❖ The Onsager Phenomenological Equations

Since the ionic mobilities of cations are not independent but affect each other as we have studied in the previous section, the expression for the flux must also be modified. In order to understand the concept, recall the general form of Nernst-Planck equation for the ionic flux of *i*th species (j_i) i.e.

$$j_i = -\frac{\bar{u}_i}{z_i F} c_i \frac{d\bar{\mu}_i}{dx} \tag{165}$$

Where $\bar{u}_i$ is the conventional ionic mobility of *i*th species and c_i represents the corresponding concentration. The symbol z_i and F are the charge number and Faraday constant, respectively. The symbol $d\bar{\mu}_i/dx$ is the total driving force for ionic transport. Correcting for the coupling between ionic mobilities arising from diffusion potential, we have

$$j_i = -\frac{\bar{u}_i}{z_i F} c_i \frac{d\bar{\mu}_i}{dx} + coupling\ correction \tag{166}$$

These mutually interactive flows can be treated by the methods of near-equilibrium thermodynamics in a phenomenological or macroscopic framework. This procedure is simple and can be covered in the postulates given below.

Statement 1: When the system is in near-equilibrium and ionic mobilities are independent of each other, the fluxes can be treated as proportional to the driving forces (Nernst-Planck flux equation). Mathematically, we can say about the ionic flux of 1st species (j_1) that

$$j_1 = L_{11}\,\vec{F}_1 \tag{167}$$

Where $L_{11} = \bar{u}_1 c_1/z_1 F$ is phenomenological constant and $\vec{F}_1 = d\bar{\mu}_1/dx$ is the corresponding driving force.

Statement 2: If the coupling between ionic mobilities is considered, the fluxes should be treated as proportional to the driving forces (Nernst-Planck flux equation) plus the contribution from the coupling. Mathematically, we can say about the ionic flux of 1st species (j_1) that

$$j_1 = L_{11}\,\vec{F}_1 + coupling\ correction \tag{168}$$

Now if there are many types of species then above equation takes the form

$$j_1 = L_{11}\,\vec{F}_1 + Flux\ of\ 1\ due\ to\ driving\ force\ of\ 2nd\ species + Flux\ of\ 1\ due\ to\ driving\ force\ of\ 3rd\ species + \cdots \tag{169}$$

Statement 3: The proportionality of fluxes is also valid for the contributions of the forces from other ionic species. Hence, equation (169) can also be written as

$$j_1 = L_{11}\,\vec{F}_1 + \left[L_{12}\,\vec{F}_2 + L_{13}\,\vec{F}_3 + L_{14}\,\vec{F}_4 \ldots\ldots L_{1n}\,\vec{F}_n\right] \tag{170}$$

Where L_{12}, L_{13} L_{14} ….. L_{1n} are the phenomenological constants for the interactions on flux from the flux of other ionic species. The symbol $\vec{F}_1, \vec{F}_2, \vec{F}_3 \ldots\ldots \vec{F}_n$ are the corresponding driving forces.

Statement 4: If a monovalent electrolyte like NaCl is dissolved into water, the fluxes of cation (j_+), anion (j_-) and water (j_0) can be written as

$$j_+ = L_{++}\,\vec{F}_+ + L_{+-}\,\vec{F}_- + L_{+0}\,\vec{F}_0 \tag{171}$$

$$j_- = L_{--}\,\vec{F}_- + L_{-+}\,\vec{F}_+ + L_{-0}\,\vec{F}_0 \tag{172}$$

$$j_0 = L_{00}\,\vec{F}_0 + L_{0+}\,\vec{F}_+ + L_{0-}\,\vec{F}_- \tag{173}$$

The equations (171-173) are typically known as the Onsager phenomenological equations.

Statement 5: According to Onsager's reciprocity relation, all symmetrical coefficients are equal. Mathematically, we can say that

$$L_{ij} = L_{ji} \tag{174}$$

Which is an experimentally proved result.

