CHEMICAL REVIEWS

VOLUME 65, NUMBER 5   SEPTEMBER 27, 1965

TRANSPORT PHENOMENA IN ARTIFICIAL MEMBRANES

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Received January 4, 1965

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PART A

I. INTRODUCTION

Transport processes occurring across artificial membranes separating different salt solutions are of great interest to chemists, chemical engineers, and biologists. Chemists and chemical engineers would like to understand the mechanism of transport so that with the knowledge so gained they would be able to fabricate membranes of any desired property or properties. Biologists, however, would like to use them as simple models for the physiological membranes in order to understand, in terms of established physical chemical principles, the behavior of complex cell membranes.

A precise and complete definition of the word "membrane" is, at present, difficult to make (490); any complete definition given to cover all the facets of membrane behavior will be inexact and any precise statement will be incomplete. So it is described in simple terms as a phase, usually heterogeneous, acting as a barrier to the flow of molecular and ionic species present in the liquids and/or vapors contacting the two surfaces. The term heterogeneous has been used to indicate the internal physical structure and external physico-chemical performance (81, 228, 272, 487, 493, 494, 519).

From this standpoint, most membranes in general, except the obvious ones as for example oil membranes, are to be considered heterogeneous, despite the fact that conventionally membranes prepared from coherent gels have been called homogeneous (155).

Functionally, no membrane exists which is completely inactive when used as a barrier to separate two solutions or phases, unless it is too porous or too fragile. It is difficult to find a membrane, artificial or natural, that would be free from carrying ionogenic groups either fixed to the membrane matrix, as seen in well-characterized ion-exchange membranes, or adsorbed, as found in some colloidal systems (234).

The presence of ionogenic groups and pores in the membrane confers certain functionality to the membrane which is described in the literature by the words permselectivity (160) and/or semipermeability. The phenomenological transport property which controls the former is the transport number $\bar{t}_i$, whereas the latter is determined by the reflection coefficient σ (ratio of the actual hydrostatic pressure required to give zero net volume flow to that which is required if the membrane were truly semipermeable) introduced by Staverman (32, 61, 84, 218, 220, 511, 512).

Grossly porous membranes (wide pores) are neither permselective nor semipermeable; whereas "ion sieve" membranes with narrow pores are semipermeable but may not be permselective if the number of fixed ionogenic groups are too few in number. As the presence of narrow pores and high fixed charge density of ionogenic groups gives high values for $\bar{t}_i$ and σ, membranes characterized by these values, *i.e.*, ion-exchange membranes, prove useful and industrially important. As a result, the bulk of the membrane literature abounds in papers describing the work on ion-exchange membranes.

Ion-exchange membranes in contact with external electrolyte solutions take up electrolytes in a way different from nonion-exchange membranes. Because of the presence of ionogenic groups fixed to the resin matrix—negative groups like $-SO_3^-$, $-COO^-$, *et seq.*, in case of cation exchangers, and positive groups like $-NH_3^+$, $>NH_2^+$, $\geqslant N^+-$, *et seq.*, in case of anion exchangers—the membrane excludes the co-ions (ions of same sign $-$ or $+$ charge as the fixed groups) by electrostatic repulsion. The amount of exclusion is governed by the concentration of the external electrolyte. At very low concentration, the amount of co-ion in the membrane is almost zero, but as the external concentration is increased, the co-ion content of the membrane phase increases. There will be less number of co-ions than counterions (ions of opposite charge to fixed groups) by an amount equal to the number of fixed groups; whereas in the nonion-exchange membrane, the distinction between co-ion and counterion being nonexistent because of the absence of fixed groups, there will be equal numbers of positive and negative ions. In the case of nonelectrolytes, both types of membranes will behave alike. The factors governing sorption of nonelectrolytes will be the relative sizes of the permeating species and the membrane pores. The ability of the ion-exchange membranes to exclude co-ions makes them permselective.

When a membrane separates two solutions, the number of forces that may normally operate to cause a flow or flux of molecular or ionic species through it are: (a) difference of chemical potential $\Delta\mu$, (b) difference of electric potential $\Delta\psi$, (c) difference of pressure ΔP, and (d) difference of temperature ΔT.

These forces when they operate severally or in combination may generate a number of phenomena, and these are indicated in Figure 1 (179, 234).

It is the purpose of this article to bring under one cover all the important literature pertaining to transport phenomena mentioned in Figure 1 and published within the last ten years. All this material is included in part A. Work connected with artificial membranes separating aqueous solutions will be discussed. Ceramic, glass, metal, and oil membranes and membrane systems involving gases (or vapors) and nonaqueous liquids will be excluded.

A prerequisite for the success of many operations indicated in Figure 1 is the availability of suitable membranes. Considerable attention therefore has been paid in recent years to the development of membranes with particular and predetermined specific properties. An account of the variety of compounds and processes that have been employed to prepare them is presented in part B.

Even though no book devoted exclusively to membranes exists, the following books contain chapters relevent to the material of this article: (a) "Diffusion and Membrane Technology" by Tuwiner (556), (b) "Demineralization by Electrodialysis," edited by Wilson (586), and (c) "Ion Exchange" by Helfferich (154). Papers of considerable interest pertaining to both artificial and natural membranes by leaders in the membrane field exist in "Electrochemistry in Biology and Medicine," edited by Shedlovsky (482), and in "Ion Transport across Membranes," edited by Clarke (48). The monograph, "Stofftransport durch Membranen" by Schlögl (455), contains a neat theoretical discussion of many of the transport phenomena indicated in Figure 1.

A symposium on membrane phenomena was held at Nottingham, England, in April 1956, and all the papers that were presented and discussed at that meeting appear in *Discussions of the Faraday Society* (71a). Papers describing the various aspects of membranes—their preparation and transport processes arising across them—are given in *Dechema Monographien* (65a).

Some brief reviews in journals, summaries as chapters of books, and small booklets or pamphlets have appeared. The reviews vary in length and importance. Some of them summarize the work of one researcher while others deal with one or two aspects of the field. In this comprehensive review, a number of articles not covered in the previous reviews and books are included. Those aspects of the subject which have already been reviewed are briefly summarized and the more recent literature is brought up to date. Papers where experiments are described just to characterize a membrane are omitted. The literature covered extends through to September 1964, with some additional references of later date.

II. BASIC CONCEPTS

The current membrane theories may be divided roughly into three groups based on the nature of the flux equation used in the treatment (*cf.* Schlögl (454)). In the first group fall many of the theories based on the Nernst–Planck flux equations or their refinements. In the second group are included all the theories using the principles of irreversible thermodynamics. In the third group is included the theory which utilizes the concepts of the theory of rate processes. In general, the theories of group one are based on the ideas of classical thermodynamics or quasi-thermodynamics which is restricted to isothermal systems. The theories of group two, apart from being more rigorous and realistic, allow a better understanding of transport phenomena in membranes and is useful in dealing with nonisothermal systems. The theories of group three contain parameters which are still unknown for the membrane and hence have restricted applicability.

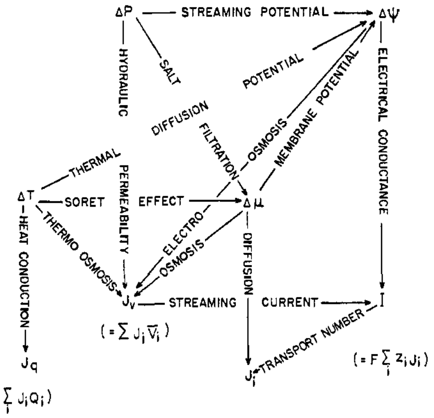


Figure 1.—Scheme of different transport phenomena across membranes.

A. NERNST–PLANCK FLUX EQUATIONS

The flux (mole cm.$^{-2}$ sec.$^{-1}$) of molecular or ionic species J_i, through a membrane is given by the product of three terms, namely concentration C_i, force, and a proportionality constant (507, 536, 538, 539).

The diffusional flux $J_{i(d)}$, caused by the force represented by the gradient of chemical potential $(-d\mu_i/dx)$, is given by

$$\begin{aligned} J_{i(d)} &= \frac{D_i}{RT} C_i\left(-\frac{d\mu_i}{dx}\right) \\ &= -D_i C_i\left(\frac{d \ln a_i}{dx}\right) \end{aligned} \qquad \text{(Eq. 1)}$$

where D_i is the diffusion coefficient, R is the gas constant, and T is the absolute temperature.

