

**Transport and Interactions in Membrane**  
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**ABSTRACT**

In this chapter non-equilibrium thermodynamic has been briefly outlined. Kedem-Katchalsky(K-K) model is used to correlate thermodynamic force and Spiegler's friction coefficient (i.e.  $F_{ik}$  and  $f_{ik}$ ) for the membrane system. The various type of interactions such as solute-membrane( $f_{sm}$ ), solute-water( $f_{sw}$ ), and water-membrane( $f_{wm}$ ) are discussed. Johnson model for the solute and solvent transport, rejection in the light of Irreversible. Thermodynamics is also summarized. Solute rejection under different conditions has been discussed. Thermodynamic Theory of membrane potential has also been given with considerable.

## Introduction :

Membranes are generally used to separate two solutions of unequal concentration. Their function is to retard the attainment of equilibrium. At equilibrium composition, pressure, electrical potential and temperature, are uniform throughout the system. A static and time invariant state of a system where no spontaneous process takes place and all macroscopic quantities remain unchanged is called “equilibrium states”.

In many situations of interest, the membrane system cannot be envisaged to be in a state of equilibrium because of the existence of gradients of composition electrical potential, pressure, etc. For the description of such non-equilibrium situations, non-equilibrium thermodynamics has been used with advantage [1-5]. All spontaneous processes are accompanied by increase in entropy. We therefore, first discuss production of entropy in irreversible processes. According to the second law of the thermodynamics entropy is defined as

$$dS = \frac{dQ_{rev}}{T} \quad (2.01)$$

However, if an irreversible process occurs in the system under consideration,  $dS > \frac{dQ}{T}$ , the entropy gain is determined by the heat which is absorbed in the reversible change,  $dQ_{rev}$ . In an irreversible process  $dS$  is always greater than  $\frac{dQ}{T}$ ;  $dQ$  being the actual heat absorbed. Thus the actual change in entropy in an irreversible process may be expressed as

$$dS = \frac{dQ}{T} + \frac{dQ_u}{T} \quad (2.02)$$

$dQ'$  is a positive quantity and is termed uncompensated heat that would have been absorbed, had the change taken place reversibly. In the actual change of state, the entropy increase  $dS$  is completed by the creation entropy  $\frac{dQ_u}{T}$ . Equation (2.02) can thus be written as

$$dS = d_e S + d_i S \quad (2.03)$$

where  $d_e S = \frac{dQ}{T}$  corresponds to “exchange” contribution to the entropy change and  $d_i S$  is an “internal” contribution, produced by occurrence of irreversible process.

### **Thermodynamic Fluxes and Forces:**

The local production of entropy  $\sigma$  is related to the rate of increase of entropy,  $d_i S/dt$  within the system by the relation.

$$\sigma = \frac{1}{V} \cdot \frac{d_i S}{dt} \quad (2.04)$$

For unit volume

$$\sigma = \frac{d_i S}{dt}$$

The entropy production  $\sigma$ , is both a thermodynamic quantity and a kinetic quantity [6].

Entropy is a single valued function of all parameters of the system. In steady state of the system wherein the macroscopic properties, temperature, pressure and composition, have time independent values at every point of the

system despite the occurrence of a dissipative process, therefore,  $\frac{dS}{dt}$  will

vanish, i.e.

$$\sigma = 0$$

It has been shown for a larger variety on non equilibrium phenomena [7-9] that ,  $\sigma$  may be expressed as a sum of products of flows and their conjugate forces.

$$\sigma = \sum_{i=1}^n J_i X_i (i = 1,2,3 \dots n) \quad (2.05)$$

$X_i$  is force conjugate with the flow  $J_i$ . The choice [10] of flows and forces, however, is to a certain extent arbitrary. When one set of variable is chosen, the set of conjugate variables is determined by the following requirements:

- a) The product of any flow and its conjugate force must have the dimension of entropy production.
- b) For a given system, the sum of the products must remain the same for any transformations of forces and flows.

### **Phenomenological Equations:**

Several relationships between fluxes and forces are known e.g. ohm's law for electric current, Fick's law for diffusion, Fourier's law for heat flow and Poiseuille's and Darcy's law for fluid flow. In each case the flux,  $J_i$  , is proportional to corresponding force.

$$J_i \propto X_i$$

$$\text{or } J_i = L_i X_i \quad (2.06)$$

where,  $L_i$  is the proportionality coefficient. In non equilibrium thermodynamics one usually deals with process involving a number of flows and forces simultaneously [11-16].

