Many biological molecules are charged. Therefore, their transport is influenced by electrical potential gradients. Such gradients arise naturally due to ifferences in ion concentration across cell membranes, as well as to localization of charges on cell membrane surfaces and the extracellular matrix. In addition, number of techniques used to characterize biological molecules in a solution apply an electric field to sepparate DNA or proteins on the basis of their charge and size. The most commonly used method is electrophoresis.

Flux of an ion Ji in a dilute solution due to applied electric field is the product of its concentration and velocity of migration vmi, i.e.

$$j_i = c_i v_{mi} \quad (1)$$

The migration velocity can be obtained by writing a force balance on an ion to yield,

$$m_i \frac{dv_{im}}{dt} = \underbrace{z_i e \left(-\frac{d\psi}{dx}\right)}_{\text{Electric Force}} - \underbrace{f v_{mi}}_{\text{Viscous Force}} \quad (2)$$

In the above equation, mi is the mass of ion, zi is the net charge (postive or negative), e is the elementary charge, ψ is the electrostatic potential and x is the direction of applied electric field. and f is the friction coefficient At steady state, the electric and viscous forces counterbalance. As a result, the net force acting on the ion is zero and the ion moves with a constant velocity. Therefore,

$$v_{mi} = \frac{z_i e (d\psi/dx)}{f} \quad (3)$$

The friction coefficient f = kT/Di. Therefore,

$$v_{mi} = \frac{z_i e D_i}{kT} \frac{d\psi}{dx} = \frac{z_i e N_A D_i}{N_A k T} \left(\frac{d\psi}{dx}\right)$$

$$\text{or, } v_{mi} = \frac{z_i F D_i}{RT} \left(\frac{d\psi}{dx}\right) \quad (4)$$

where NA is the Avagadro number, F=eNa is the Faraday constant and R is the gas constant.

The flux of ith ion is the sum of flux due to electric field as given by eq. (4) plus the diffusive flux as a result of concentration gradient. Therefore, the flux Ni is given by

$$N_i = -D_i \frac{dc_i}{dx} - \frac{D_i z_i F}{RT} c_i \left(\frac{d\psi}{dx}\right) \quad (5)$$

Eq. (5) is known as Nernst Planck equation. This equation is valid for dilute solutions. For more concentrated solutions, the fluxes and ionic currents interact. We need additional relations to solve for flux. These relations are obtained by imposing the condition of electroneutrality.

$$\sum c_i z_i = 0 \quad (6)$$

The net current is the sum of ion fluxes, i.e.

$$i = F \sum N_i z_i \quad (7)$$

Let us consider transport of ions across a membrane with imposed potential gradient. The potential can be assumed to be linear across the membrane since the membrane is thin. Therefore,

$$\frac{d\psi}{dx} = -\frac{\psi_0 - \psi_L}{L} = \frac{V_m}{L} \quad (8)$$

Vm being the potential drop across the membrane and L is the membrane thickness. At steady state, mass balance of an ionic species gives

$$\frac{dN_i}{dx} = 0 \quad (9)$$

From eqs. (5) and (9), one obtains,

$$0 = -D_i \frac{d^2 c_i}{dx^2} - \frac{D_i z_i F}{RT} \frac{V_m}{L} \frac{dc_i}{dx} \quad (10)$$

or,

$$D_i \frac{dc_i}{dx} + D_i \frac{z_i F}{RT}\frac{V_m}{L} c_i = A' = \text{constant}$$

$$\frac{dc_i}{dx} + \frac{z_i F}{RT}\frac{V_m}{L} c_i = \frac{A'}{D_i} = A$$

$$\frac{dc_i}{dx} \exp\left(\frac{z_i F V_m}{RT\,L} x\right) + \frac{z_i F}{RT} c_i \exp\left(\frac{z_i F V_m}{RT\,L} x\right) = A \exp\left(\frac{z_i F}{RT} x\right)$$

$$\frac{d}{dx}\left[c_i \exp\left(\frac{z_i F V_m}{RT\,L} x\right)\right] = A \exp\left(\frac{z_i F}{RT}\frac{V_m}{L} x\right)$$

$$\int_0^L \frac{d}{dx}\left[c_i \exp\left(\frac{z_i F V_m}{RT\,L} x\right)\right] dx = A \int_0^L \exp\left(\frac{z_i F V_m}{RT\,L} x\right) dx$$

$$c_L \exp\left(\frac{z_i F V_m}{RT}\right) - c_0 = \frac{A\,RT}{z_i F}\left[\exp\left(\frac{z_i F}{RT} V_m\right) - 1\right] \quad (11)$$

$$c_L = c_0 \exp\left(-\frac{z_i F V_m}{RT}\right) + \frac{ART}{z_i F}\left[1 - \exp\left(-\frac{z_i F V_m}{RT}\right)\right] \quad (12)$$

From (11),

$$N_i = A' = A D_i = \frac{D_i z_i F}{RT} \frac{\left\{\exp\left(\frac{z_i F}{RT} V_m\right) c_L - c_0\right\}}{\left\{\exp\left(\frac{z_i F V_m}{RT}\right) - 1\right\}} \quad (13)$$