Substituting for a_i ($a_i = C_i\gamma_i$; γ_i is the activity coefficient)

$$\begin{aligned} J_{i(d)} &= -D_i C_i\left[\frac{d \ln C_i}{dx} + \frac{d \ln \gamma_i}{dx}\right] \\ J_{i(d)} &= -D_i\left[\frac{dC_i}{dx} + C_i \frac{d \ln \gamma_i}{dx}\right] \end{aligned} \qquad \text{(Eq. 2)}$$

when γ_i is constant (ideal case), the flux equation reduces to the Fick's first law

$$J_{i(d)} = -D_i \frac{dC_i}{dx} \qquad \text{(Eq. 3)}$$

The diffusion generates an electric field (diffusion potential) which acts as another driving force. Thus the flux due to an electric field $(-d\psi/dx)$ is given by

$$J_{i(e)} = -u_i z_i C_i \frac{d\psi}{dx} \qquad \text{(Eq. 4)}$$

where u_i is the electrochemical mobility and z_i is the valence. Assuming that the Nernst–Einstein equation relating mobility to diffusion coefficient (ideal solution), *viz.*

$$u_i = D_i \frac{F}{RT} \qquad \text{(Eq. 5)}$$

is applicable to membrane systems, then

$$J_{i(e)} = -D_i \frac{F}{RT} z_i C_i \frac{d\psi}{dx}$$

Therefore the total flux in an ideal system is given by

$$J_i = J_{i(d)} + J_{i(e)} = -D_i \left[\frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\psi}{dx} \right] \qquad \text{(Eq. 6)}$$

This equation may be refined by introducing the activity coefficient term (157); thus

$$J_i = -D_i \left[\frac{dC_i}{dx} + z_i C_i \frac{F}{RT} \frac{d\psi}{dx} + C_i \frac{d \ln \gamma_i}{dx} \right] \qquad \text{(Eq. 7)}$$

When a constant electric field acts on an electrolyte solution, cations move to the cathode and anions move to the anode. Transfer of momentum between the moving ions and the surrounding solvent molecules takes place. Except for the difference in the solvation shells of cations and anions, there will be no net transfer of solvent. When a membrane is interposed, the situation is altered. This alteration is governed by the nature of the membrane. If the membrane is grossly porous, there may not be any change different from the ordinary aqueous solution as far as the movement of the solvent is concerned. But if the membrane is a cross-linked polyelectrolyte gel acting selectively to certain ions, the counterions are in large numbers in the membrane phase. So, counterions impart more momentum to solvent than do co-ions and as a result solvent transfer takes place to the respective electrode chamber (cathode in case of a negatively charged membrane). The velocity of this solvent transfer will be proportional to the strength of the electric field and the resistance to flow of the membrane material. The counterions in their movement experience less resistance than do co-ions. In relation to membrane matrix, the counterions move faster than they would if the liquid were standing still. Consequently, the convection of pore liquid brings about increased flux of the counterions which may be written as (454)

$$J_{i(c)} = \bar{C}_i V^* \qquad \text{(Eq. 8)}$$

where $\bar{C}_i$ is the concentration of counterions in the membrane phase (barred terms refer always to membrane phase) and V^* is the velocity of movement of the center of gravity of the pore liquid. V^* is determined by the electric field acting on the pore liquid. If ρ_0 is the specific flow resistance of the membrane and v_0 is the fractional pore volume, the electric charge associated with unit volume of the pore liquid is given by $-\omega \cdot XF/v_0$ where X is the concentration of fixed charge and ω is the sign of the fixed charge ($-$ for negatively charged membranes and $+$ for positively charged membranes).

The convection velocity is given by (453, 458)

$$V^* = \frac{\omega XF}{\rho_0 v_0} \frac{d\psi}{dx} = \omega \bar{u}_0 \frac{d\psi}{dx} \qquad \text{(Eq. 9)}$$

where $\bar{u}_0 = XF/\rho_0 v_0$ is the "mobility" of pore liquid.

Equation 8 must be added to Eq. 7 to give the total flux J_i. These equations are applicable to ideal cases where there are no complicating factors arising from molecular or ionic interactions. They apply to all mobile species and are governed by the condition of electroneutrality

$$\sum_i z_i \bar{C}_i + \omega X = 0 \qquad \text{(Eq. 10)}$$

Further in the steady state, the concentrations are independent of time, and therefore

$$\frac{dJ_i}{dx} = 0 \qquad \text{(Eq. 11)}$$

The species present in the system invariably carry electric charges and as they move under an electric field give electric current I, which is represented by

$$I = F \sum_i z_i J_i \qquad \text{(Eq. 12)}$$

The observable parameters like specific conductivity $\bar{\kappa}$ and transport number $\bar{t}_i$ may be written as

$$\bar{\kappa} = -\left(\frac{I}{d\psi} \right) \qquad \text{(Eq. 13)}$$

$$\bar{t}_i = FJ_i/I \qquad \text{(Eq. 14)}$$

B. THERMODYNAMICS OF IRREVERSIBLE PROCESSES

A membrane acting as a restrictive barrier to the flow of various chemical species between two subsystems (′) and (″) contacting the two membrane faces is considered to maintain differences in concentration, temperature, pressure, and electric potential across it. The two subsystems are kept so well stirred as to obtain uniform values of these variables throughout each subsystem and to have the whole difference occurring only across the membrane. These quantities $\Delta\mu$, ΔT, ΔP, and $\Delta\psi$ are the forces denoted by X_i ($i = 1, 2, \ldots, n$) causing the flows or fluxes J_i ($i = 1, 2, \ldots, n$).

The fundamental theorem of the thermodynamics of irreversible process is (66, 123) that the forces and the fluxes are so chosen as to conform to the equation

$$T\Theta = \sum_i J_i X_i \qquad \text{(Eq. 15)}$$

and the phenomenological coefficients L_{ik} ($i, k = 1, 2, \ldots, n$) in the equations

$$J_i = \sum_{k=1}^{n} L_{ik} X_k \qquad \text{(Eq. 16)}$$

satisfy the Onsagar reciprocal relations

$$L_{\mathrm{ik}} = L_{\mathrm{ki}} \qquad \text{(Eq. 17)}$$

A recent review of the existing data by Miller (347) gives the experimental justification for regarding the Onsagar law as a law of nature (218). The description of transport processes in a system of n components therefore requires the measurement of only $n(n + 1)/2$ coefficients and not all n^2 coefficients.

$\Theta = \mathrm{d_i}S/\mathrm{d}t$ is the rate of entropy production due to irreversible processes within the system. The first task then is to evaluate Θ. This requires the use of the laws of conservation of mass and energy and the second law of thermodynamics (the Gibbs equation) (123).

Conservation of mass for the system, subsystem (′)/membrane/subsystem (″), is expressed by

$$\mathrm{d}n_{\mathrm{k}}' + \mathrm{d}n_{\mathrm{k}}'' = 0 \ (\mathrm{k} = 1, 2, \ldots, n) \qquad \text{(Eq. 18)}$$

where n_{k} is the number of moles of species k.