Onsager [17] assumed that any flow is linearly dependent not only on its conjugate force but in principle on all other forces operative in the system. The situation can be expressed, if it is assumed that  $n$  forces are operative in any system, but following set of equations.

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \dots + L_{1n}X_n \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \dots + L_{2n}X_n \\ &\dots\dots\dots \\ &\dots\dots\dots \\ J_n &= L_{n1}X_1 + L_{n2}X_2 + \dots + L_{nn}X_n \end{aligned} \quad (2.07)$$

The above set of equation represent that each flow,  $J_i$ , ( $i = 1,2,3,\dots$ ) is dependent on its conjugate force,  $X_i$ , through straight coefficient,  $L_{ii}$ , which is always positive, and to force  $X_j$  ( $j = 1,2,\dots$ ) through the cross coefficients,  $L_{ij}$  ( $i \neq j$ ) which may be positive, negative or zero. The coefficients  $L_{ij}$  are not necessarily constant but independent of the forces  $X_j$ .

Eckart [10] called these equations as phenomenological equations. In general.

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1,2,3,\dots,n) \quad (2.08)$$

Coefficients  $L_{iK}$  denote the phenomenological coefficients. The phenomenological rate equation (2.08) describes the interaction, i.e., energy transfer between various processes.

### **Onsager's Reciprocal Relationship:**

In 1931, Onsager on statistical mechanical consideration showed that if conjugate fluxes and forces obeying:

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (2.09)$$

are defined so that the expression for the entropy production is of the form

$$\sigma = \sum_i X_i J_i \quad (2.10)$$

The matrix of the coefficients is symmetric, i.e.,

$$L_{iJ} = L_{Ji} (i \neq J) \quad (2.11)$$

when external magnetic field acts on the system, the Onsager relation becomes.

$$L_{iJ}(\mathbf{B}) = L_{Ji}(-\mathbf{B}) \quad (2.12)$$

$\mathbf{B}$  is magnetic induction. Similarly in a rotating system the relationship takes the form  $L_{iJ}(\omega) = L_{Ji}(-\omega)$  (2.13)

$-\omega$  denotes the angular velocity of rotation. Onsager's reciprocal relations reduce the number of coefficients needed for the description of any process. It also allows correlation between different cross effects.

The Onsager's reciprocal relations are valid [18-25] as long as the expression for the entropy production is of the form given by equation (2.07). A good account of earlier efforts at testing the applicability of Onsager's reciprocal relation [3,26] is available in the review of Miller [27].

In classical thermodynamics, time invariant state of the system, the so called equilibrium state is endowed with minimum free energy production of the system attains a minimum value. The positive definite nature of the entropy production also requires that the straight coefficients,

$$L_{ii} > 0$$

The magnitude of the cross phenomenological coefficient is determined by these, straight coefficients. For example, for a process involving two fluxes and two forces it is shown that

$$L_{11} L_{22} > L_{12} L_{21}$$

The L coefficients can be translated into frictional coefficients  $f$  which is performed by balancing the thermodynamic forces  $X_i$  by the algebraic sum of the frictional forces  $F_{ik}$ . According to Kedem and Katchalsky [28], the thermodynamic force  $X_i$  acting on the solute ( $X_s$ ) existing with water in the membrane is counter balanced by the sum of the frictional forces between solute and water, and between solute and membrane, i.e.,

$$X_s = -F_{sw} - F_{sm} \quad (2.14)$$

Similarly, the thermodynamic force on water is given by

$$X_w = -F_{ws} - F_{wm} \quad (2.15)$$

where w and m indicate water and membrane, respectively.

The friction force  $F_{ik}$  which slows down the motion of an object (i) moving or gliding on another object (k) is proportional to the relative velocity of i with respect to k, i.e.,

$$F_{ik} = -f_{ik}(u_i - u_k) \quad (2.16)$$

The values of the proportionality constant  $f_{ik}$  are determined by the difference in the values of  $u_i$  and  $u_k$  (the velocities of i and k), unlike L values, are independent of the frame of reference to which velocities are related and are also concentration independent and thus it brings out the specific interaction of i with k. Hence,

$$F_{sw} = -f_{sw}(u_s - u_w); F_{sm} = -f_{sw}(u_s - u_m)$$

If the membrane is chosen as the frame of reference, then  $u_m = 0$  and  $F_{sm} = -f_{sm}u_s$

The friction coefficients may be related easily to either the L coefficients of the linear rate law is expressed as

$$J_i = \sum_{k=1}^n L_{ik} \cdot X_k$$

or to R coefficients (macroscopic) if the resistance formulation is employed, i.e.



