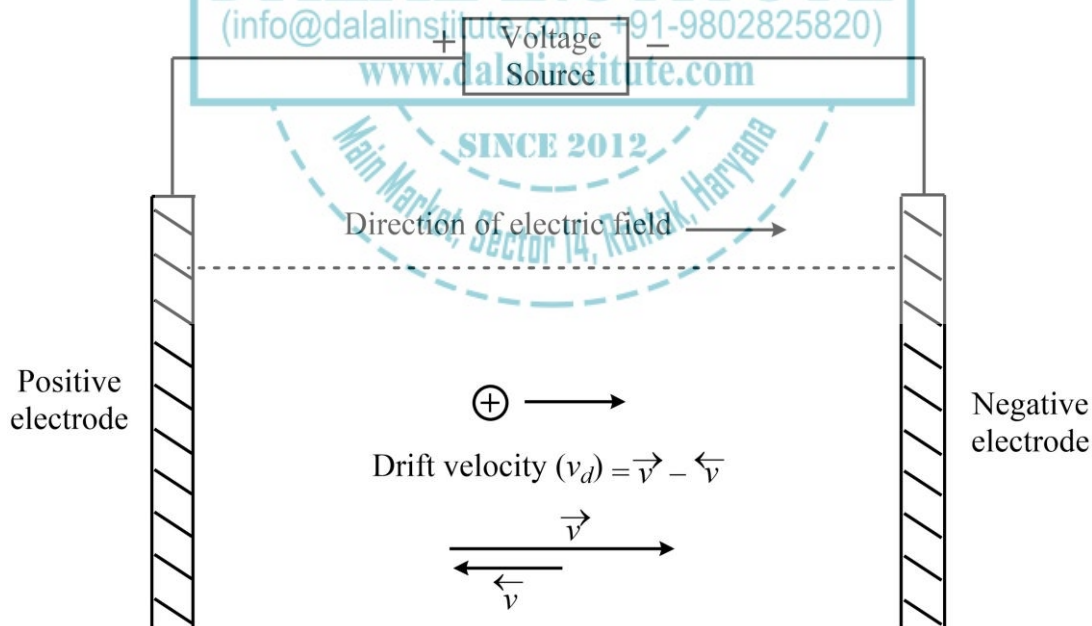


Figure 5. The general depiction of the rate-process approach to ionic migration under the influence of an external electric field.