Conservation of energy is expressed by

$$\mathrm{d}U' = \mathrm{d_e}U' + \mathrm{d_i}U'; \ \mathrm{d}U'' = \mathrm{d_e}U'' + \mathrm{d_i}U''$$

and

$$\mathrm{d_i}U' + \mathrm{d_i}U'' = 0 \qquad \text{(Eq. 19)}$$

where $\mathrm{d_e}U'$ is the energy exchanged by (′) with surroundings and $\mathrm{d_i}U'$ the energy exchanged with (″). Thus

$$\mathrm{d}U = \mathrm{d_e}U' + \mathrm{d_e}U''$$

$$\mathrm{d}U = \mathrm{d_e}Q' + \mathrm{d_e}Q'' - P'\mathrm{d}V' - P''\mathrm{d}V'' \qquad \text{(Eq. 20)}$$

is the total energy received by the whole system. $\mathrm{d_e}Q$ is the heat absorbed from the surroundings, and P and V have their usual thermodynamic significance. $\mathrm{d_e}Q'$ and $\mathrm{d_e}Q''$ are independent and so are $\mathrm{d}V'$ and $\mathrm{d}V''$ and therefore

$$\mathrm{d_e}U' = \mathrm{d_e}Q' - P'\mathrm{d}V'$$

$$\mathrm{d_e}U'' = \mathrm{d_e}Q'' - P''\mathrm{d}V'' \qquad \text{(Eq. 21)}$$

Taking the Gibbs equation

$$T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V - \sum_{\mathrm{k}} \mu_{\mathrm{k}}\mathrm{d}n_{\mathrm{k}} \qquad \text{(Eq. 22)}$$

as being applicable to systems not in thermodynamic equilibrium, a fundamental tenet of the theory of thermodynamics of irreversible processes and applying it to the subsystems (′) and (″)

$$T'\mathrm{d}S' = \mathrm{d}U' + P'\mathrm{d}V' - \sum_{\mathrm{k}} \mu_{\mathrm{k}}'\mathrm{d}n_{\mathrm{k}}'$$

$$T''\mathrm{d}S'' = \mathrm{d}U'' + P''\mathrm{d}V'' - \sum_{\mathrm{k}} \mu_{\mathrm{k}}''\mathrm{d}n_{\mathrm{k}}'' \qquad \text{(Eq. 23)}$$

The change of entropy of the total system is given by

$$\mathrm{d}S = \mathrm{d}S' + \mathrm{d}S''$$

Substituting from Eq. 23

$$\mathrm{d}S = \frac{\mathrm{d_e}U' + P'\mathrm{d}V'}{T'} + \frac{\mathrm{d_e}U'' + P''\mathrm{d}V''}{T''} + \frac{\mathrm{d_i}U'}{T'} + \frac{\mathrm{d_i}U''}{T''} - \sum_{\mathrm{k}} \frac{\mu_{\mathrm{k}}'\mathrm{d}n_{\mathrm{k}}'}{T'} - \sum_{\mathrm{k}} \frac{\mu_{\mathrm{k}}''\mathrm{d}n_{\mathrm{k}}''}{T''} \qquad \text{(Eq. 24)}$$

This expression for the total change of entropy can be split into two parts; one giving the entropy received from the surroundings (first two terms), *i.e.*

$$\mathrm{d_e}S = \frac{\mathrm{d_e}Q'}{T'} + \frac{\mathrm{d_e}Q''}{T''}$$

and the other giving the interproduction of entropy resulting from the action of irreversible processes in the system (last four terms), *i.e.*

$$\mathrm{d_i}S = \frac{\mathrm{d_i}U'}{T'} + \frac{\mathrm{d_i}U''}{T''} - \sum_{\mathrm{k}} \frac{\mu_{\mathrm{k}}'\mathrm{d}n_{\mathrm{k}}'}{T'} - \sum_{\mathrm{k}} \frac{\mu_{\mathrm{k}}''\mathrm{d}n_{\mathrm{k}}''}{T''} \qquad \text{(Eq. 25)}$$

Substitution of Eq. 18 and 19 into Eq. 25 gives

$$\mathrm{d_i}S = -\mathrm{d_i}U'\Delta(1/T) + \sum_{\mathrm{k}=1}^{n} \mathrm{d}n_{\mathrm{k}}'\Delta(\mu_{\mathrm{k}}/T) \qquad \text{(Eq. 26)}$$

where symbol Δ indicates the difference of quantities in (″) and (′). But

$$T(\mathrm{d_i}S/\mathrm{d}t) = J_{\mathrm{u}}X_{\mathrm{u}} + \sum_{\mathrm{k}=1}^{n} J_{\mathrm{k}}X_{\mathrm{k}} \qquad \text{(Eq. 27)}$$

where J_{u} and J_{k} are energy flux and matter flux, respectively. These are given by

$$J_{\mathrm{u}} = -(\mathrm{d_i}U'/\mathrm{d}t) \text{ and } J_{\mathrm{k}} = -(\mathrm{d}n_{\mathrm{k}}'/\mathrm{d}t) \qquad \text{(Eq. 28)}$$

Substituting Eq. 28 into Eq. 27 and equating the resultant to Eq. 26, the forces are given by

$$X_{\mathrm{u}} = T\Delta(1/T) \text{ and } X_{\mathrm{k}} = -T\Delta(\mu_{\mathrm{k}}/T) \qquad \text{(Eq. 29)}$$

The phenomenological law being linear relations bearing between fluxes and forces

$$\begin{aligned} J_{\mathrm{i}} &= \sum_{\mathrm{k}=1}^{n} L_{\mathrm{ik}}X_{\mathrm{k}} + L_{\mathrm{iu}}X_{\mathrm{u}} \\ J_{\mathrm{u}} &= \sum_{\mathrm{k}=1}^{n} L_{\mathrm{uk}}X_{\mathrm{k}} + L_{\mathrm{uu}}X_{\mathrm{u}} \end{aligned} \qquad \text{(Eq. 30)}$$

the Onsagar relations

$$L_{\mathrm{ik}} = L_{\mathrm{ki}} \text{ and } L_{\mathrm{ku}} = L_{\mathrm{uk}} \qquad \text{(Eq. 31)}$$

are valid between the phenomenological coefficients.

The coefficient L_{iu} from Eq. 30 may be eliminated by defining the energy of transfer U_{k}^* (energy carried by unit flow of k at uniform temperature T, $X_{\mathrm{u}} = 0$, and $J_{\mathrm{k}} = 1$) by

$$L_{\mathrm{iu}} = \sum_{\mathrm{k}=1}^{n} L_{\mathrm{ik}}U_{\mathrm{k}}^* \quad \mathrm{i} = 1, 2, \ldots, n \qquad \text{(Eq. 32)}$$

J_i is therefore given by

$$J_i = \sum_{k=1}^{n} L_{ik}(X_k + U_k^* X_u) \qquad \text{(Eq. 33)}$$

Substitution of Eq. 29 in Eq. 33 gives

$$J_i = \sum_{k=1}^{n} L_{ik}[\{-T\Delta(\mu_k/T)\} + \{U_k^* T\Delta(1/T)\}] \qquad \text{(Eq. 34)}$$

i.e., $J_i = \sum_{k=1}^{n} L_{ik}\bar{X}_k$, thus defining $\bar{X}_k$. For infinitesimal forces

$$\begin{aligned}\bar{X}_k &= -T\mathrm{d}(\mu_k/T) + U_k^* T\mathrm{d}(1/T)\\ &= -\mathrm{d}\mu_k - (\mathrm{d}T/T)(U_k^* - \mu_k) \qquad \text{(Eq. 35)}\end{aligned}$$

but

$$\mathrm{d}\mu_k = -\bar{S}_k\mathrm{d}T + \bar{V}_k\mathrm{d}P + RT\mathrm{d}\ln a_k + z_kF\mathrm{d}\psi \ (456) \qquad \text{(Eq. 36)}$$

where z_k is valence including sign of species k. Therefore

$$\bar{X}_k = -\bar{V}_k\mathrm{d}P - RT\mathrm{d}\ln a_k - z_kF d\psi - (\mathrm{d}T/T)(U_k^* - H_k^*) \qquad \text{(Eq. 37)}$$

where $H_k^* = \mu_k + T\bar{S}_k$. The difference between U_k^* and H_k^* is called heat of transport Q_k^*. Q_k^* may be positive, negative, or zero. If it is zero, thermoosmosis will not occur.

The final general expression for the material fluxes is given by

$$J_i = \sum_k L_{ik}\left(-\bar{V}_k\mathrm{d}P - RT\mathrm{d}\ln a_k - z_kF\mathrm{d}\psi - Q_k^*\frac{\mathrm{d}T}{T}\right) \qquad \text{(Eq. 38)}$$

The observable electrical parameters may be written in terms of the phenomenological coefficients (73, 180, 290, 513). (1) Current density $I = F\sum_i z_iJ_i$ and substituting for J_i from Eq. 38

$$I = \sum_i\sum_k z_iFL_{ik}(-\bar{V}_k\mathrm{d}P - RT\mathrm{d}\ln a_k - Q_k^*\mathrm{d}\ln T) - \sum_i\sum_k z_iz_kL_{ik}F^2\mathrm{d}\psi \qquad \text{(Eq. 39)}$$

(2) Electrical conductance $\bar{\kappa} = -(I/\mathrm{d}\psi)(\mathrm{d}P = 0, \mathrm{d}T = 0, \mathrm{d}\ln a_k = 0)$

$$\bar{\kappa} = \sum_i\sum_k z_iz_kF^2L_{ik} \qquad \text{(Eq. 40)}$$

(3) Transport number $\bar{t}_k = (Fz_kJ_k/I)(\mathrm{d}P = 0, \mathrm{d}T = 0, \mathrm{d}\ln a_k = 0)$

$$\bar{t}_k = \frac{F\sum_i z_iz_kFL_{ik}\mathrm{d}\psi}{\sum_i\sum_k z_iz_kL_{ik}F^2\mathrm{d}\psi} = \frac{F^2\sum_i z_kz_iL_{ik}}{\bar{\kappa}} \qquad \text{(Eq. 41)}$$

Staverman (513) has defined a useful quantity, the reduced electrical transport number $\bar{t}_k^r$ which has also been called mass transport number (290). Thus

$$\bar{t}_k^r = (\bar{t}_k/z_k) = F^2\sum_i z_iL_{ik}/\bar{\kappa} \qquad \text{(Eq. 42)}$$

The flow of uncharged molecules, *e.g.*, water, may be expressed in terms of their reduced transport numbers where $\sum_k z_k\bar{t}_k^r = 1$.