$$X_i = \sum_{k=1}^n R_{ik} \cdot J_k$$

The Onsager relation holds for either formula

$$L_{ik} = L_{ki} \quad \text{and} \quad R_{ik} = R_{ki}$$

### Application of Macroscopic $R_{ik}$ Coefficients :

The macroscopic  $R_{ik}$  coefficients formulation is used in the explanation of anomalous osmosis. It is an electrochemical phenomenon which depends on the electrokinetic charge of the membrane and the dynamic membrane potential which results from the diffusion of electrolyte across the membrane. In anomalous osmosis, reflection coefficient  $\sigma$  becomes negative and  $\Delta P = 0$ , that is,

$$\left( \frac{J_w}{X_w \Delta P} \right) < 0 \quad (2.17)$$

For the two components (solvent w and solute s) as

$$X_w = R_{ww}J_w + R_{ws} \cdot J_s \quad (2.18)$$

$$X_s = R_{ws}J_w + R_{ss} \cdot J_s \quad (2.19)$$

Using the Gibbs – Duhem – Margules equation, we get

$$\left( \frac{J_w}{X_w} \right) = \frac{[R_{ss} + (C_w R_{ws} / C_s)]}{(R_{ss} \cdot R_{ww} - R_{sw}^2)} \quad (2.20)$$

For  $\left( \frac{J_w}{X_w} \right) < 0$ ,  $(R_{ss} \cdot R_{ww} - R_{sw}^2) > 0$  and  $R_{ss} + (C_w \cdot R_{ws} / C_s) < 0$

In terms of frictional coefficient and the microscopic friction coefficients  $r_{ik}$ , the condition for anomalous osmosis is obtained as

$$\frac{f_{sm} + r_{ws} \bar{\epsilon}_w}{\bar{\epsilon}_s} - \frac{\bar{\epsilon}_w}{\epsilon_s} \cdot r_{ws} < 0 \quad (2.21)$$

### Spiegler Formalism:[29]

When system comprises three components (w = water, s = solute, m = membrane) the formal hydrodynamic description of the frictional forces is as follows

$$F_{sm} = -f_{sm}(\bar{V}_s - \bar{V}_m) \quad (2.22)$$

$$F_{sw} = -f_{sw}(\bar{V}_s - \bar{V}_w) \quad (2.23)$$

$$F_{wm} = -f_{wm}(\bar{V}_w - \bar{V}_m) \quad (2.24)$$

where  $F_{ik}$  denotes frictional force,  $f_{sw}$  is the friction coefficient characterizing the friction between a mole of solute and an infinite amount of water,  $f_{sm}$  is the friction coefficient characterizing the solute-membrane interaction, whereas  $f_{wm}$  determines the friction between water and the membrane matrix. The membrane is considered as the reference system,  $\bar{V}_m$  is zero.

Assuming thus with Spiegler that forces acting on every molecule are additive, the following relationships for the force balances result from

$$X_i - \sum_k F_{ik} = 0$$

$$X_s = F_{sm} + F_{sw} = \bar{V}_s(f_{sm} + f_{sw}) - \bar{V}_w \cdot f_{sw} \quad (2.25)$$

$$X_w = F_{wm} + F_{ws} = \bar{V}_w(f_{wm} + f_{ws}) - \bar{V}_s \cdot f_{ws} \quad (2.26)$$

Where  $X_i$  denotes generalized thermodynamic force. The friction coefficient  $f_{ws}$  differs from  $f_{sw}$  since  $f_{ws}$  characterizes the friction between one mole of water and the amount of solute in unit volume of the membrane. The thermodynamic driving force  $X_i = \frac{\bar{\mu}_i}{\delta x}$  where  $\frac{\bar{\mu}_i}{\delta x}$  is the gradient of the

chemical potential within the membrane complying with the frictional formalism, Kedem and Katchalsky derived formula for the permeation/ reflection coefficients ( $\omega, \sigma$ ) which is valid for dilute solutions.

$$\omega = \left( \frac{\epsilon_2}{\epsilon_{sd}} \right) \left[ \frac{1}{f_{2w} + f_{2m}} \right] \quad (2.27)$$

$$\sigma = 1 - \frac{\omega d}{V_w \epsilon_w} [f_{1w} + f_{2w} + f_{wm} \cdot \frac{V_s}{V_w}] \quad (2.28)$$

The general solution for  $\omega$  and  $\sigma$  valid for any concentration range may be found elsewhere [29].

$$m = \left( \frac{\epsilon_2}{\epsilon_{sd}} \right) \left[ \frac{1}{f_{21} \cdot A_m + f_{2w}(1+B_2) + f_{2m} + f_{1w}(A_2+B_2) + f_{1m} A_2} \right] \quad (2.29)$$

$$\sigma = 1 - \frac{\omega d}{V_m \epsilon_w} [f_{1w}(1+B_1) + f_{2w}(1+B_2) + f_{wm} \cdot B_w] \quad (2.30)$$

$$\text{where } A_i = \frac{\epsilon_i}{\epsilon_1} ; \quad B_i = \frac{V_s \epsilon_i}{V_w \epsilon_w} \quad i=1,2,w,m$$

1 = counterion ; 2 = coion ; w = water ; m = membrane.