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

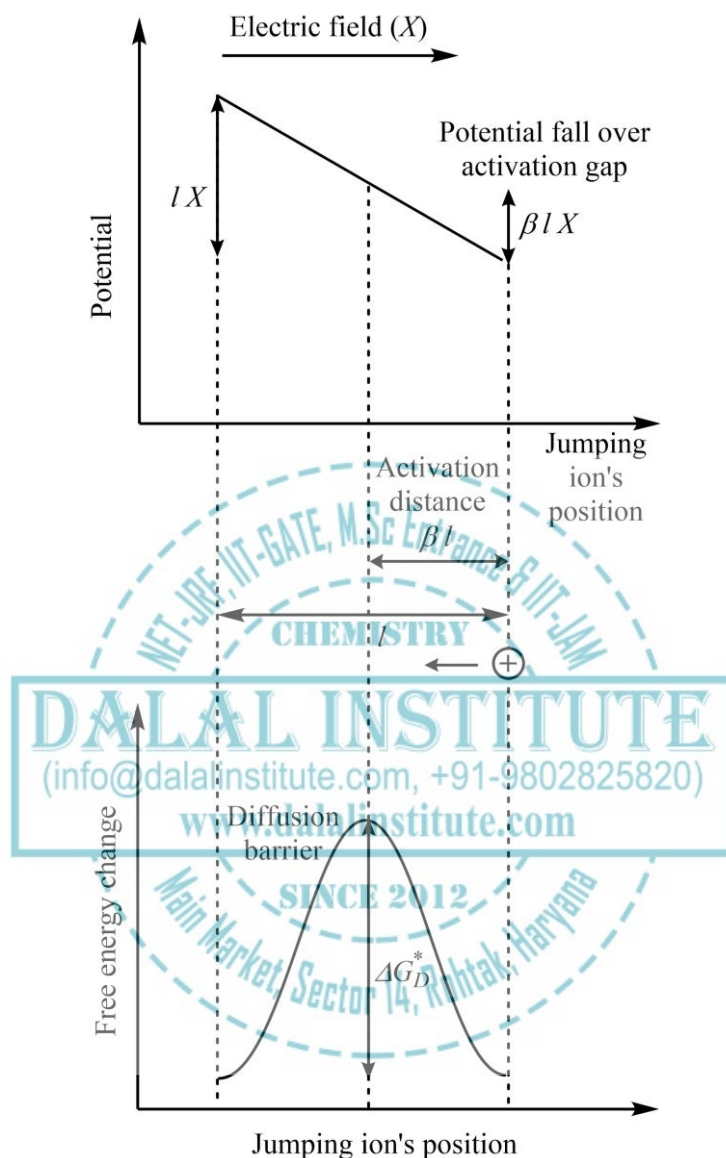


Figure 6. The general depiction ionic movement from the right to left facing the activation barrier under the influence of an external electric field.

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.,

$$\Delta G_{total}^* = \Delta G_D^* + \Delta G_e^* \quad (102)$$

or

$$\Delta G_{total}^* = \Delta G_D^* + z_+ F \beta X l \quad (103)$$

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

$$\bar{k} = \frac{kT}{h} e^{-(\Delta G_D^* + z_+ F \beta X l)/RT} \quad (104)$$

or

$$\bar{k} = \frac{kT}{h} e^{-\Delta G_D^*/RT} e^{-z_+ F \beta X l/RT} \quad (105)$$

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

$$\bar{k} = k_D e^{-z_+ F \beta X l/RT} \quad (106)$$

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

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

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

$$\bar{k} = k_D e^{-pX} \quad (108)$$

and

$$\vec{k} = k_D e^{pX} \quad (109)$$

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

Hence, we can conclude that the jumping frequency becomes anisotropic in the presence of externally applied field. 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.

❖ The Rate-Process Equation for Equivalent Conductivity

The rate-process equation for equivalent conductivity can be derived by recalling the fundamental relation between the ionic drift velocity (v_d) and current density (J) for cation first i.e.

$$J = z_+ c F v_d \quad (110)$$

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 (\tilde{v}). Mathematically, we can say as given below.

$$v_d = \vec{v} - \tilde{v} \quad (111)$$

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

$$\vec{v} = \frac{l}{\tau} \quad (112)$$

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

$$\vec{v} = l \vec{k} \quad (113)$$

$$\tilde{v} = l \tilde{k} \quad (114)$$

From the rate-process approach to ionic migration, the values of \vec{k} and \tilde{k} were found to be

$$\tilde{k} = k_D e^{-pX} \quad (115)$$

and

$$\vec{k} = k_D e^{pX} \quad (116)$$

Where k_D is the jumping frequency for diffusion and X is simply the electric field. The expression for symbol $p = z_+ Fl/2RT$. Using values of \vec{k} and \tilde{k} in equation (113, 114), we get

$$\vec{v} = l k_D e^{pX} \quad (117)$$

$$\tilde{v} = l k_D e^{-pX} \quad (118)$$

Now substituting the value of \vec{v} and \tilde{v} in equation (111), we have

$$v_d = l k_D e^{pX} - l k_D e^{-pX} \quad (119)$$

$$v_d = l k_D (e^{pX} - e^{-pX}) \quad (120)$$

Since $e^{pX} - e^{-pX} = 2 \sinh pX$, the equation (120) can also be written as

$$v_d = 2l k_D 2 \sinh pX \quad (121)$$

Now using the value of drift velocity from equation (121) in equation (110), we get the current density as

$$J = z_+ c F (2l k_D 2 \sinh pX) \quad (122)$$

Therefore, it is obvious from the above expression that the current density varies hyperbolically with the applied electric field.



Figure 7. The variation of current density with the applied electric field.

Now since the J/X is equal to specific conductivity (σ), the above equation takes the form

$$\sigma = \frac{J}{X} = z_+ c F \frac{(2l k_D 2 \sinh pX)}{X} \quad (123)$$

Since molar conductivity is $\Lambda_m = \sigma/c$ and equivalent conductivity is $\Lambda_{eq} = \Lambda_m/z_+$; the equation (123) gives

$$\Lambda_{eq} = \frac{\Lambda_m}{z_+} = \frac{\sigma}{z_+ c} = z_+ c F \frac{(2l k_D 2 \sinh pX)}{z_+ c X} \quad (124)$$

$$\Lambda_{eq} = F \frac{(2l k_D 2 \sinh pX)}{X} \quad (125)$$

Which is the equation for equivalent conductivity.