Rearranging Eq. 39 for dψ and substituting from Eq. 40 and 42, the potential gradient at any point in the membrane may be obtained. Thus

$$\mathrm{d}\psi = -(I/\bar{\kappa}) - (1/F)\sum_k \bar{t}_k^r(\bar{V}_k\mathrm{d}P + RT\mathrm{d}\ln a_k + Q_k^*\mathrm{d}\ln T_k) \qquad \text{(Eq. 43)}$$

The first term is given by the purely electrical part and the second term is due to the chemical part.

Various special cases follow directly from Eq. 43. (a) Isothermal diffusion potential is obtained at uniform temperature and pressure

$$\mathrm{d}\psi = -\frac{RT}{F}\sum_k \bar{t}_k^r\mathrm{d}\ln a_k \qquad \text{(Eq. 44)}$$

This has been derived many years ago by Nernst using Thomson's method and more recently by Staverman (513) and Kirkwood (225). (b) Streaming potential is obtained at uniform temperature and chemical potential

$$\mathrm{d}\psi = -\frac{1}{F}\sum_k \bar{t}_k^r\bar{V}_k\mathrm{d}P \qquad \text{(Eq. 45)}$$

(c) Thermal diffusion potential is obtained at uniform pressure and activity

$$\mathrm{d}\psi = -\frac{1}{F}\sum_k \bar{t}_k^rQ_k^*\mathrm{d}\ln T \qquad \text{(Eq. 46)}$$

In the considerations given above, nothing has been said explicitly about the reference framework to which the fluxes are referred. It is implied that the reference frame was the membrane (449). Some choices about the frame of reference are possible. For example the solvent in the membrane phase may be considered stationary and therefore taken as one of the frames of reference. Hills, Jacobs, and Lakshminarayanaiah (180) have given a treatment choosing for reference framework, the plane normal to the direction of fluxes and passing through the center of mass of the system. The values of the phenomenological coefficients in this type of treatment which is rigorous, depend on the reference framework chosen. This being very unsatisfactory, attempts have been made to translate these coefficients into parameters (frictional coefficients) which are independent of the motion of the reference frame and thus give a clearer physical picture of the membrane processes. The classical work of Lord Raleigh (421) and the investigations of Klemm (229) and Laity (269) have laid the foundations for the successful applications of these principles to membrane processes (61, 194, 335), pioneered by Spiegler (507) and illustrated by Spiegler (507) and Meares (298, 335) and expounded by Kedem and Katchalsky (217, 218, 220–224) taking different membrane systems into consideration.

The translation of the L coefficients (Eq. 16) into frictional coefficients, f, is performed by balancing the thermodynamic forces X_i by the algebraic sum of the frictional forces F_{ik}. Taking the illustration of Kedem and Katchalsky (221), the thermodynamic force X_i acting on the solute (X_s) existing with water in the membrane is counterbalanced by the sum of the frictional forces between solute and water and between solute and membrane, *i.e.*

$$X_s = -F_{sw} - F_{sm}$$

Similarly

$$X_w = -F_{ws} - F_{wm} \qquad \text{(Eq. 47)}$$

where subscripts w and m indicate water and membrane, respectively.

The frictional forces F_{ik}'s are proportional to the relative velocity of i with respect to k, *i.e.*

$$F_{ik} = -f_{ik}(u_i - u_k) \qquad \text{(Eq. 48)}$$

The values of the proportionality constant f_{ik}, being determined by the difference in the values if 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 defined and will also be concentration independent and bring out the specific interaction of i with k.

The frictional coefficients may be related easily to either the L coefficients (conductance formulation) if the linear rate law is expressed as (see Spiegler (507))

$$J_i = \sum_{k=1}^{n} L_{ik}X_k \qquad \text{(Eq. 16)}$$

or to R coefficients if the resistance formulation is employed (see Kedem and Katchalsky (221)), *i.e.*

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

The Onsagar relation holds for either formulation: $L_{ik} = L_{ki}$; $R_{ik} = R_{ki}$.

C. THEORY OF ABSOLUTE REACTION RATES

A membrane is considered as a series of potential energy barriers existing one behind the other, across which material must pass to cross the membrane (62, 89, 213, 609). To do so, the permeating species must have a certain minimum energy. A typical potential energy diagram is shown in Figure 2 (89), where λ indicates the mean jump distance. If C_1 is the initial concentration of the substance (molecules per cc.), the velocity of forward diffusion is

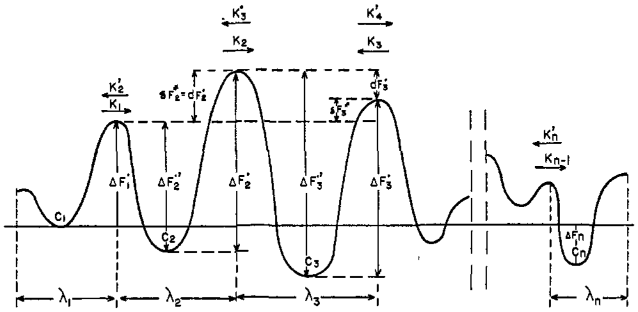


Figure 2.—Potential energy diagram representing permeation in a membrane.

$$q_f = k_1C_1\lambda_1 \quad (\text{molecules/cm.}^2) \qquad \text{(Eq. 49)}$$

where k_1 is the specific velocity for crossing the barrier 1, and

$$k_1 = \dot{k}\,\frac{kT}{h}\,e^{-\Delta F_1^{\ddagger}/RT} \qquad \text{(Eq. 50)}$$

where $\dot{k}$ is the transmission coefficient for which a value of unity is assumed. k is the Boltzmann constant, h is the Planck constant, and $\Delta F_1^{\ddagger}$ is the free energy of activation necessary for crossing the barrier 1.

Similarly, the velocity of the backward diffusion over the barrier 1 is

$$q_b = k_2'C_2\lambda_2 \qquad \text{(Eq. 51)}$$

The net rate of diffusion or flux is

$$J = k_1C_1\lambda_1 - k_2'C_2\lambda_2 \qquad \text{(Eq. 52)}$$

In the steady state (Eq. 11), the diffusional flux is the same over every barrier

$J = k_2C_2\lambda_2 - k_3'C_3\lambda_3$ for second barrier
$J = k_3C_3\lambda_3 - k_4'C_4\lambda_4$ for third barrier
$J = k_{n-1}C_{n-1}\lambda_{n-1} - k_n'C_n\lambda_n$ for $(n - 1)$ barrier

Consecutive substitutions using $(n - 1)$ equations give upon rearrangement

$$J = \frac{k_1C_1\lambda_1 - \dfrac{k_2'\cdot k_3'\cdots k_{n-1}'}{k_2\cdot k_3\cdots k_{n-1}}\,k_n'C_n\lambda_n}{1 + \dfrac{k_2'}{k_2} + \dfrac{k_2'\cdot k_3'}{k_2\cdot k_3} + \cdots + \dfrac{k_2'\cdots k_{n-1}'}{k_2\cdots k_{n-1}}} \qquad \text{(Eq. 53)}$$

But according to Eq. 50

$$\frac{k_2'}{k_2} = e^{(\Delta F_2^{\ddagger} - \Delta F_2^{\ddagger\prime})/RT} = e^{\delta F_2^*/RT} \qquad \text{(Eq. 54)}$$

where δF_2^* is the difference in energy of barriers 1 and 2.