Evaluation of the friction coefficients  $f_{sw}$ ,  $f_{sm}$ , and  $f_{wm}$  were calculated from the following equations-[30]

$$f_{sw} = \frac{[1 - \frac{m_s \bar{v}_s}{L_P}] \epsilon_w}{m_{sd}} \quad (2.31)$$

$$f_{sm} = \frac{[\frac{m_s \bar{v}_s}{L_P}]}{1 - (\frac{m_s \bar{v}_s}{L_P})} f_{sw} \quad (2.32)$$

$$f_{wm} = \frac{\epsilon_w}{d} \left[ \frac{1}{L_P} - \frac{(1 - \frac{m_s \bar{v}_s}{L_P}) \epsilon_s}{m_s} \right] \quad (2.33)$$

### Test of Possibility of Anomalous Osmosis under Spiegler Formalism:

Membrane anomalous osmosis behavior can be tested employing the friction coefficients and membrane semipermeability parameters. The satisfactory in equality relation is

$$f_{sm} < \left( \frac{\bar{\epsilon}_s}{\epsilon_s} \cdot C_w - \bar{C}_w \right) \cdot r_{ws} \quad (2.34)$$

The cause of anomalous osmosis can be understood as when a membrane maintained at its isoelectric point gave only the normal flow but when it is put into a charged state by changing the pH, it gives a total flow which have the abnormal component. The difference between the two flows is known as anomalous osmosis.

Johnson Model for the solute and solvent transport rejection and coupling through the membrane in the light of Irreversible Thermodynamics:

The water and salt fluxes through the membrane are given by

$$J_w = -L_{ww} \frac{d\mu_w}{dx} - L_{ws} \frac{d\mu_s}{dx} \quad (2.35)$$

$$J_s = -L_{sw} \frac{d\mu_w}{dx} - L_{ss} \frac{d\mu_s}{dx} \quad (2.36)$$

and  $L_{ws} = L_{sw} \quad (2.37)$

According to Johnson et. al.

$$L_{ww} = \frac{\bar{\epsilon}_w \bar{D}_w}{RT} \times 10^{-3} \quad (2.38)$$

$$L_{ss} = \frac{\bar{\epsilon}_s \bar{D}_s}{vRT} \times 10^{-3} \quad (2.39)$$

$$\text{and } L_{sw} = L_{ws} = \frac{\bar{\epsilon}_w \bar{\epsilon}_s \bar{D}_{sw}}{RT} \times 10^{-6}$$

where  $\bar{C}_w$  and  $\bar{C}_s$  are local concentrations of water and salt in membrane.

$\bar{D}_{sw}$  denotes the proportionality constants having the properties of diffusion coefficient and is the number of ions per mole of salt. For the case

$$\begin{aligned} d\mu_s / dx &\rightarrow 0 \\ \left( \frac{J_s}{J_w} \right)_{d\mu_s/dx=0} &= \frac{L_{ws}}{L_{ww}} = \beta \frac{\bar{\epsilon}_s}{\bar{\epsilon}_w} \end{aligned} \quad (2.40)$$

where  $\beta = (\bar{D}_{sw} \times 10^{-3} / \bar{D}_w) \cdot \bar{C}_w$  and can have values between 0 and 1. It indicates the ratio of salt velocity to water velocity in the membrane. After rearranging above equations one gets

$$J_s = \beta \frac{\bar{\epsilon}_s}{\bar{\epsilon}_w} J_w - \frac{\bar{D}_s}{1000v} \cdot \frac{\bar{\epsilon}_s}{dx} d(\mu_s / RT) \quad (2.41)$$

It is known that  $d(\mu_s / RT) = v \ln \bar{C}_s$ , one gets

$$J_s = \beta \bar{m} \cdot J_w - \bar{D}_s^* \frac{d\bar{m}}{dx} \quad (2.42)$$

where  $\bar{D}_s^* = (\rho_m \cdot \phi_w / 1000) \cdot \bar{D}_s$ ,  $\rho_m$  is the density of the membrane, and

$\phi_w$  is the weight fraction of water in the membrane.  $\bar{m}$  denotes molality of water in the membrane. Above equation is integrated under steady state

condition for two extreme cases when  $\beta=1$  (complete coupling of salt and water)

and  $\beta = 0$  (independent transport of salt and water through the membrane).

