

❖ 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.

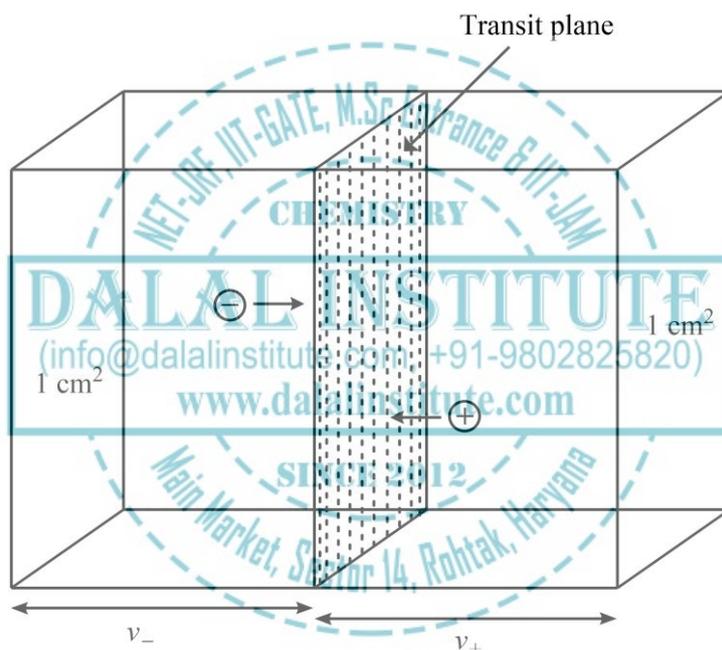


Figure 3. The general depiction ionic movement through transit plane under applied field.

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.

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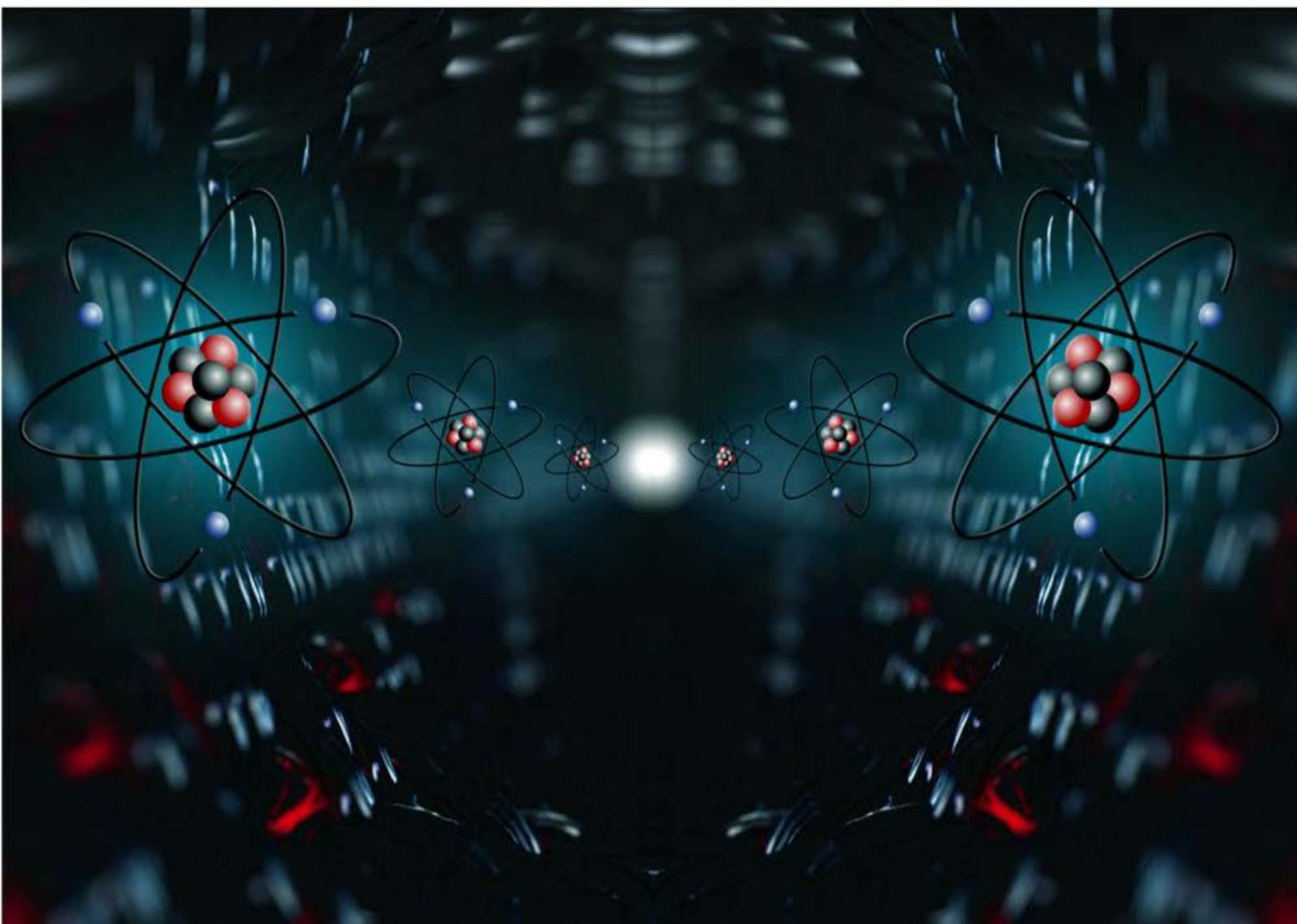
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Volume I

MANDEEP DALAL



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ISBN: 978-81-938720-1-7



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