❖ 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.

$$J = z_+ cFv_d \tag{110}$$

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

$$v_d = \vec{v} - \overleftarrow{v} \tag{111}$$

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

$$\vec{v} = \frac{l}{\tau} \tag{112}$$

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

$$\vec{v} = l\,\vec{k} \tag{113}$$

$$\overleftarrow{v} = l\,\overleftarrow{k} \tag{114}$$

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

$$\overleftarrow{k} = k_D\, e^{-pX} \tag{115}$$

and

$$\vec{k} = k_D e^{pX} \tag{116}$$

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 $\overleftarrow{k}$ in equation (113, 114), we get

$$\vec{v} = l\, k_D e^{pX} \tag{117}$$

$$\overleftarrow{v} = l\, k_D\, e^{-pX} \tag{118}$$

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

$$v_d = l\, k_D\, e^{pX} - l\, k_D\, e^{-pX} \tag{119}$$

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

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

$$v_d = 2l\,k_D\,2\,Sinh\,pX \tag{121}$$

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

$$J = z_+cF\,(2l\,k_D\,2\,Sinh\,pX) \tag{122}$$

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

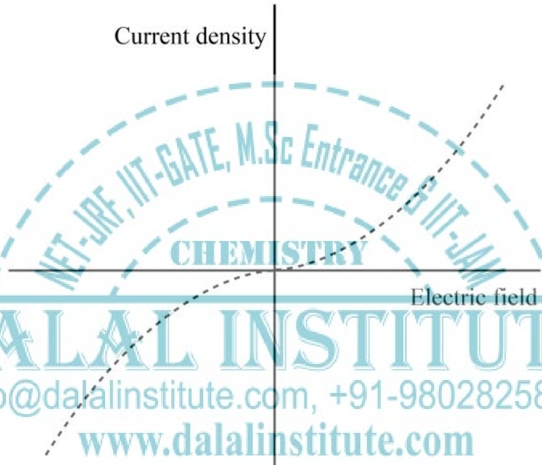

Figure 7. The variation of current density with the applied electric field.

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

$$\sigma = \frac{J}{X} = z_+cF\,\frac{(2l\,k_D\,2\,Sinh\,pX)}{X} \tag{123}$$

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

$$\Lambda_{eq} = \frac{\Lambda_m}{z_+} = \frac{\sigma}{z_+c} = z_+cF\,\frac{(2l\,k_D\,2\,Sinh\,pX)}{z_+cX} \tag{124}$$

$$\Lambda_{eq} = F\,\frac{(2l\,k_D\,2\,Sinh\,pX)}{X} \tag{125}$$

Which is the equation for equivalent conductivity.

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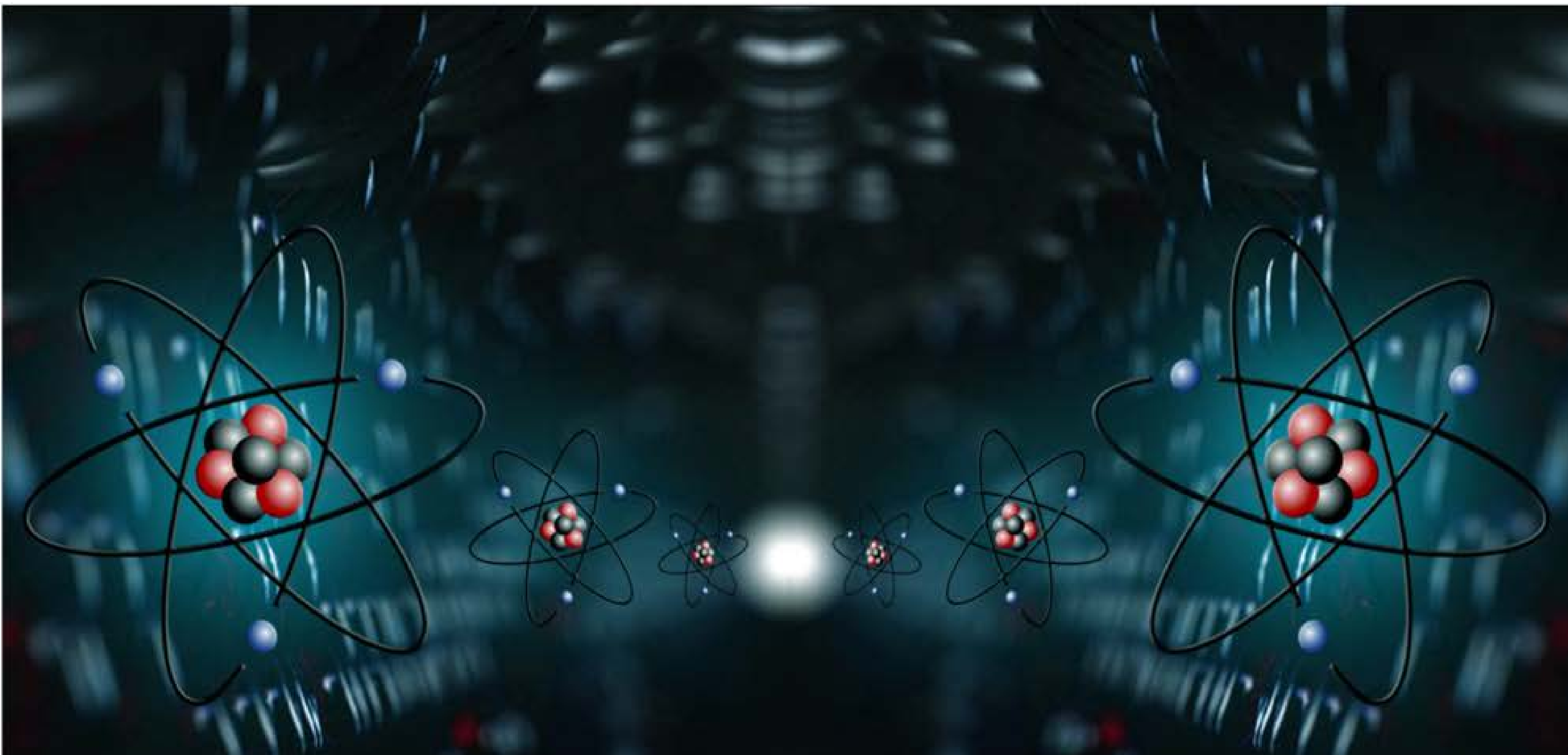

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

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