For the case when,  $\beta=1$ , above equation integration becomes:

$$\frac{J_w}{\bar{D}_s^*} (x - d) = \ln \left( \frac{m_e - \bar{m}}{m_e - \bar{m}_e} \right) = \ln \left\{ \frac{1 - (\bar{m}/m_e)}{1 - K} \right\} \quad (2.43)$$

where  $K$  is the distribution coefficient and is given by

$$K = \frac{\bar{m}_e}{m_e} = \frac{\bar{m}_f}{m_f} \quad (2.44)$$

where  $m_e$  and  $\bar{m}_e$  denote effluent molality in the bulk and at the membrane interface;  $m_f$  and  $\bar{m}_f$  denote molality of the feed and at the membrane interface respectively.

Equation(2.43) on rearrangement gives the equation for the concentration

profile in the membrane. That is

$$e^{a[(x/d)-1]}(1-k) = 1 - \frac{\bar{m}}{m_e} \quad (2.45)$$

$$\text{or } \bar{m}/m_e = 1 - (1-k)e^{a[(x/d)-1]} \quad (2.46)$$

where  $\alpha = J_w (d/\bar{D}^*)$  and is dimensionless For  $x = 0, \bar{m} = \bar{m}_f$ , the salt rejection  $S$  is given by

$$S = 1 - \frac{K}{(\bar{m}_f/m_e)} \quad (2.47)$$

In term  $\alpha$ , and  $k$  salt rejection can be rearranged as

$$\frac{1-S}{K} = \frac{e^{\alpha} - 1}{e^{\alpha} - 1} \left( \frac{K}{1-K} \right) \quad (2.48)$$

when  $e^{\alpha} \gg 1$ , Eq(2.48) becomes

$$1 - S_{\alpha} \approx K \quad (2.49)$$

For the other extreme case,  $\beta=0$  (no coupling of salt and water flows)

$$\frac{1-S}{K} = \frac{K}{a} = \left( \frac{K}{d} \right) \cdot \frac{1}{J_w} \quad (2.50)$$

For intermediate value of  $\beta$ , the corresponding equations are

$$\frac{1-S}{K} = \frac{e^{\beta\alpha} - 1}{e^{\beta\alpha} - 1} \left( \frac{\beta k}{1-\beta k} \right) \quad (2.51)$$

$$\text{and } 1 - S_{\alpha} \approx \beta K \quad (2.52)$$

when  $e^{\beta\alpha} \gg 1$

Regarding the salt rejection, the following conclusions arise from this



treatment.

- (i) When there is no coupling ( $\beta=0$ ), salt rejection to unity for large  $a$
- (ii) For both ( $\beta=0$ ) and ( $\beta=1$ ), rejection at a given  $a$  is higher the lower the value of  $k$ .
- (iii) The rejection is higher the larger the value of  $a$ , the thicker the rejecting layer of the membrane, and the lower the diffusion coefficient of the salt in the membrane.

**Thermodynamic Theory of Membrane Potential :[31]**

The TMS theory of membrane potential depends on internal structure and properties of the membrane. The thermodynamic theories do not need this information. Staverman [32] derived the relation

$$-FdE = \sum t_i/z_i d\mu_i \tag{2.53}$$

using the principles of irreversible thermodynamics. In a similar way, scatchard [33] discarding considerations of membrane properties or structure, expressed membrane potential

$$E = - \frac{RT}{F} \sum_i^i \frac{t_i}{z_i} \ln a_i \tag{2.54}$$

The solutions of activity  $a_i^u$  and  $a_i^{uu}$  extend up to each interface. Equation(2.54) may be applied to all components moving across the membrane, those for a 1:1 electrolyte are counterion, coion, water and fixed charges of the membrane.

