❖ Walden's Rule

The Walden's rule states that the product of the equivalent conductivity and the viscosity of the solvent for a specific electrolyte at a given temperature is constant.

The Stokes-Einstein relation found the connection between the viscosity (η) and the diffusion coefficient (D); whereas the Nernst-Einstein relation correlates the equivalent conductivity (Λ) and diffusion coefficient. Therefore, a remarkable possibility is to eliminate the diffusion coefficient to correlate the viscosity of the solvent with the equivalent conductivity. In order to do so, recall the Stokes-Einstein relation first i.e.

$$D = \frac{kT}{6\pi r\eta} \tag{82}$$

Where k is the Boltzmann constant and η is the coefficient of viscosity. The symbol r represents the radius of the ion and T is the temperature of the electrolytic solution. Now, recall the Nernst-Einstein relation i.e.

$$D = \frac{\Lambda_{eq}RT}{zF^2} \tag{83}$$

Where z is the charge number and F is the Faraday constant. From equation (82) and equation (83), we get

$$\frac{kT}{6\pi r\eta} = \frac{\Lambda_{eq}RT}{zF^2} \tag{84}$$

$$\Lambda_{eq} = \frac{kTzF^2}{6\pi r\eta RT} \tag{85}$$

Since $e_0N_A = F$ and $kN_A = R$, the above equation can be written in the following form

$$\Lambda_{eq} = \frac{kTzFe_0N_A}{6\pi r\eta TkN_A} = \frac{zFe_0}{6\pi r\eta} \tag{86}$$

$$\Lambda_{eq}\eta = \frac{zFe_0}{6\pi r} \tag{87}$$

Putting $zFe_0/6\pi = constant$, the above equation can also be written as

$$\Lambda_{eq}\eta = \frac{constant}{r} \tag{88}$$

Now, if the radius of the ion the solvated ion is same in solvents of different viscosities, the equation (88) is reduced to

$$\Lambda_{eq}\eta = constant = \frac{zFe_0}{6\pi r} \tag{89}$$

Which is the empirical Walden's rule. The experimental data for potassium iodide in various solvents is given for more clear picture is given below.

Table 1. The experimental data for KI in different solvents.

Solvent used	Equivalent conductivity (Λ_{eq})	Viscocity of the solvent (η)	$\Lambda_{eq}\eta$
Acetophenone	39.8	0.01620	0.64476
Ethanol	50.9	0.01096	0.55786
Pyridine	71.4	0.00958	0.68401
Methanol	114.5	0.00545	0.62403
Propanone	185.4	0.00316	0.58586
Acetonitrile	198.3	0.00345	0.68414

It is obvious for the data listed in 'Table 1' that the product of equivalent conductivity and viscosity of the solvent is almost constant with slight deviation, which can be attributed to different solvated radii in different solvents.

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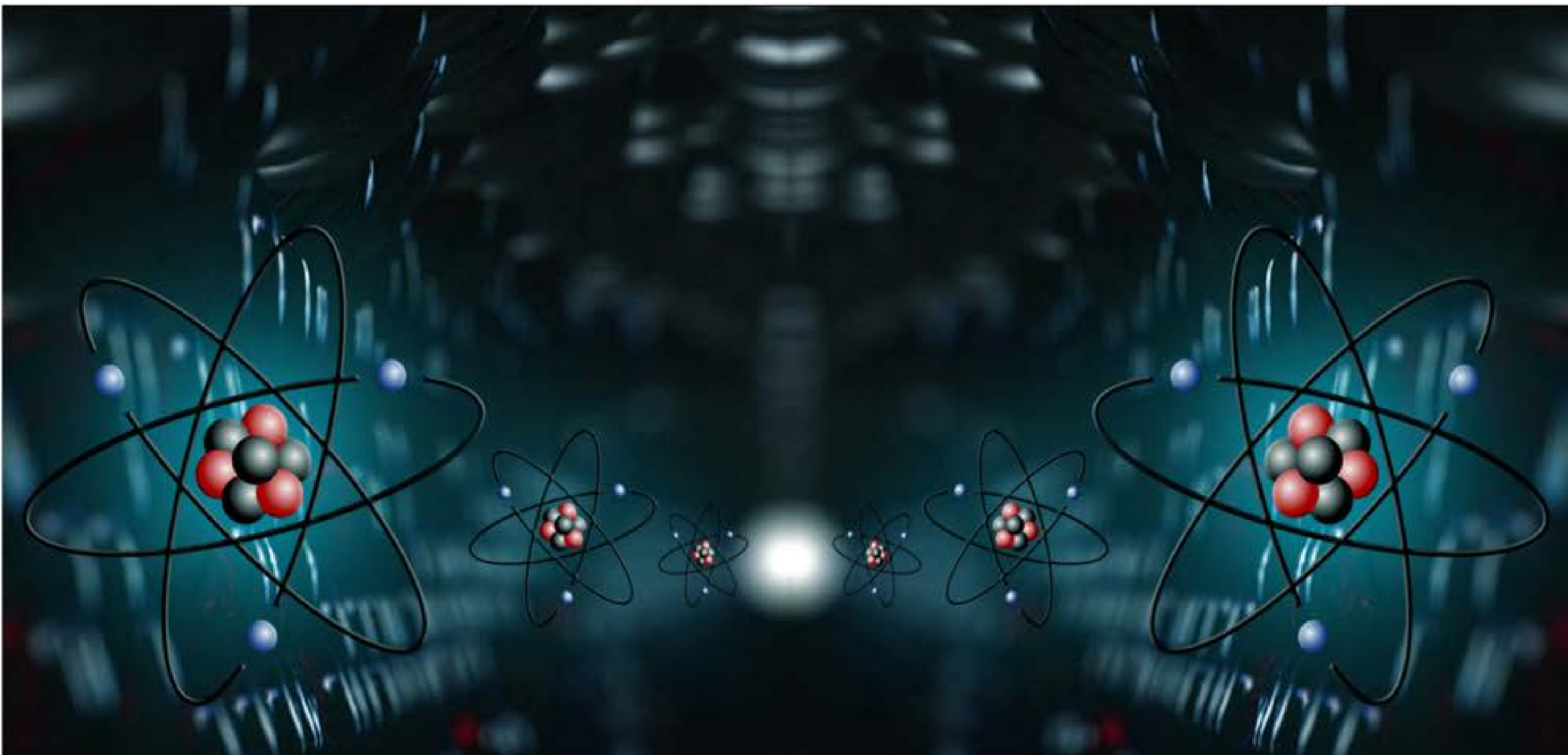

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