$$\frac{k_2'\cdot k_3'}{k_2\cdot k_3} = e^{(\Delta F_2^{\ddagger} - \Delta F_2^{\ddagger\prime}) + (\Delta F_3^{\ddagger} - \Delta F_3^{\ddagger\prime})/RT}$$
$$= e^{\delta F_3^*/RT} \qquad \text{(Eq. 55)}$$

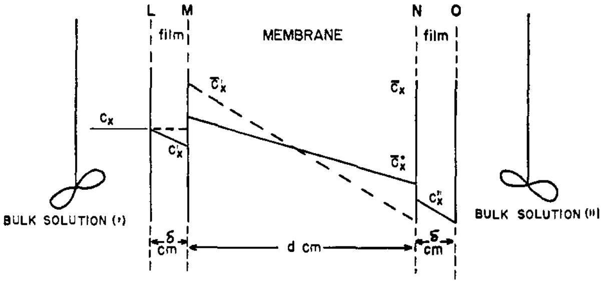


Figure 3.—Isotopic diffusion across a membrane: broken line, ideal membrane diffusion; solid line, partial film diffusion. L, M, N, and O demarcate the respective regions, bulk solution–film ('), film–membrane interface ('), membrane–film interface (''), and film–bulk solution (''). C_x is the concentration of the tracer on side (').

where δF_3^* is the algebraic sum of $dF_2^{\cdot}$ and $dF_3^{\cdot}$ and is the difference in height of barriers 1 and 3. Similarly

$$\frac{k_2'k_3'\cdots k_{n-1}'}{k_2k_3\cdots k_{n-1}} = e^{\delta F_{n-1}^*/RT} \qquad \text{(Eq. 56)}$$

and

$$\frac{k_2'k_3'\cdots k_{n-1}'k_n'}{k_1k_2k_3\cdots k_{n-1}} = e^{(\Delta F\text{i} + \delta F_{n-1}^* - \Delta F_n^{\cdot\prime})/RT} \qquad \text{(Eq. 57)}$$

But $\Delta F_i + \delta F_{n-1}^* - \Delta F_n^{\cdot\prime} = \Delta F_n$, the difference in free energy between position 1 and n.

Substituting Eq. 54–57 into Eq. 53

$$J = \frac{\lambda_1 k_1\left(C_1 - \frac{\lambda_n}{\lambda_1} e^{\Delta F_n/RT} C_n\right)}{1 + e^{\delta F_2^*/RT} + e^{\delta F_3^*/RT} + \cdots + e^{\delta F_{n-1}^*/RT}} \qquad \text{(Eq. 58)}$$

A number of special cases have been considered by Parlin and Eyring (408). In all these considerations, considerable skill to manipulate Eq. 58 is called for. An analogous type of kinetic approach to membrane processes has been presented by Laidler and Schuler (268) and applied to experimental osmotic results by Schuler, Dames, and Laidler (470). Similar ideas prevail in the theory of membrane potential discussed by Nagasawa and Kobatake (366).

III. FLUX DUE TO GRADIENT OF ELECTROCHEMICAL POTENTIAL

Conditions arising across a membrane separating two aqueous solutions of equal or different concentration are considered. When the concentrations of the two solutions are equal, two types of phenomena arise depending on the species present in the two solutions. If one of the solutions contains a radioactive isotope, the phenomenon of self-diffusion takes place; or, if the two solutions contain different cations and the same anion, interdiffusion of cations sets in. If the concentrations are different, diffusion of the species in the direction of their gradients takes place. The diffusing species may be electrolytes, nonelectrolytes, or mixtures of both.

A. GENERAL CONSIDERATIONS

Whatever the nature of the diffusing species, a feature common to all these diffusion processes is the role the liquid layers adhering to the membrane faces play in controlling the over-all rates of permeation of the species across the membrane. The bulk solutions on either side of the membrane are kept very well stirred. Despite this, a zone of defined thickness without any convection will exist on either side. The diffusional flux may be controlled either by the membrane or by the liquid layer; that across which the slowest rate of flow takes place determines the over-all rate of diffusion. Besides these extremes, coupled membrane–film diffusion mechanism might also operate to control diffusion across the membrane.

Self-diffusion across a membrane in equilibrium with the outside solutions may be considered (Figure 3).

Equation 3 is applicable to both the membrane and the liquid films (158). In the steady state, *i.e.*, Eq. 11

$$J_x = D\frac{C_x - C_x'}{\delta} = \bar{D}\frac{\bar{C}_x' - \bar{C}_x''}{d} = D\frac{C_x''}{\delta} \qquad \text{(Eq. 59)}$$

It is assumed that little resistance is offered by the two interfaces. Then

$$\frac{C_x'}{C_x} = \frac{\bar{C}_x'}{\bar{C}_x}\,;\ \frac{C_x''}{C_x} = \frac{\bar{C}_x''}{\bar{C}_x} \qquad \text{(Eq. 60)}$$

Combining Eq. 59 and 60 (150)

$$J_x = \frac{\bar{D}\bar{C}_x}{d\left(1 + \frac{2\bar{D}\bar{C}_x\delta}{DC_xd}\right)} \qquad \text{(Eq. 61)}$$

This equation is applicable to all species that move through the membrane. In the case of self-diffusion, $\bar{C}_x$ will be the concentration of the radioactive species in the membrane in equilibrium with the surroundings.

Peterson and Gregor (414) applied similar considerations for two diffusing species (interdiffusion) and by applying Fick's law under some simplifying conditions calculated the concentrations of the mobile species at the interfaces. Using these values, they calculated the fluxes of the species in the diffusion layers and the final equation was identical with Eq. 61.

The factors controlling the rate-determining step of diffusion can be easily deduced from Eq. 61.

$$\text{When } (DC_xd/\bar{D}\bar{C}_x\delta) \gg 2 \quad J_x = (\bar{D}\bar{C}_x/d) \qquad \text{(Eq. 62)}$$

$$\text{When } (DC_xd/\bar{D}\bar{C}_x\delta) \ll 2 \quad J_x = (DC_x/2\delta) \qquad \text{(Eq. 63)}$$

In the first case membrane controls the diffusion process and in the second case films control the rate of the diffusional flux. It follows then that the ratio $DC_xd/\bar{D}\bar{C}_x\,\delta$ controls the rate-determining step. Lower values of d (thin membranes) and higher values of δ (thicker films, *i.e.*, little stirring or forced convection), higher diffusion coefficients in the membrane (greater porosity and little permselectivity), and low values of $C_x/\bar{C}_x$ (*i.e.*, high value of $\bar{C}_x$, higher concentration in the membrane) favor film diffusion control.

A simple calculation using some probable values in the ratio $Dd/\bar{D}\delta$ show that the value of the ratio is almost the same for most permeating species and probably for most membranes, charged or uncharged, assuming no specific interactions between the membrane and the diffusing species. Helfferich (159) has estimated the value to be between 100 and 200. The prime factor determining the diffusion control is the ratio $C/\bar{C}$. In uncharged membranes both electrolytes and nonelectrolytes are likely to have $C/\bar{C} \approx 1$; as such, membrane control of diffusion will be expected. In the case of charged membranes, because of their permselective nature the conditions will be different. For co-ions, $\bar{C}$ is always less than C; therefore, $C/\bar{C}$ is always greater than unity and will become very large at high dilutions due to Donnan exclusion of co-ions from the membrane phase. Film diffusion control is likely to be very rare. In the case of counterions, $C/\bar{C}$ is less than unity and will become very small at high dilutions, and hence diffusion will be controlled by the film. As C is increased, $\bar{C}$ will approach C and when it does, membrane diffusion control will set in. So in case of counterions, flux rate will change from film control to membrane control as the external concentration is increased. In between coupled membrane–film mechanism will prevail. With nonelectrolytes, $C/\bar{C}$ will be nearly unity and like the flux of co-ions, the flux rate will be controlled by the membrane.

In the consideration given above, it was assumed that the concentration profile in the diffusion layer (Figure 3) was linear. This would be so if the rates of stirring employed were high enough to give only a thin diffusion layer. Špan and Ribarič (504) have presented a theoretical model for self-diffusion suitable for arbitrary thick boundary layers with nonlinear concentration profiles. The equation derived is claimed to be of a general character and shown to be applicable in case of self-diffusion of ions (Cs^{137} tracer) into ion exchangers (Dowex 50), over a wide range of concentrations of the flowing solution.