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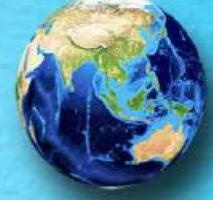

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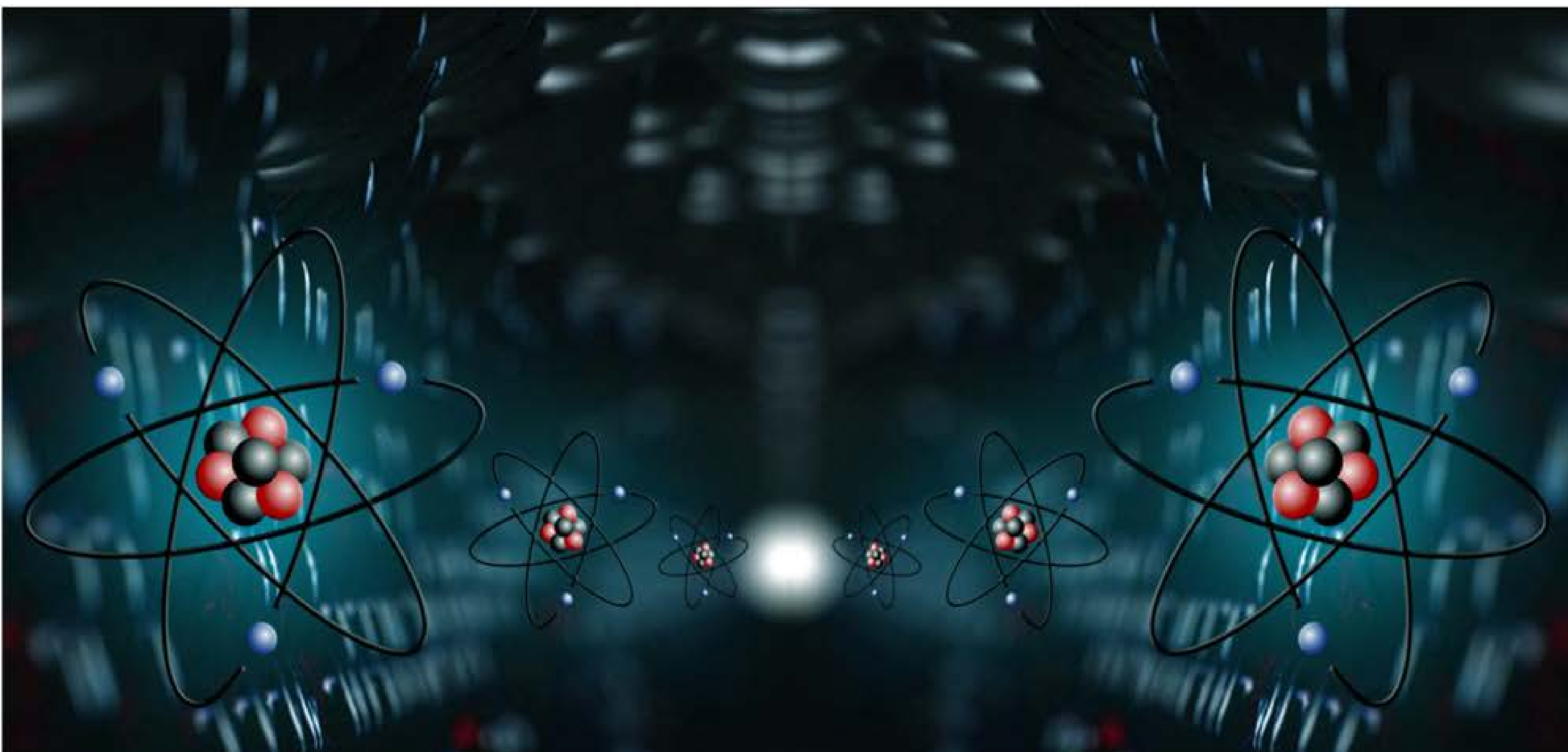

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ISBN: 978-81-938720-1-7
9 788193 872017
MRP: Rs 800.00

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