❖ 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

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

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

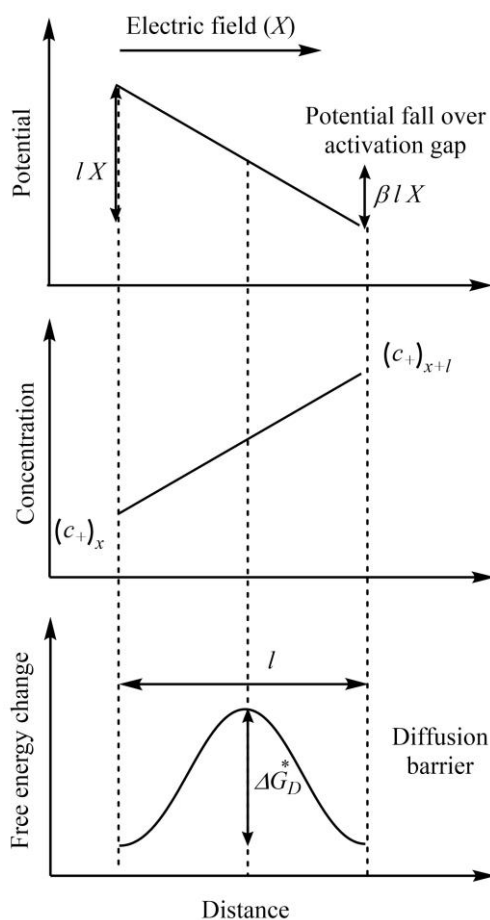


Figure 8. The general depiction of the ionic movement from right to left due to diffusion facing activation barrier under the influence of the external electric field.

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

$$J = z_+ c F v_d \quad (127)$$

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 (\tilde{v}). Mathematically, we can say as given below.

$$v_d = \vec{v} - \tilde{v} \quad (128)$$

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

$$J = z_+ c F (\vec{v} - \tilde{v}) \quad (129)$$

$$J = z_+ c F \vec{v} - z_+ c F \tilde{v}$$

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

$$J = z_+ (c_+)_{x+l} F \vec{v} - z_+ (c_+)_{x+l} F \tilde{v} \quad (130)$$

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

$$J = z_+ (c_+)_{x+l} F \vec{v} - z_+ \left((c_+)_{x+l} + \frac{d(c_+)_{x+l}}{dx} \times l \right) F \tilde{v} \quad (131)$$

For simplicity, the label $(c_+)_{x+l}$ with c_+ i.e.

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

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

$$\vec{v} = l k_D e^{pX} \quad (133)$$

$$\tilde{v} = l k_D e^{-pX} \quad (134)$$

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 expanded as given below.

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

$$\tilde{v} = l k_D (1 - pX) \quad (136)$$

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

$$J = z_+ c_+ F \bar{v} - c_+ z_+ F \bar{v} - \frac{dc_+}{dx} l z_+ F \bar{v} \quad (137)$$

$$J = z_+ c_+ F l k_D (1 + pX) - c_+ z_+ F l k_D (1 - pX) - \frac{dc_+}{dx} l z_+ F l k_D (1 - pX) \quad (138)$$

$$J = 2z_+ c_+ F l k_D pX - z_+ F l^2 k_D (1 - pX) \frac{dc_+}{dx} \quad (139)$$

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

$$J = 2z_+ c_+ F l k_D pX - z_+ F l^2 k_D \frac{dc_+}{dx} \quad (140)$$

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

$$J = 2z_+ c_+ F l k_D \frac{z_+ F l}{2RT} X - z_+ F l^2 k_D \frac{dc_+}{dx} \quad (141)$$

$$J = z_+^2 c_+ F^2 \frac{l^2 k_D}{RT} X - z_+ F l^2 k_D \frac{dc_+}{dx} \quad (142)$$