Regarding the polymer network to which the fixed charges are attached as the reference framework to which the movements of all other species are

referred, the summation in equation (2.54) refers only to three species, i.e., counter ion (+), coion (-), and water (w). Thus equation (2.54) becomes

$$E = -\frac{RT}{F} \sum_I t_{\pm} \ln a_{\pm} + t_w \ln a_w \quad (2.55)$$

If anion – reversible electrodes are used in the membrane cell to measure the cell emf, E, then the electrode potential  $E_{ref}$  between two such electrodes is given by equation.

$$E_{\pm} = E^{0\pm} + \frac{RT}{Z_{\pm}F} \ln a_{\pm}$$

i.e.,

$$E_{ref} = \frac{RT}{F} \cdot \ln \frac{a_{\pm}^I}{a_{\pm}^{II}} \quad (2.56)$$

substitution of equation (2.56) together with the use of relations ( $\bar{t}_+ + \bar{t}_- = 1$ ) and  $\ln a_w = -2 \times 10^{-3} m M_1 \ln a_{\pm}$  into (2.55) gives [34],

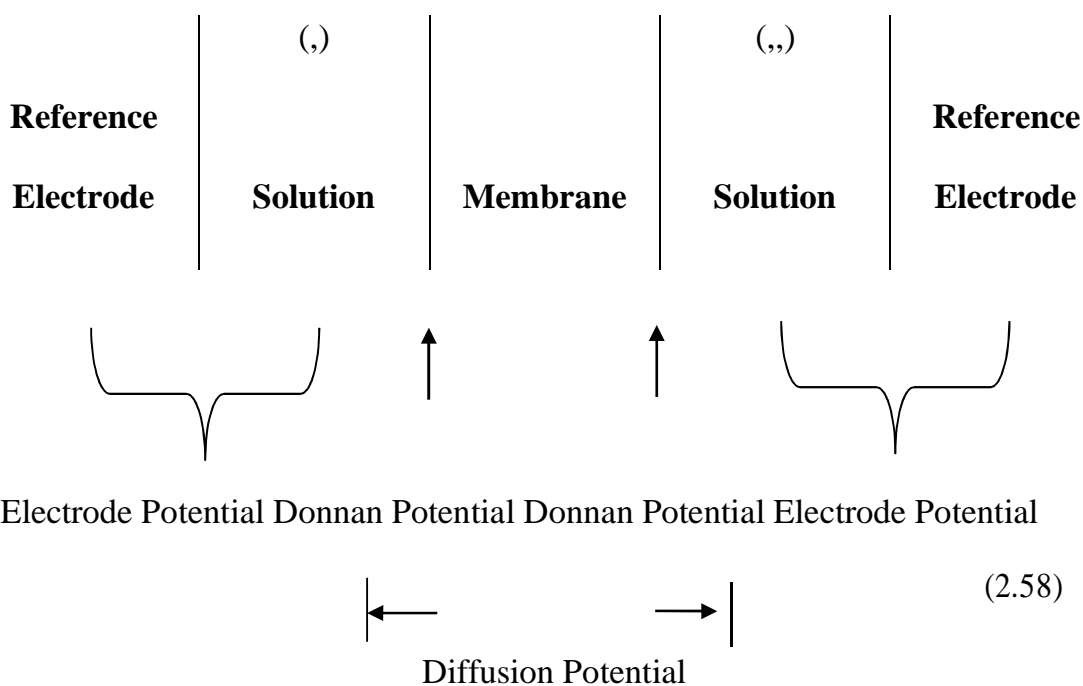
$$E = -\frac{2RT}{F} \sum_I t_{\pm} \ln a_{\pm} - 10^{-3} m M_1 \ln a_{\pm} \quad (2.57)$$

where,  $M_1$  is the molecular weight of the solvent and  $m$  is the molality of the solution. Equation (2.57) has been derived by Lorimer et al.[35] using the principles of irreversible thermodynamics. An experimental test of equation (2.57) carried out by Lakshminarayanaiah [30, 36, 37] has shown that it satisfactorily describes the electrical potentials arising across membranes when they separate solution of the same 1:1 electrolyte but of different concentration.

### **Modellistic Approach : T.M.S. Theory of Membrane Potentials :**

In general an electrical potential difference existing across a membrane separating two electrolyte solutions is called membrane potential. This

potential difference arises as a consequence of electroneutrality requirement. Initially an extremely small net charge transfer may occur, but this charge transfer results in an electric potential difference and enforces their compensation [38-40]. The permeability of ion species migrating across a membrane depends upon the properties of the ion and the membrane. If the membrane has no fixed charges, the membrane potential is equivalent to diffusion potential [41-42]. On the other hand if the membrane carries some fixed charges, donnan potential in addition to the diffusion potential may constitute the membrane potential [43-45] as shown.



