

❖ 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

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

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

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).

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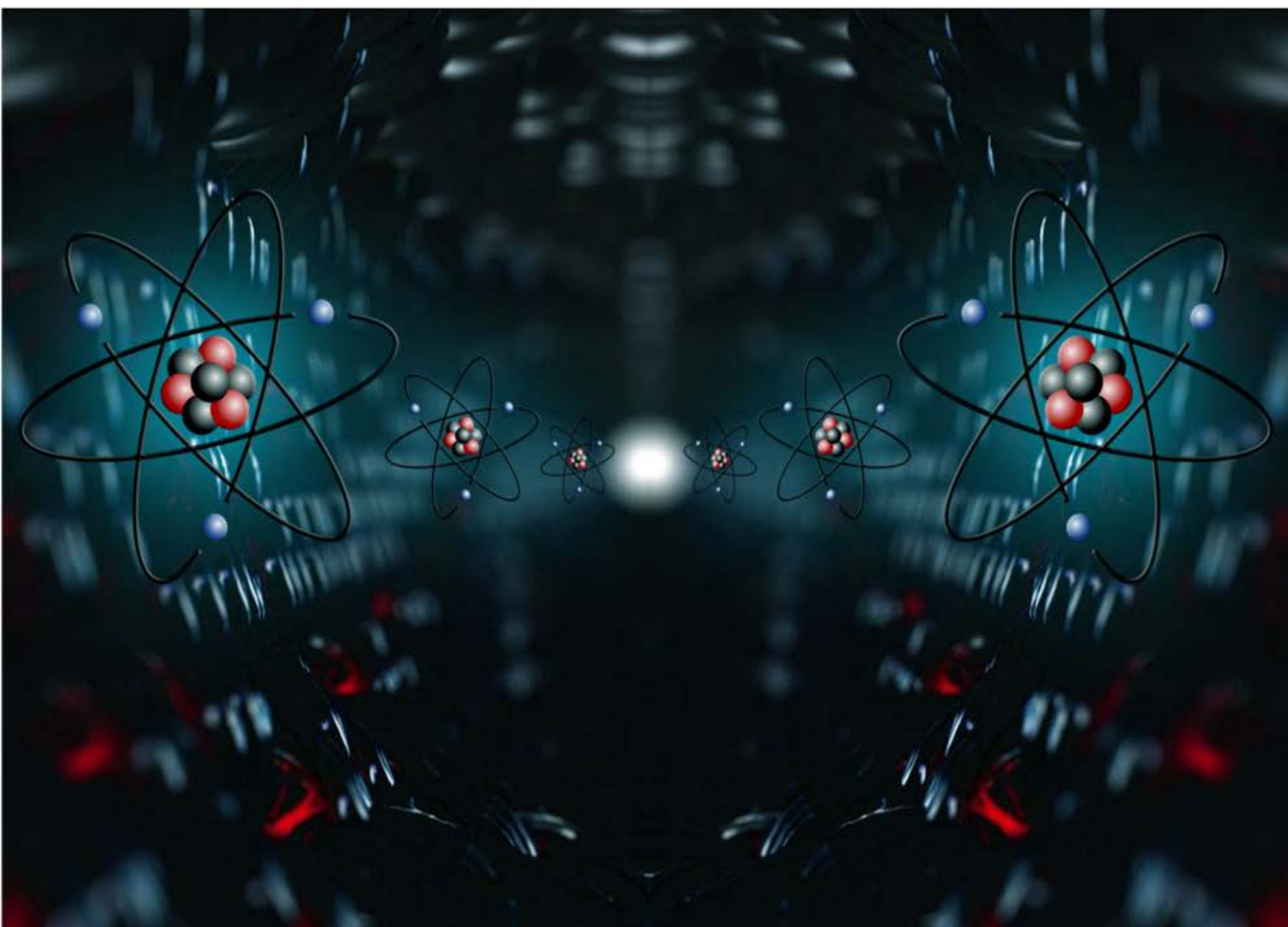
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Volume I

MANDEEP DALAL



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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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