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

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

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

$$j_+ = \frac{J_+}{z_+ F} \quad (144)$$

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

$$j_+ = \frac{z_+^2 c_+ F^2 D_+ X}{z_+ F R T} - \frac{z_+ F D_+}{z_+ F} \frac{dc_+}{dx} \quad (145)$$

$$j_+ = \frac{c_+ D_+}{RT} z_+ F X - D_+ \frac{dc_+}{dx} \quad (146)$$

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

$$j_+ = \frac{c_+ D_+}{RT} z_+ F X - \frac{D_+ c_+ RT}{RT c_+} \frac{dc_+}{dx} \quad (147)$$

$$j_+ = \frac{c_+ D_+}{RT} z_+ F X - \frac{D_+ c_+}{RT} \frac{d(RT \ln c_+)}{dx} \quad (148)$$

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

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

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

$$j_+ = \frac{c_+ D_+}{RT} z_+ F X - \frac{D_+ c_+}{RT} \frac{d\mu_+}{dx} \quad (151)$$

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

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

or

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

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

$$\bar{\mu}_+ = z_+ F \psi + \mu_+ \quad (154)$$

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

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

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

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

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

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

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

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

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

$$j_+ = -\frac{c_+(\bar{u}_{conv})_+k}{z_+e_0R} \frac{d\bar{\mu}_+}{dx} \quad (159)$$

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

$$j_+ = -\frac{c_+(\bar{u}_{conv})_+}{z_+e_0N_A} \frac{d\bar{\mu}_+}{dx} \quad (160)$$

Putting $e_0N_A = F$, we have

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

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

❖ Ionic Drift and Diffusion Potential

In order to understand the link between ionic drift and diffusion potential, consider a solution of monovalent electrolyte with concentration c . Now assume that this solution is brought in contact with pure water and the boundary of contact is assumed to be $x = 0$. Owing to the concentration gradient, both cation as well anions will start moving into pure water immediately.

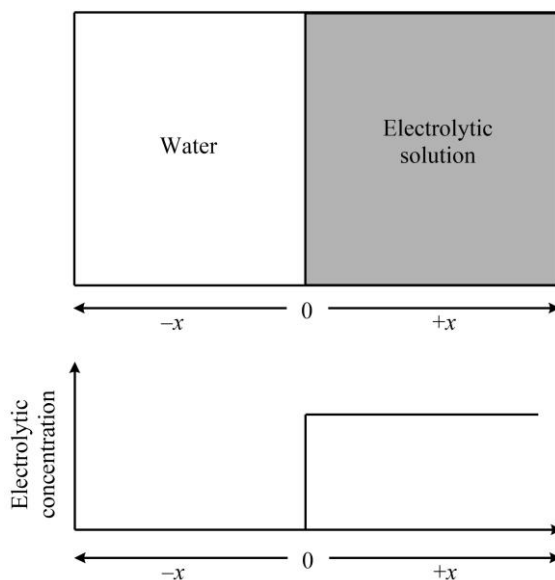


Figure 9. The general depiction electrolytic solution and concentration in contact with water in start.

Now owing to different absolute ionic mobilities of cations and anions (say $\bar{u}_+ > \bar{u}_-$), the Einstein relation can be written for cations and anions as given below.

$$D_+ = \bar{u}_+ kT \quad (162)$$

and

$$D_- = \bar{u}_- kT \quad (163)$$

Where D_+ and D_- are the diffusion coefficients for cations and anions, respectively. The symbol k is simply the Boltzmann constant and T is the temperature. The symbol \bar{u}_+ and \bar{u}_- represent the absolute ionic mobilities for cation and anion, respectively. Since we have assumed that $\bar{u}_+ > \bar{u}_-$, the following must be true

$$D_+ > D_- \quad (164)$$

This implies that the cations will move faster in comparison to anions, will lead the anions in their diffusion race. Now consider two unit-volume-elements at distance $-x_1$ and $-x_2$ in the water phase with $-x_2$ on more left than $-x_1$. Since the cations are moving faster than anions, the concentration ratio of the two (c_+/c_-) will be higher in volume element at $-x_2$ than in the volume element at $-x_1$ distance. In other words, the ratio c_+/c_- will increase as we move from the boundary to the waterside of the system.