The membrane potential of cell (2.58) is the algebraic sum of two Donnan potentials and a diffusion potential. The two membrane surfaces are assumed to be in a state of equilibrium. The condition for equilibrium between two phases such as the aqueous and the membrane phases is that the electrochemical

potentials of any mobile species  $i$  in the two phases are equal. Accordingly, for a univalent species  $i$ ,

$$\mu_1^0 + RT \ln a_i + PV_i + FE = \mu_1^0 + RT \ln \bar{a}_i + \bar{P}V_i + F\bar{E} \quad (2.59)$$

where the terms with over bars refers to the membrane phase. Thus when the membrane is in a 1 : 1 electrolyte solution of activity  $a_{\pm}$ , equation (2.59) can be written as

$$F(E - \bar{E}) = RT \ln \frac{\bar{a}_+}{a_+} + V_+(\bar{P} - P) \quad (2.60)$$

$$-F(\bar{E} - E) = RT \ln \frac{\bar{a}_-}{a_-} + V_-(\bar{P} - P) \quad (2.61)$$

Addition of equations (2.60) and (2.61) gives the relation

$$\frac{\bar{a}_+\bar{a}_-}{a_+a_-} = \exp \frac{\pi V}{RT} \quad (2.62)$$

Where  $\pi = P - \bar{P}$ , the difference between the hydrostatic pressure in the outside solution and the swelling pressure in the membrane and  $V = V_+ + V_-$ , the molal volume of the electrolyte. It has been shown that the term  $\exp \left( \frac{\pi V}{RT} \right)$  is approximately unity [46, 47] and so equation (2.62) becomes

$$\bar{m}_+\bar{\gamma}_+\bar{m}_-\bar{\gamma}_- = a_{\pm}^2 \quad (2.63)$$

If the concentration of ionogenic groups in the membrane is  $\bar{X}$ , then for a negatively charged membrane, the electroneutrality condition gives

$$\bar{m}_+ = \bar{m}_- + \bar{X} \quad (2.64)$$

Substituting equations (2.64) into equation (2.63) and solving the quadratic gives

$$\bar{m}_+ = \frac{\bar{x}}{2} + \mathbf{J} \frac{\sqrt{\bar{x}^2 - a^2}}{4 \bar{y}^2} \quad (2.65)$$

$$\bar{m}_- = \frac{\bar{x}}{2} - \mathbf{J} \frac{\sqrt{\bar{x}^2 - a^2}}{4 \bar{y}^2} \quad (2.66)$$

Teorell [41,48] and Meyer and Sievers [42] assumed  $\bar{\gamma}_+$  and  $\bar{\gamma}_-$  to be unity and so equation (2.65) and (2.66) becomes

$$\bar{m}_+ = \frac{\bar{x}}{2} + \frac{\sqrt{\bar{x}^2 - a^2}}{4} \quad (2.67)$$

$$\bar{m}_- = \frac{\bar{x}}{2} - \frac{\sqrt{\bar{x}^2 - a^2}}{4} \quad (2.68)$$

The Donnan ratio  $r$  given by equation (2.63) becomes

$$r = \frac{\bar{m}_+}{a_+} = \frac{a_-}{\bar{m}_-} = \dots = \frac{\bar{m}_+}{a} = \frac{a}{\bar{m}_-} \quad (2.69)$$

when the ionic membrane is bounded by a 1 : 1 electrolyte of activities  $a'$  and  $a''$ , the two Donnan potential,  $E'_{\text{Don}}$  and  $E''_{\text{Don}}$  at the two interfaces (') and (") are given according to equations (2.59) and (2.60) by (the PV terms are ignored)

$$E'_{\text{Don}} = E^{\text{I}} - \bar{E}^{\text{I}} = \frac{RT}{F} \ln \frac{\bar{a}'_+}{a'_+} = \frac{RT}{F} \ln \frac{a'_-}{a'_+} \quad (2.70)$$

$$E''_{\text{Don}} = E^{\text{II}} - \bar{E}^{\text{II}} = \frac{RT}{F} \ln \frac{\bar{a}''_+}{a''_+} = \frac{RT}{F} \ln \frac{a''_-}{a''_+} \quad (2.71)$$

The net Donnan potential therefore is given by

$$E'_{\text{Don}} - E''_{\text{Don}} = \frac{RT}{F} \ln \frac{\bar{a}_{\text{a}^+}}{\bar{a}'_{\text{a}^+}} - \frac{RT}{F} \ln \frac{\bar{a}_{\text{a}^+}}{\bar{a}''_{\text{a}^+}} \quad (2.72)$$

$$= \frac{RT}{F} \ln \frac{a'_+}{a'_-} - \frac{RT}{F} \ln \frac{a''_+}{a''_-} \quad (2.73)$$