B. THICKNESS OF NERNST DIFFUSION LAYER

The existence of a thin liquid layer between the well-stirred bulk solution and the membrane face being a reality, attempts have been made to estimate its thickness. A direct measurement is difficult to make but has been estimated from kinetic measurements. Tetenbaum and Gregor (545) estimated the thickness by applying Fick's law to the diffusion process occurring through ion-exchange particles and their bounding unstirred films. Using radioactive solutions of KCl and polystyrene sulfonic acid (PSSA) particles (12% cross linked) in a shallow bed, they measured the amount of radioactive substance diffusing out with time. If Q_0 is the amount of active species present initially in the sphere (particle) and Q is the amount diffused out in time t, the rate equation is given by

$$1 - (Q/Q_0) = \exp(-3Dt/r^\circ\delta K) \qquad \text{(Eq. 64)}$$

where r° is the radius of the homogeneous particle and K is the distribution coefficient given by $\bar{C}/C$.

Putting $3D/r^\circ\delta K = F$, Q/Q_0 values were calculated for assumed values of Ft, and Q/Q_0 was plotted against Ft. For the experimental values of Q/Q_0 at time t, Ft was read off and F was calculated. As D, r°, and K were independently determined, δ can be evaluated. The values obtained were 1.3 μ for a linear flow rate of 282 cm. sec.$^{-1}$ and 2.5 μ for a flow rate of 161 with 0.001 M KCl solution. Values of δ depended very strongly on the rates of stirring; the higher the rate of stirring, the smaller was the thickness. They evaluated δ by the limited bath technique also and obtained a value of 11 μ (concentration range 0.001-0.1 M) with stirring rates between 500–750 r.p.m. These values are nearly ten times the values realized for the shallow bed runs.

Peterson and Gregor (414) applied Nernst–Planck flux equations to the system (0.001 M KCl) $\rightleftharpoons$ membrane $\rightleftharpoons$ (0.001 M NH_4NO_3) and calculated the film thickness using both anion- and cation-exchange membranes by measuring the flux of K cation or Cl anion at different time intervals and extrapolating the flux to zero time.

Rearrangement of Eq. 61 gives

$$\delta = \frac{DC_x}{2}\left(\frac{1}{J_x} - \frac{d}{\bar{D}\bar{C}_x}\right)$$

where J_x was obtained by extrapolation. $\bar{D}$ was determined by conductance measurement of the membrane. As dilute solutions were used, Eq. 5 was employed to calculate $\bar{D}_k$. Thus

$$\bar{D}_k = 2.66 \times 10^{-7}\, \bar{\lambda}_k \text{ and } \bar{\lambda}_k = (\bar{\kappa}_k \times 10^3/\bar{C})$$

As D, C_x, and $\bar{C}_x$ were known, δ was evaluated. The values realized as a function of stirring rate are given in Table I.

A similar procedure was used by Stewart and Graydon (515) who measured the changes in concentration across the membrane in a known period of time. Using the unintegrated form of the Fick's equation, *viz.*

$$\bar{D}_{app} = (\Delta C \cdot V \cdot d/A \cdot C_t \cdot t)$$

where $\bar{D}_{app}$ is the apparent diffusion coefficient, ΔC is the change in concentration in time t, C_t is the concentration after time t, V is the volume of the solution, and A is the area of the membrane, the apparent diffusion coefficient was calculated. With this value, ΔC_L, the average concentration difference across either of two liquid layers was calculated from the equation

TABLE I

THICKNESS OF DIFFUSION LAYER AS A FUNCTION OF RATE OF STIRRING AND OF EXTERNAL CONCENTRATION

Concentration C_{x1}	C_{x2}	Rate of stirring, r.p.m.	μ	Ref.
0.001	0.001	1200	1.04	414
		800	4.25	
		400	14.40	
		300	19.70	
		200	30.10	
0.01	0.05	180	57	299
0.02	0.05		51	
0.01	0.02		60	
0.01	0.05		50	
0.02	0.05		57	
0.01	0.02		45	

$$\Delta C_L = (C_t/2) - (d\Delta C/2\bar{D}_{app}At)$$

The thickness of the liquid film, therefore, is given by

$$\delta = (D/2)[(AtC_t/V\Delta C) - (d/\bar{D}_{app})]$$

where D is the diffusion coefficient in water. δ was estimated as a function of the shaking rate and was about 330 μ at 30 oscillations/min. δ decreased with increase in the shaking rate and reached a value of about 10 μ at 110 oscillations/min.

Mackay and Meares (299) like other workers applied the Nernst–Planck flux Eq. 7 to the system

$$C = C_1 + C_2 \begin{array}{r|c|l} \text{solution} & & \text{solution} \\ C & & C \\ \vdots C_1\ \text{NaCl} & \text{membrane} & \text{NaCl}\ C_3\vdots \\ \vdots C_2\ \text{HCl} & & \text{HCl}\ C_4\vdots \end{array} C_3 + C_4 = C$$

and derived the equation for the fluxes across the membrane. For identical membranes of different thickness, they obtained

$$\delta = \frac{CD(Q_1^O - Q_1^L)(J_{x_1}d_{x_1} - J_{x_2}d_{x_2})}{2J_{x_1}J_{x_2}(d_{x_1} - d_{x_2})} \qquad \text{(Eq. 65)}$$

where

$$D = [(RTu_1u_2)/(Q_1^Ou_1 + Q_2^Ou_2)]$$
$$Q_1^O = {}^1/_2(Q_1^L + Q_1^O)$$
$$Q_2^O = {}^1/_2(Q_2^L + Q_2^O)$$

and Q is the ionic fraction of the species 1 or 2 in bulk solutions L and O. By measuring the fluxes J_{x_1} and J_{x_2} across the two membranes of thickness d_{x_1} and d_{x_2}, δ was evaluated and found to be 44 μ with solutions in the concentration range 0.01–0.05 M (180 r.p.m.).

They also measured, for the same membrane, fluxes with different external concentrations and using the equation

$$\delta = \frac{C_{x_1}C_{x_2}D(Q_1^O - Q_1^L)(J_{x_1} - J_{x_2})}{2J_{x_1}J_{x_2}(C_{x_1} - C_{x_2})} \qquad \text{(Eq. 66)}$$

calculated δ (Table I). It was assumed that D and $\bar{D}$ were independent of external concentration.

An elegant method has been described by Peers (411). A Permutit C-10 cation-exchange membrane bisected two half-cells, each containing 0.01 N NaCl solution flowed over the membrane faces. D.c. current was passed through the system and, using two Ag-AgCl probes, the potential was measured. The current–voltage characteristic for the membrane was thus determined (Figure 4).

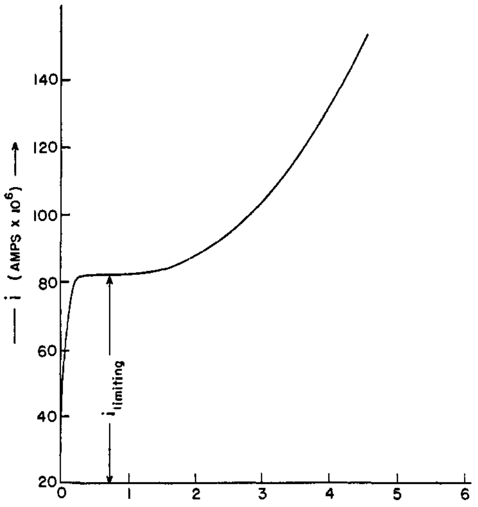


Figure 4.—Current–voltage characteristics of an ion-exchange membrane.

The current density, i, is given by the ionic current and the diffusion current through the stationary layer, i_d (409)

$$i = i_d + it_+ \qquad \text{(Eq. 67)}$$

where t_+ is the transport number of the Na$^+$ in bulk solution and $t_+ + t_- = 1$.

The bulk solution concentration was practically constant. The current in excess of i_d is carried partly by H$^+$ ions and mostly by Cl$^-$ ions.

$$i_d = FDC/\delta$$
$$i(1 - t_+) = FDC/\delta$$
$$i = i_{\text{lim}} = FDC/\delta t_- \qquad \text{(Eq. 68)}$$

i_{lim} can be determined and as D, C, and t_- are known, δ may be calculated.