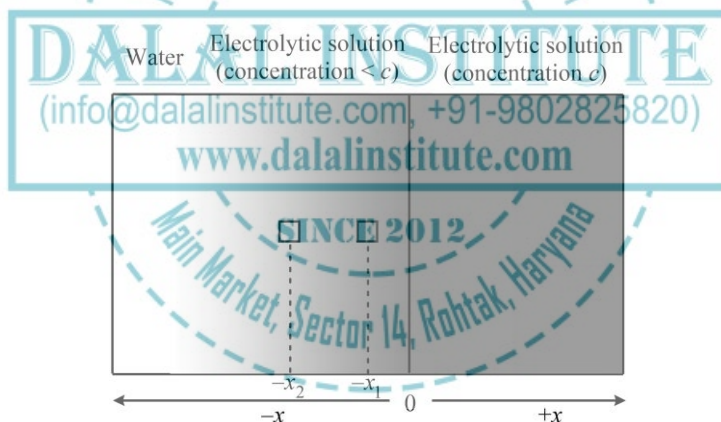


Figure 10. The development of diffusion potential due to different ionic mobilities.

Consequently, a situation will arise in which the positive and negative charges are separated with a negative layer on the left and positive layer on the right. All this will lead to the development of a potential difference that will oppose the faster movement of cations and will reinforce the slower movement of anions. This potential is generally called as the “diffusion potential” and tries to level the ionic mobilities of cations and anions; and hence, tries to maintain the electroneutrality in different parts of the solution. It should also be noted that diffusion potential is also called as the “liquid junction potential” in the case of concentration cells and “membrane potential” if the two solutions are separated by an uncharged membrane.

❖ The Onsager Phenomenological Equations

Since the ionic mobilities of cations are not independent but affect each other as we have studied in the previous section, the expression for the flux must also be modified. In order to understand the concept, recall the general form of Nernst-Planck equation for the ionic flux of i th species (j_i) i.e.

$$j_i = -\frac{\bar{u}_i}{z_i F} c_i \frac{d\bar{\mu}_i}{dx} \quad (165)$$

Where \bar{u}_i is the conventional ionic mobility of i th species and c_i represents the corresponding concentration. The symbol z_i and F are the charge number and Faraday constant, respectively. The symbol $d\bar{\mu}_i/dx$ is the total driving force for ionic transport. Correcting for the coupling between ionic mobilities arising from diffusion potential, we have

$$j_i = -\frac{\bar{u}_i}{z_i F} c_i \frac{d\bar{\mu}_i}{dx} + \text{coupling correction} \quad (166)$$

These mutually interactive flows can be treated by the methods of near-equilibrium thermodynamics in a phenomenological or macroscopic framework. This procedure is simple and can be covered in the postulates given below.

Statement 1: When the system is in near-equilibrium and ionic mobilities are independent of each other, the fluxes can be treated as proportional to the driving forces (Nernst-Planck flux equation). Mathematically, we can say about the ionic flux of 1st species (j_1) that

$$j_1 = L_{11} \vec{F}_1 \quad (167)$$

Where $L_{11} = \bar{u}_1 c_1 / z_1 F$ is phenomenological constant and $\vec{F}_1 = d\bar{\mu}_1/dx$ is the corresponding driving force.

Statement 2: If the coupling between ionic mobilities is considered, the fluxes should be treated as proportional to the driving forces (Nernst-Planck flux equation) plus the contribution from the coupling. Mathematically, we can say about the ionic flux of 1st species (j_1) that

$$j_1 = L_{11} \vec{F}_1 + \text{coupling correction} \quad (168)$$

Now if there are many types of species then above equation takes the form

$$j_1 = L_{11} \vec{F}_1 + \text{Flux of 1 due to driving force of 2nd species} \quad (169) \\ + \text{Flux of 1 due to driving force of 3rd species} + \dots$$

Statement 3: The proportionality of fluxes is also valid for the contributions of the forces from other ionic species. Hence, equation (169) can also be written as

$$j_1 = L_{11} \vec{F}_1 + [L_{12} \vec{F}_2 + L_{13} \vec{F}_3 + L_{14} \vec{F}_4 \dots L_{1n} \vec{F}_n] \quad (170)$$

Where $L_{12}, L_{13}, L_{14}, \dots, L_{1n}$ are the phenomenological constants for the interactions on flux from the flux of other ionic species. The symbol $\vec{F}_1, \vec{F}_2, \vec{F}_3, \dots, \vec{F}_n$ are the corresponding driving forces.

