❖ 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.,

$$\Lambda_{eq} = F[(u_{conv})_+ + (u_{conv})_-] \tag{71}$$

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

$$(u_{conv})_+ = z_+e_0(\bar{u}_{abs})_+ = ze_0(\bar{u}_{abs})_+ \tag{72}$$

$$(u_{conv})_- = z_-e_0(\bar{u}_{abs})_+ = ze_0(\bar{u}_{abs})_- \tag{73}$$

Using equation (72, 73) in equation (71), we get

$$\Lambda_{eq} = F[ze_0(\bar{u}_{abs})_+ + ze_0(\bar{u}_{abs})_-] \tag{74}$$

$$\Lambda_{eq} = ze_0F[(\bar{u}_{abs})_+ + (\bar{u}_{abs})_-] \tag{75}$$

From Einstein's relation, we know that

$$(\bar{u}_{abs})_+ = \frac{D_+}{kT} \tag{76}$$

also

$$(\bar{u}_{abs})_- = \frac{D_-}{kT} \tag{77}$$

Using equation (76, 77) in equation (75), we get

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

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

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.

$$\Lambda_{eq} = \frac{ze_0FN_A}{kTN_A}(D_+ + D_-) \tag{80}$$

Since $e_0N_A = F$ and $kN_A = R$, the above equation takes the form

$$\Lambda_{eq} = \frac{zF^2}{RT}(D_+ + D_-) \tag{81}$$

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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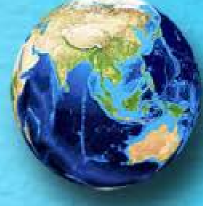

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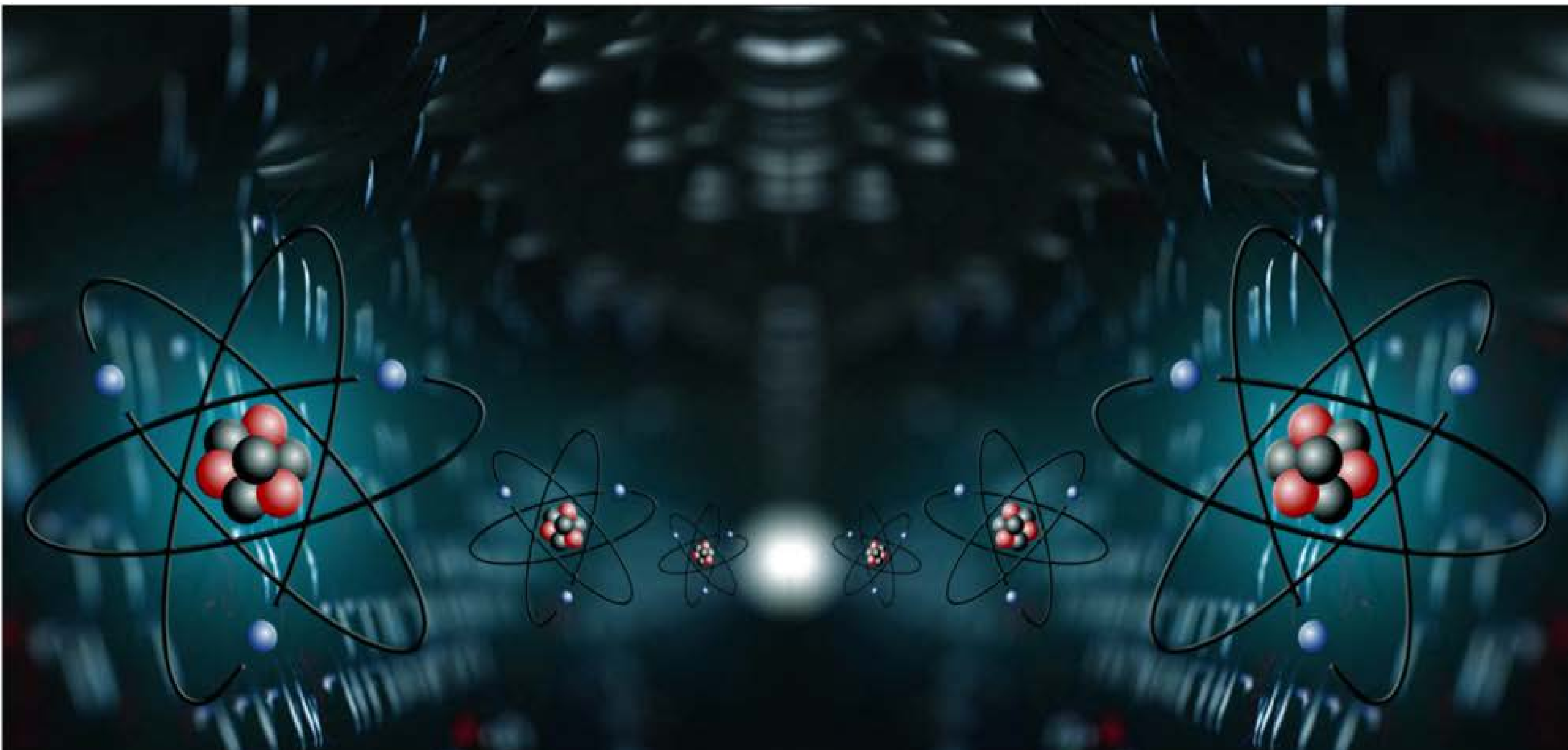

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