It is apparent that it is impossible to get rid of these adhering liquid layers completely by stirring. Even by blotting an equilibrated membrane, liquid on either side of the membrane surface could not be completely removed. Glueckauf and Watts (107) estimated the thickness of this adhering liquid to be about 1 μ. They also suggested the possibility that this might be the liquid present in the micropores on the surface of the membrane.

Another method to estimate the thickness of the liquid films has been suggested by Ginzburg and Katchalsky (102). It consists in determining the solute permeability (mole sec.$^{-1}$ dyne^{-1}) ω_s, through two membranes independently. The membranes are arranged in series and then the over-all permeability is measured.

Apparent solute permeability (ω_s') through a membrane is given by

$$\frac{1}{\omega_s'} = \frac{1}{\omega_s} + (2RT/D)\delta \qquad \text{(Eq. 69)}$$

where ω_s is the true permeability through the membrane. For two membranes 1 and 2

$$(1/\omega_{s_1}') = (1/\omega_{s_1}) + (2RT/D)\delta \qquad \text{(Eq. 70)}$$

$$(1/\omega_{s_2}') = (1/\omega_{s_2}) + (2RT/D)\delta \qquad \text{(Eq. 71)}$$

It is shown by Kedem and Katchalsky (224) that the permeability through a composite membrane is given by

$$(1/\omega_{s_{12}}') = (1/\omega_{s_1}) + (1/\omega_{s_2}) + (2RT/D)\delta \qquad \text{(Eq. 72)}$$

Substituting Eq. 70 and 71 into Eq. 72, gives after rearrangement

$$\delta = (D/2RT)[(1/\omega_{s_1}') + (1/\omega_{s_2}') - (1/\omega_{s_{12}}')] \qquad \text{(Eq. 73)}$$

This is a very direct method to evaluate δ.

Rearranging Eq. 69

$$D/2RT\omega_s' = (D/2RT\omega_s) + \delta \qquad \text{(Eq. 74)}$$

The apparent permeability was determined for the solute, tritiated water, by Ginzburg and Katchalsky at various rates of stirring. On extrapolation of $D/2RT\omega_s'$ to zero stirring, they obtained for Sylvania wet gel a value of 100 μ. The permeability of tritiated water was calculated using an approximation (221) given by

$$\omega_{\mathrm{THO}} = (\vartheta\varphi_{\mathrm{w}}\, D_{\mathrm{THO}}\,/dRT) \qquad \text{(Eq. 75)}$$

where ϑ is the tortuosity factor of the capillaries in the membrane, φ_{w} is the volume fraction of water in the membrane (0.77; same as v_0 of Eq. 9), and d is the thickness of the membrane (84.2×10^{-4} cm.). Substituting Eq. 75 into Eq. 74

$$100\mu = (d/2\vartheta\varphi_{\mathrm{w}}) + \delta$$

$$(d/2\varphi_{\mathrm{w}}) = 52.5\mu$$

$$\delta = 100\,\mu - (52.5/\vartheta)\mu$$

As the limits of ϑ are set at 0.6 and 1, the δ-values vary from 12 to 47.5 μ.

The role that δ plays in determining the permeability of substances through membranes can be assessed from the values of ω_s. If this value is small, $D/2RT\omega_s$ becomes very large and the value of δ becomes negligible. δ therefore plays only a minor role in determining the real permeability of less penetrating substances like glucose and sucrose; whereas, its contribution becomes significant for highly penetrating substances like heavy water.

C. SELF-DIFFUSION

This subject matter has been treated in great detail by Helfferich (156). Mathematical theories and experimental procedures for determining self-diffusion coefficients in ion-exchange resin rods, ribbons, and membranes are discussed at length. Both Helfferich and Tuwiner (558) have reviewed the early work connected with self-diffusion studies. There seems to be little work done with nonion-exchange membranes; but from the considerations of ion-exchange membranes, general understanding of how nonselective membranes control self-diffusion is possible.

The work reviewed by Helfferich and Tuwiner is concerned mostly with ion-exchanger particles (28, 30, 31, 486) except for the work of Schlögl who used membranes (451). The work is briefly recounted to bring out the general principles governing self-diffusion in membranes.

Self-diffusion coefficient in the membrane phase depends on the size of the solvated ion and follows the order of mobility observed in aqueous solutions. But in membranes their values are 1/5 to 1/20 lower than corresponding coefficients in water. The sequence of mobility for alkali metal ions increase in the order Li < Na < K < Rb < Cs. The retardation increases as the valency of the species is increased; thus, $\mathrm{Na^+} > \mathrm{Ca^{2+}} > \mathrm{Y^{3+}} > \mathrm{Th^{4+}}$. This effect is more for counterions in cation exchangers than it is for counterions in anion exchangers. Retardation is stronger for counterions than for co-ions. This is due to the electrostatic attraction of counterions to the fixed charges of the membrane network. For co-ions, this attraction is negligible. On this basis it may be inferred that cations and anions move in nonion-exchange membranes at reduced mobilities but follow the sequence observed in ordinary aqueous solutions.

The degree of cross linking of the membrane also controls diffusion. In general, higher the cross linking greater the retardation. Mobilities of the mobile species depend on the free water and not the total water present in the membrane phase. It is considered that the pore liquid is the medium in which diffusion took place. The composition of the medium will then affect the moving species as also their interactions with the other existing ions in the medium.

Self-diffusion coefficient of a species is increased if a species of higher mobility existed in the medium and the reverse happens in presence of a slower one (486). Self-diffusion coefficient of $\mathrm{Sr^{85}}$ through Amberplex C-1 with (100% Sr + 0% H) solution changed from 0.85×10^{-8} to 1.5×10^{-8} cm.^{2} sec.$^{-1}$ when the solution was changed to (22.5% Sr + 77.5% H) at 16° (289).

The effect of fixed ionic groups is difficult to assess. Boyd, Soldano, and Bonner (31), by desulfonating the resin, determined the self-diffusion coefficients whose values increased with decrease of fixed charge, reached a maximum, and decreased with further decrease in

TABLE II

SELF-DIFFUSION COEFFICIENTS IN PSA MEMBRANES

	Ishibashi, Seiyama, and Sakai (205)		Mackay and Meares (298)			
External concn., mole/l.	$\bar{D} \times 10^7$, cm.^{2} sec.$^{-1}$		$\bar{D} \times 10^6$ cm.^{2} sec.$^{-1}$		$(\bar{D}_{obsd}/\bar{D}_{calcd})$	
	Ca^{2+}	Cl^-	Na^+	Cl^-	Na^+	Cl^-
0.01			2.33	7.50 (obsd.)	0.51	1.07
0.02			2.97	7.46 (calcd.)	0.65	
0.05			3.51	7.42 (calcd.)	0.77	
0.06	0.66	61.5				
0.10			3.72	7.37 (calcd.)	0.83	
0.12	0.95	19.8				
0.50	1.68	6.0	4.75	7.23 (calcd.)	1.07	
1.00			4.70	7.08 (calcd.)	1.08	
1.44	2.24	4.1				
3.00	1.40	2.2				

fixed groups. In the desulfonation process, cross linking and, following it, the swelling were also affected. On just theoretical grounds, because of the absence of electrostatic attraction, the counterion mobility will increase with decrease in capacity provided the swelling remained constant. These aspects have received detailed consideration in the work of Despić and Hills (69) and Jakubovic, Hills, and Kitchener (209).

Nepton CR 51 (phenolsulfonic acid, PSA) membrane has been used by Spiegler and Coryell (509) and by autoradiographing the radioactivity, the movement of the species was followed, and their concentration estimated. By a graphical method the diffusion coefficients were evaluated. The values obtained were: Na $= 1.95 \times 10^{-6}$, Zn $= 0.41 \times 10^{-6}$, and Ca $= 0.31 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. Tetenbaum and Gregor (545) with PSSA particles obtained for Na $= 4.68 \times 10^{-6}$ in 0.1 *M* solution and 8.1×10^{-6} cm.^{2} sec.$^{-1}$ for Cl^-. The co-ion has a higher value than the counterion.