The diffusion potential  $\psi = \bar{E}'' - \bar{E}'$  with in the membrane is assumed to be that existing in a constrained liquid junction. Teorell [41,47] used the expression

$$\psi = \frac{\bar{u}_+ - \bar{u}_-}{F} \ln \frac{\bar{u}_+ \bar{m}'_+ + \bar{u}_- \bar{m}'_-}{\bar{u}_+ \bar{m}''_+ + \bar{u}_- \bar{m}''_-} \quad (2.74)$$

Substituting for  $\bar{m}_+$  and  $\bar{m}_-$  from equations (2.67) and (2.68). Equation (2.74) becomes on rearrangement

$$\psi = \bar{U} \frac{RT}{F} \ln \frac{\bar{U} \bar{X}_+ + \sqrt{J \bar{X}^2 + 4a'^2}}{\bar{U} \bar{X}_- + \sqrt{J \bar{X}^2 + 4a''^2}} \quad (2.75)$$

where  $U = (\bar{u}_+ - \bar{u}_-)/(\bar{u}_+ + \bar{u}_-)$ . Assuming that  $\bar{X}$  is independent of the external electrolyte solution, the total membrane potential is given by the sum of equation (2.72) or (2.73) and equation (2.75). Thus for a highly idealized membrane system  $\bar{\gamma}_+ = \bar{\gamma}_- = 1$  the total membrane potential when agar KCl salt bridges are used in the measurement is given by

$$E = E'_{\text{Don}} - E''_{\text{Don}} + \psi$$

so

$$E = \frac{RT}{F} \left[ \ln \frac{a'' (4a'^2 + \bar{X}^2)^{1/2} + \bar{X}}{a' (4a''^2 + \bar{X}^2)^{1/2} + \bar{X}} + \bar{U} \ln \frac{(4a'^2 + \bar{X}^2)^{1/2} + \bar{U} \bar{X}}{(4a''^2 + \bar{X}^2)^{1/2} + \bar{U} \bar{X}} \right] \quad (2.76)$$

An equation exactly similar to equation (2.76) has been derived by Kobatake and coworkers [38]. However, their equation has a parameter  $\phi \bar{X}$  ( $0 < \phi < 1$ ,



the thermodynamically effective charge density) in place of  $\bar{x}$  and mobility values corresponding to the bulk aqueous phase in place of  $\bar{U}$ , i.e,

$$\bar{U} = (\bar{u}_+ - \bar{u}_-) / (\bar{u}_+ + \bar{u}_-)$$

Three special cases of equation (2.76) are of interest.

(i) when  $a \ll \bar{X}/2$ , equation (2.76) reduces to the Nernst equation

$$E = \frac{RT}{F} \ln \frac{a'}{a''} \quad (2.77)$$

(ii) when  $a \gg \bar{X}/2$ , equation (2.76) reduces to

$$E_L = (1 - 2t_+) \frac{RT}{F} \ln \frac{a'}{a''} \quad (2.78)$$

which gives the value for a diffusion potential between two solutions of activities  $a'$  and  $a''$ . The mobility values would correspond to those prevailing in the aqueous solution although diffusion would be occurring across the

membrane. When  $a \gg \frac{\bar{X}}{2}$ , the sorption of the electrolyte by the membrane is so

high that the ionogenic group (i.e.,  $\bar{X}$ ) in the membrane are unable to distinguish between counter ions and coions.

(ii) when  $a = \frac{\bar{X}}{2}$ , the ionogenic groups are able to distinguish between counter

ions and coions to some extent so that the mobility values correspond to the membrane phase. Thus equation (2.76) reduces to

$$E = \frac{RT}{F} \frac{\bar{u}_+ - \bar{u}_-}{\bar{u}_+ + \bar{u}_-} \ln \frac{a'}{a''}$$

or

$$E = \frac{RT}{F} (\bar{t}_+ - \bar{t}_-) \ln \frac{a'}{a''} \quad (2.79)$$

where  $\bar{t}_+$  and  $\bar{t}_-$  are the transport numbers of counterion and coion for a negatively charged membrane in the membrane phase equation (2.79) may be rearranged to give

$$\frac{E}{E_{\max}} = 2\bar{t}_+ - 1 \text{ or } \bar{t}_+ = \left[ \frac{E}{2E_{\max}} + 0.5 \right] \quad (2.80)$$

where  $E_{\max} = \frac{RT}{F} \ln \frac{a_+}{a_-}$ . Equation (2.80) has often been used to calculate the transport numbers in the membrane phase from measurements of membrane potential [49-51].

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