Statement 4: If a monovalent electrolyte like NaCl is dissolved into water, the fluxes of cation (j_+), anion (j_-) and water (j_0) can be written as

$$j_+ = L_{++} \vec{F}_+ + L_{+-} \vec{F}_- + L_{+0} \vec{F}_0 \quad (171)$$

$$j_- = L_{--} \vec{F}_- + L_{-+} \vec{F}_+ + L_{-0} \vec{F}_0 \quad (172)$$

$$j_0 = L_{00} \vec{F}_0 + L_{0+} \vec{F}_+ + L_{0-} \vec{F}_- \quad (173)$$

The equations (171-173) are typically known as the Onsager phenomenological equations.

Statement 5: According to Onsager's reciprocity relation, all symmetrical coefficients are equal. Mathematically, we can say that

$$L_{ij} = L_{ji} \quad (174)$$

Which is an experimentally proved result.

❖ 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.

$$j_+ = L_{++} \vec{F}_+ + L_{+-} \vec{F}_- \quad (175)$$

$$j_- = L_{--} \vec{F}_- + L_{-+} \vec{F}_+ \quad (176)$$

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

$$z_+ F j_+ = -(z_- F j_-) \quad (177)$$

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

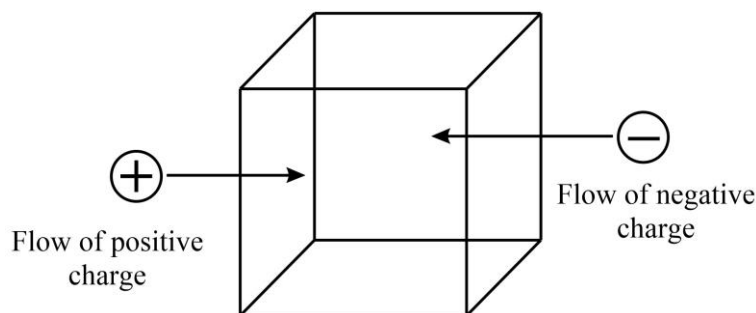


Figure 11. The flow of charge under steady-state approximation.

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

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

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

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

$$q_+L_{++}\vec{F}_+ + q_+L_{+-}\vec{F}_- + q_-L_{--}\vec{F}_- + q_-L_{-+}\vec{F}_+ = 0 \quad (180)$$

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

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

$$p_+\vec{F}_+ + p_-\vec{F}_- = 0 \quad (182)$$

Now recalling the expressions for driving forces i.e.

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

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

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

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

or

$$-p_+q_+ \frac{d\psi}{dx} - p_-q_- \frac{d\psi}{dx} = p_+ \frac{d\mu_+}{dx} + p_- \frac{d\mu_-}{dx} \quad (186)$$

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

$$-\frac{d\psi}{dx} = \frac{p_+}{p_+q_+ + p_-q_-} \frac{d\mu_+}{dx} + \frac{p_-}{p_+q_+ + p_-q_-} \frac{d\mu_-}{dx} \quad (188)$$

Since we know that

$$\frac{p_+}{p_+q_+ + p_-q_-} = \frac{t_+}{z_+F} \quad (189)$$

or

$$\frac{p_-}{p_+q_+ + p_-q_-} = \frac{t_-}{z_-F} \quad (190)$$

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

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

Or in general, we can conclude as

$$-\frac{d\psi}{dx} = \sum \frac{t_i}{z_iF} \frac{d\mu_i}{dx} \quad (192)$$

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

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

or

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

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

$$-d\psi = \frac{RT}{F} \sum \frac{t_i}{z_i} d \ln a_i \quad (194)$$

Which is the basic equation of diffusion potential.

❖ Planck-Henderson Equation for the Diffusion Potential

The basic equation for diffusion potential is applicable only if the potential difference ($d\psi$) is considered over a very small distance (dx). However, the problem of obtaining an overall potential difference ($\Delta\psi = \psi^0 - \psi^l$) that develops from $x = 0$ to $x = l$ was still there.

