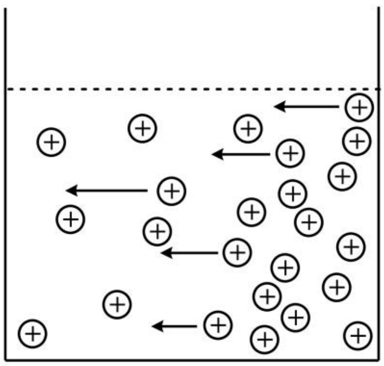
CHAPTER 8

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.

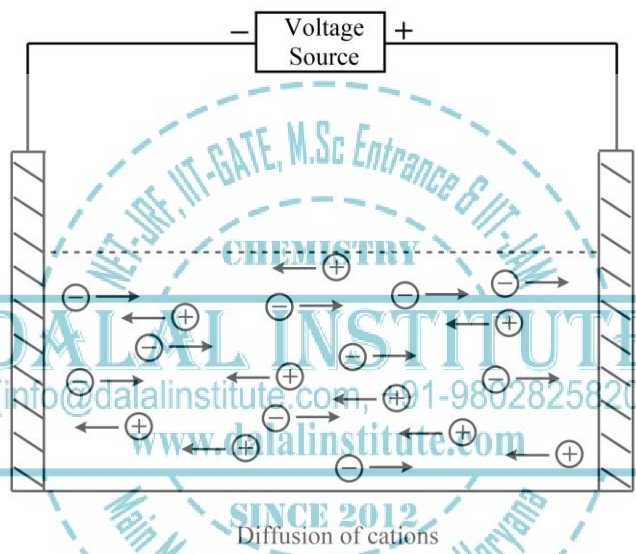


Figure 2. The general depiction movement of ions under the influence of the external electric field.

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

$$a = \frac{dv}{dt} \tag{1}$$

And

$$a = \frac{\vec{F}}{m} \tag{2}$$

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

$$\frac{\vec{F}}{m} = \frac{dv}{dt} \tag{3}$$

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.

$$\tau = \frac{t}{N} \tag{4}$$

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.,

$$v_d = \frac{dv}{dt}\tau \tag{5}$$

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

$$v_d = \frac{\vec{F}}{m}\tau \tag{6}$$

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.

$$Flux = Ionic\ concentration \times Drift\ velocity \tag{7}$$

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.,

$$Flux \propto Electric\ field \tag{8}$$

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.

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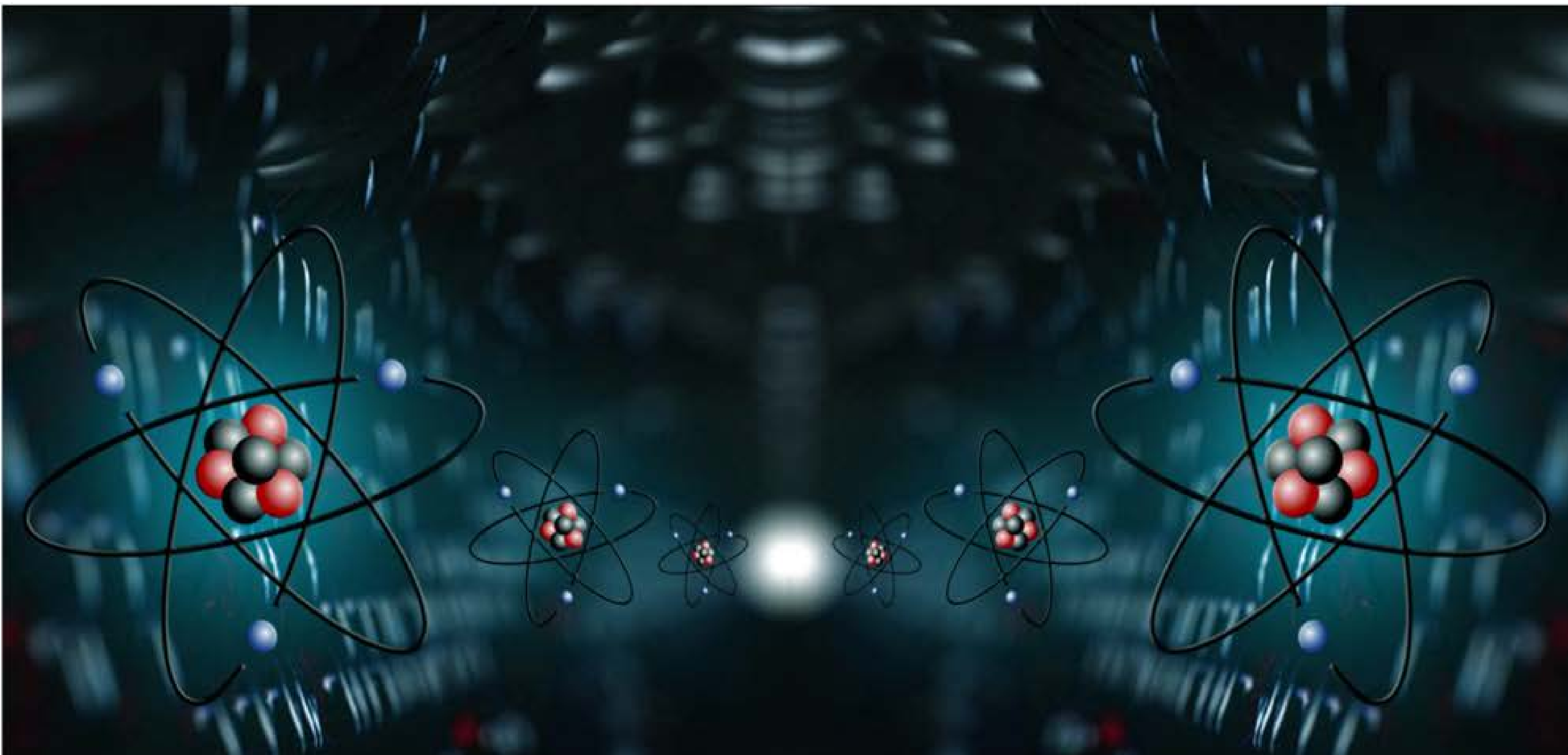

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