❖ 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

$$j_D = -D\frac{dc}{dx} \tag{39}$$

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

$$v_d = \bar{u}_{abs}\vec{F} \tag{40}$$

The current density produced by this drift velocity is

$$J = z_+ cFv_d \tag{41}$$

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

$$j_c = \frac{z_+ cFv_d}{z_+ F} \tag{42}$$

or

$$j_c = cv_d \tag{43}$$

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

$$j_c = c\,\bar{u}_{abs}\vec{F} \tag{44}$$

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

$$j_c = -j_D \tag{45}$$

$$j_c + j_D = 0 \tag{46}$$

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

$$c\,\bar{u}_{abs}\vec{F} - D\frac{dc}{dx} = 0 \tag{47}$$

or

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

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

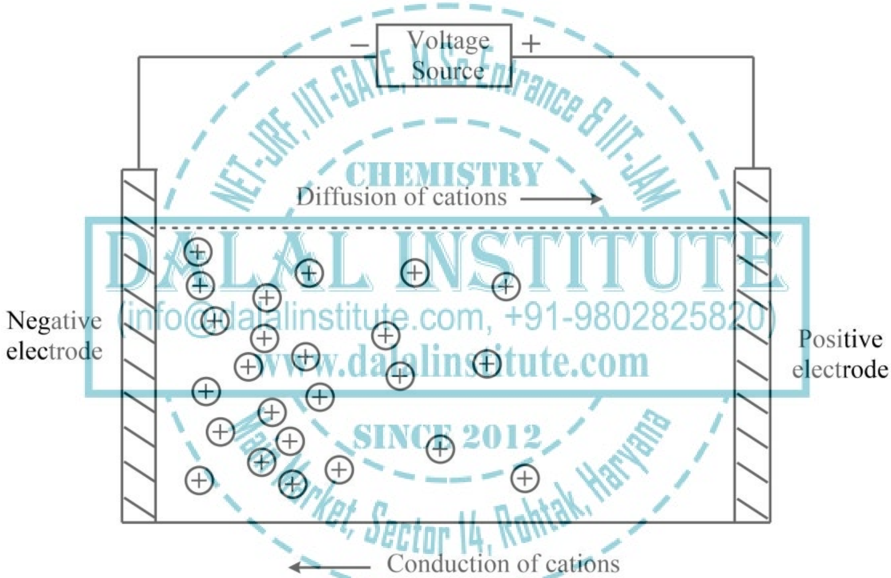

Figure 4. The pseudo-equilibrium when diffusion flux and conduction flux are equal and opposite.

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

$$c = c_0\,e^{-U/kT} \tag{49}$$

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

$$\frac{dc}{dx} = -c_0\,e^{-U/kT}\frac{1}{kT}\frac{dU}{dx} \tag{50}$$

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

$$\frac{dc}{dx} = -\frac{c}{kT}\frac{dU}{dx} \tag{51}$$

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

$$\frac{dc}{dx} = \frac{c}{kT}F \tag{52}$$

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

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

$$\frac{\bar{u}_{abs}}{D} = \frac{1}{kT} \tag{54}$$

or

$$D = \bar{u}_{abs}kT \tag{54}$$

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

$$D = BRT \tag{55}$$

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

$$\bar{u}_{abs}kT = BRT \tag{56}$$

or

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

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

$$B = \frac{\bar{u}_{abs}}{N} \tag{58}$$

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).

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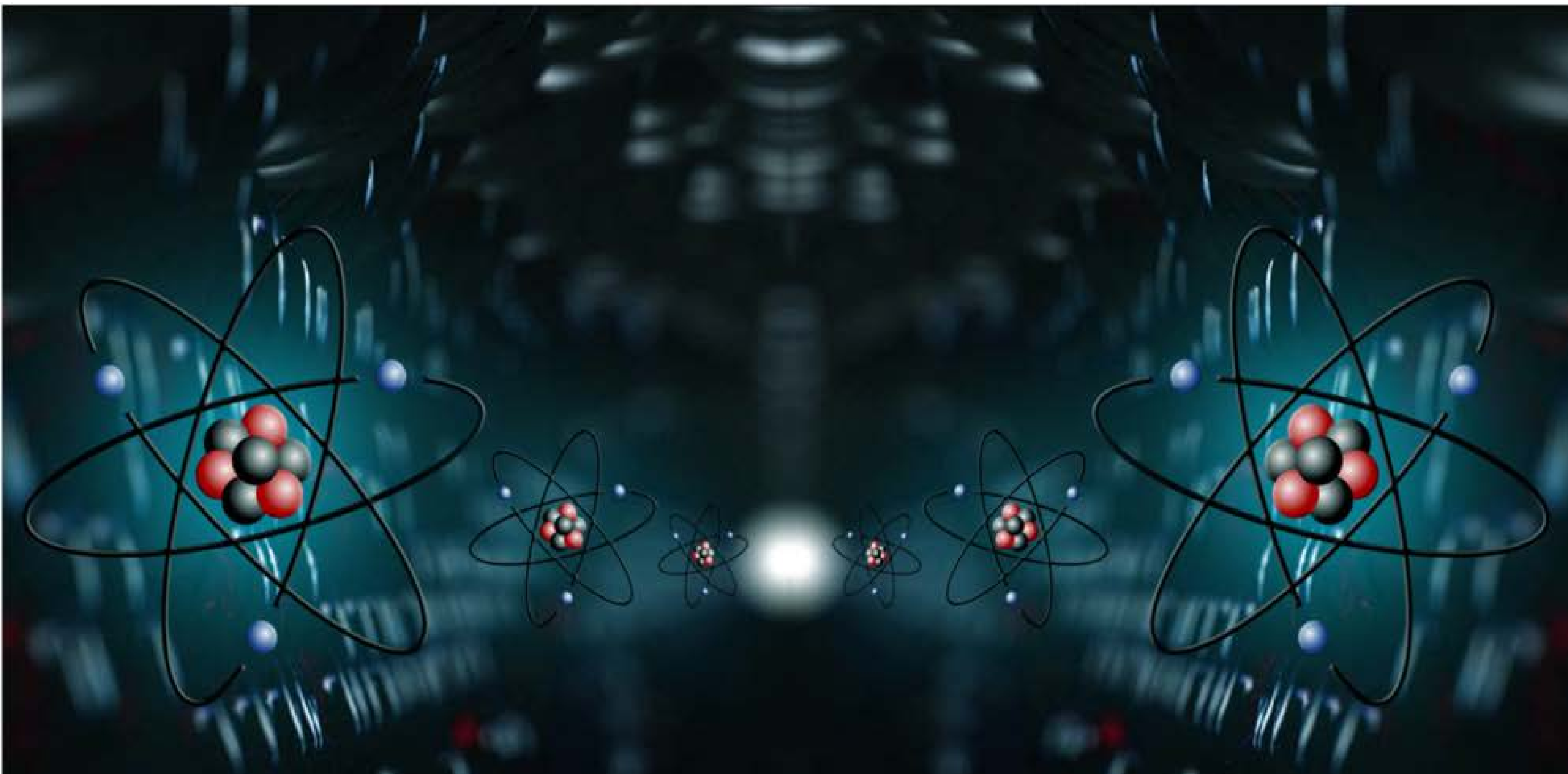

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ISBN: 978-81-938720-1-7
9 788193 872017
MRP: Rs 800.00

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