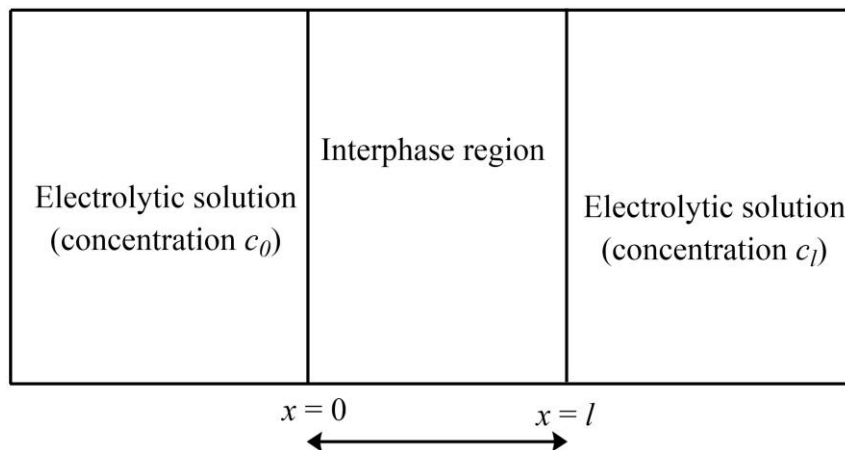


Figure 12. The overall potential difference across the complete interphase domain between electrolytes with concentration c_0 and c_l .

This was overcome by Planck-Henderson equation which can be obtained by recalling the basic equation for diffusion first i.e.

$$-d\psi = \frac{1}{F} \sum \frac{t_i}{z_i} d\mu_i \quad (195)$$

Where t_i and z_i are the charge number of i th species whereas F represents the Faraday constant. Integrating equation (195), we get

$$-\Delta\psi = \psi^0 - \psi^l = \frac{1}{F} \sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d\mu_i}{dx} dx \quad (196)$$

or

$$-\Delta\psi = \frac{RT}{F} \sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{d \ln a_i}{dx} dx \quad (197)$$

or

$$-\Delta\psi = \frac{RT}{F} \sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{1}{f_i c_i} \frac{d(f_i c_i)}{dx} dx \quad (198)$$

At this stage, the things we need to evaluate the equation (198) are the concentration of all species in the interphase region, the variation of activity coefficient and transport number with concentration. For simplicity, the activity coefficients can be taken as unity and transport numbers as constant. In addition to these assumptions, the variation of concentration of i th species with distance is considered as linear i.e.

$$c_i(x) = k_i x + c_i(0) \quad (199)$$

For constant k_i , differentiate above equation i.e.

$$\frac{dc_i}{dx} = k_i = \frac{c_i(l) - c_i(0)}{l} \quad (200)$$

Now using equation (199, 200) in equation (198), we get

$$-\Delta\psi = \frac{RT}{F} \sum_i \int_{x=0}^{x=l} \frac{t_i}{z_i} \frac{k_i}{c_i(0) + k_i x} dx \quad (201)$$

or

$$-\Delta\psi = \frac{RT}{F} \sum_i \frac{t_i}{z_i} \int_{x=0}^{x=l} \frac{d[k_1 x + c_i(0)]}{k_1 x + c_i(0)} \quad (202)$$

or

$$-\Delta\psi = \frac{RT}{F} \sum_i \frac{t_i}{z_i} \left\{ \ln [k_1 x + c_i(0)] \right\}_{x=0}^{x=l} \quad (203)$$

or

$$-\Delta\psi = \frac{RT}{F} \sum_i \frac{t_i}{z_i} \ln \frac{c_i(l)}{c_i(0)} \quad (204)$$

Which is the general form of the Planck-Henderson equation for diffusion potential. Using $c_+ = c_- = c$ and $z_+ = z_- = z$ for $z:z$ electrolyte, we have

$$-\Delta\psi = \frac{RT}{zF} (t_+ - t_-) \ln \frac{c_i(l)}{c_i(0)} \quad (205)$$

Furthermore, putting $t_+ + t_- = 1$, the equation (205) takes the form

$$-\Delta\psi = \frac{RT}{zF} (2t_+ - 1) \ln \frac{c_i(l)}{c_i(0)} \quad (206)$$

Which is the another form of Planck-Henderson equation for simple systems.



❖ Problems

- Q 1. Discuss the ionic movement under the influence of an electric field.
- Q 2. What are absolute and conventional ionic mobilities? How they are related?
- Q 3. Derive and discuss the relationship between ionic drift velocity and current density.
- Q 4. Define the diffusion coefficient. How it is related to the absolute mobility.
- Q 5. Derive Stokes-Einstein relation.
- Q 6. What is the Nernst-Einstein relation? What is its significance?
- Q 7. State and explain Walden's rule.
- Q 8. Explain the rate process approach to ionic migration in detail.
- Q 9. Derive the relationship between ionic drift and diffusion potential.
- Q 10. What are Onsager phenomenological equations? How they can be used to derive the basic equation of diffusion potential?
- Q 11. Write down the Planck-Henderson equation for monovalent electrolytes.

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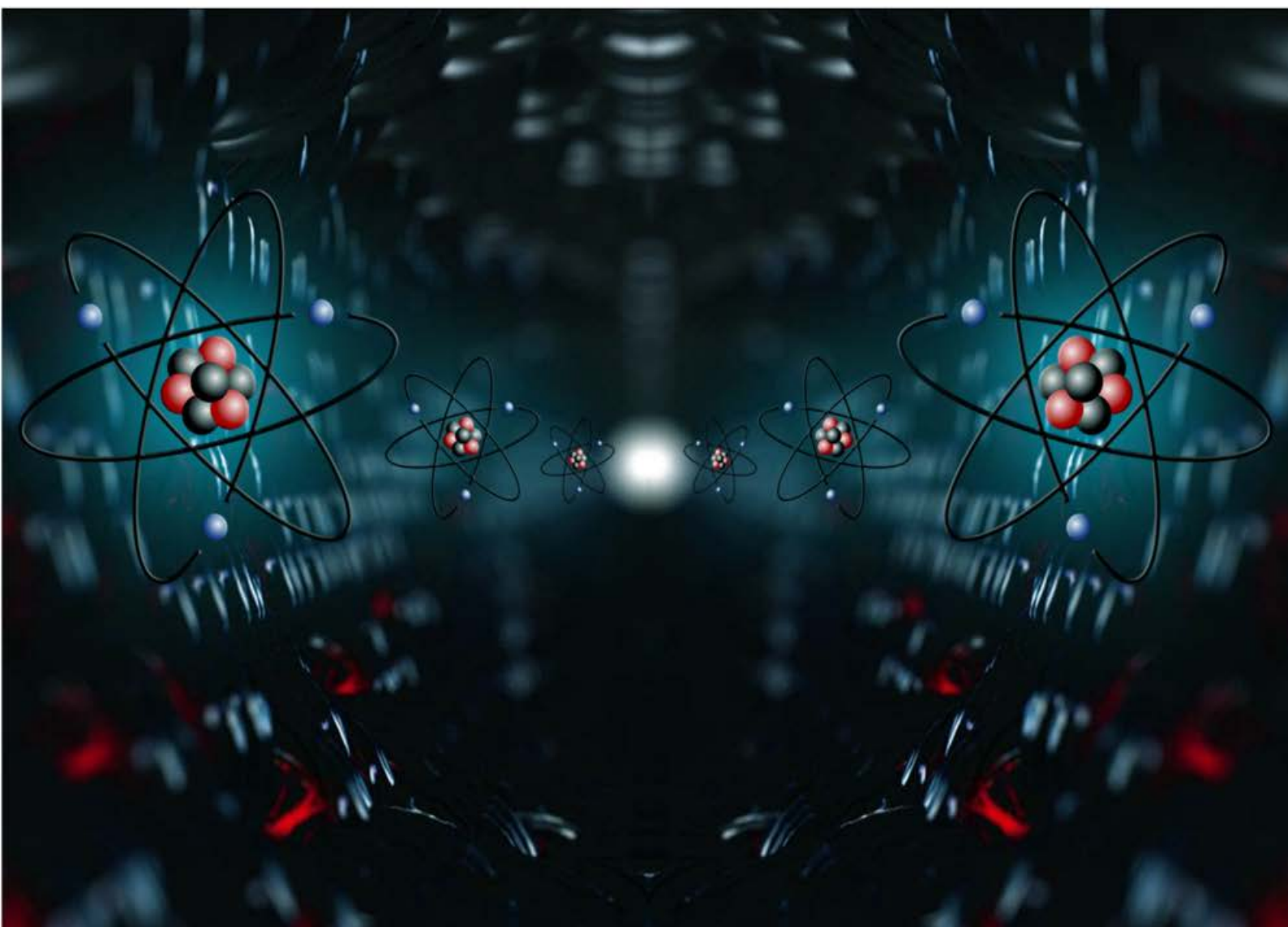
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MANDEEP DALAL



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