Richman and Thomas (434) evolved a technique whereby they could use a cylindrical rod and studied self-diffusion in Nepton CR 51 as a function of external NaCl concentration. The solution was kept in a very well-stirred bath and so the diffusion took place from a limited bath into the end of an infinite uniform rod. The self-diffusion coefficients of Na^+ increased with increase in the concentration of the external electrolyte solution. Schlögl (451) observed a similar behavior for the counterion, whereas for the co-ion he found the diffusion coefficient to decrease with increase in the external concentration. Similarly, Ishibashi, Seiyama, and Sakai (205) determined the diffusion coefficient of Ca^{2+} in a calcium PSA membrane in equilibrium with external $CaCl_2$ solutions using Ca^{45} employing the Schlögl and Helfferich technique (149, 457). Ca^{2+} diffusion coefficient varied between 1/120 and 1/35 of the estimated conductivity values in the solution at infinite dilution. The values are given in Table II.

$\bar{D}_{Cl^-}$ values in the case of $CaCl_2$ solutions were calculated from conductivity data and Ca^{2+} counterion self-diffusion coefficients. These data confirm the findings of Schlögl. In the context of the considerations presented earlier (diffusion coefficient to increase with increase in water content), it is surprising that the counterion diffusion should increase instead of decreasing due to decrease of free water. But the co-ion diffusion, as expected, decreased. The counterion diffusional increase with external concentration, reaching a maximum and then decreasing with further increase in external concentration, recorded by the Japanese workers, but not very seriously considered by them, has been observed by Jakubovic, Hills, and Kitchener (209, 210) who used an elegant technique for determining self-diffusion coefficients in ion-exchange resin rods. This method is an improved technique of Richman and Thomas (434) effectively used for the first time by Despić and Hills (67, 69) to study self-diffusion of Na^+ counterions in cross-linked polymethacrylic acid (PMA) polymer in the form of a rod. They used a tiny drop of a highly radioactive Na or Cs at one end of an upright rod and allowed it to diffuse for a predetermined time. They were able to eliminate the interfering effects arising from the contact of the polymer material with the external solution. Further, they were able to isolate the effects of the resin matrix and of the interstitial ionic concentration on the counterion diffusion coefficients. In most of these rods the co-ion did not exist, as it was leached out. Their values are given in Tables III and IV. Jakubovic, Hills, and Kitchener (209) used PSA resin rods free from co-ions in Na^+ or Cs^+ form and found that the self-diffusion coefficient of the counterion increased with increase in the water content of the resin (*i.e.*, decreasing volume fraction of the resin V_r) reached a maximum, and decreased with further increase in the water content. Meares (334) using Zeokarb 315 studied the self-diffusion of Na^+ ion as a function of the external electrolyte concentration. The diffusion of ions in a membrane was considered to take place in the aqueous medium. The polymer matrix would only act to hinder its movement by increasing the tortuosity of the diffusion path. Meares considered this factor in great detail (298, 303, 304, 333, 334) and has expressed the diffusion coefficient in the membrane as

TABLE III

IONIC SELF-DIFFUSION COEFFICIENTS OF Na^+ COUNTERIONS IN CROSS-LINKED PMA RODS

Interstitial concentration, C_1	$\bar{D}_{obsd} \times 10^6$, cm.^{2} sec.$^{-1}$	$\frac{\bar{\eta}}{\eta}$	$\bar{D}\left(\frac{\bar{\eta}}{\eta}\right)\left(\frac{1 + V_r}{1 - V_r}\right)^2 \times 10^6$	$D \times 10^6$, cm.^{2} sec. ^{1}
1.03	3.92	1.10	9.98	
1.76	3.88	1.17	9.08	
2.02	3.09	1.21	7.40	
2.66	2.72	1.30	9.31	
3.38	2.12	1.41	8.41	
6.08	0.95	2.00	7.27	
6.94	0.52	2.20	10.01	
		Average	9	13.34

TABLE IV

IONIC SELF-DIFFUSION COEFFICIENTS OF Cs^+ COUNTERIONS IN CROSS-LINKED PMA RODS

Interstitial concentration, C_1	$\bar{D}_{obsd} \times 10^6$, cm.^{2} sec.$^{-1}$	$\frac{\bar{\eta}}{\eta}$	$\bar{D}\left(\frac{\bar{\eta}}{\eta}\right)\left(\frac{1 + V_r}{1 - V_r}\right)^2 \times 10^6$	$D \times 10^6$, cm.^{2} sec.$^{-1}$
0.726	7.15	1		
0.756			15.07	
0.786	2.33		14.35	
0.792	7.06		12.72	
0.799	7.33		13.50	
0.814			13.60	
0.875	6.20			
0.953	4.44		15.60	
1.202	3.39		14.88	
1.244			15.92	
1.405			14.64	
1.469	3.49			
		Average	14.48	20.71

$$\bar{D} = D\left(\frac{1 - V_r}{1 + V_r}\right)^2 \qquad \text{(Eq. 76)}$$

Accordingly, $\bar{D}$ values calculated using Eq. 76 were compared with the experimental values (Table II). In dilute solutions calculated values were higher than the observed values, but with solutions above 0.3 *M* there was some agreement. In this treatment the specific or other effects of the fixed charge on the mobile species is not considered. In dilute solutions at least, the fixed charge must tend to attract the counterion and thus slow it down. Using the above correction term for various external concentrations, Meares calculated the $\bar{D}$ values for the Cl^- ion at various concentrations taking the value of $\bar{D}_{obsd}/\bar{D}_{calcd}$ as 1.07 (298). These calculated values for the Cl^- ion are given in Table II.

A critical check of Eq. 76 has been made by Jakubovic, Hills, and Kitchener (209, 210). Their data point to the inadequacy of the treatment exhibited by the disagreement between the calculated diffusion coefficients (or $\bar{\lambda}$) and their observed values. Calculated values are all consistently higher. Further the observed values show a variation with water content of the resin which has a maximum. This has been attributed to the migration of ions along the polymer chains. This type of movement has to overcome to a greater extent the friction between the moving ion and the pore wall. Despić and Hills (69) tried applying corrections to the Meares function by taking the viscosity of the medium into account as proposed by Elton (87). Even with this correction it is found (Tables III and IV) that

$$\bar{D}\left(\frac{\bar{\eta}}{\eta}\right)\left(\frac{1 + V_r}{1 - V_r}\right)^2$$

(η, $\bar{\eta}$, viscosity of water and interstitial solution, respectively), which should be equal to the limiting value of D in very dilute aqueous solution, is too low. This discrepancy has been attributed to (1) a relaxation effect, (2) mechanism of ionic diffusion along the chains, being similar to surface conduction, is probably different from that in aqueous solution, and (3) the polymer chains may not be continuous.

TABLE V

APPARENT AND TRUE DIFFUSION COEFFICIENTS AND CHECK OF SPIEGLER'S MEMBRANE MODEL

External soln. (NaCl), concn., *m*	$\bar{D}_{app} \times 10^7$	$\bar{D} \times 10^7$	$L_{22} \times 10^9$ (calcd. Eq. 77)	$L_{22} \times 10^{11}$ (obsd.) Method 1	Method 2
0.21	1.95	7.6	0.5		
0.61	2.82	5.6	2.0		
0.95	3.91	6.2	4.4		
1.00				0.94	0.86
1.39	4.34	5.7	7.2		
1.50				1.12	0.90
1.75				1.32	1.00
1.83	4.48	5.6	9.8		
2.25				1.74	1.13
2.50				1.05	1.00
3.42				3.09	1.04

A further test has been made by Lagos and Kitchener (267) who studied self-diffusion of Na^+, Cs^+, Ag^+, and Ca^{2+} ions in PSSA resin ribbons as a function of degree of cross linking and water content. Unlike the previous study with PSA material (209, 210), no maximum in the diffusion coefficient (or $\bar{\lambda}$) with the water content was observed. They were not able to prepare resins which were highly swollen to contain as large a quantity of water as the PSA resins. Due to this practical limitation, existence or complete absence of a maximum in the diffusion coefficient could not be detected. They point out another factor which the Meares function should take into consideration in accounting for the observed variation of $\bar{D}$, *viz.*, the size of the diffusing species itself. They consider tortuosity to be less for smaller diffusing species than for larger species. However, the interesting results of Ginzburg and Katchalsky (102) are opposed to this view, and it is found that tortuosity for heavy water is larger than it is for sucrose (Table XXXII).

Caramazza, Dorst, Hoeve, and Staverman (38) measured the self-diffusion of co-ion (Cl^{36}) in PSSA membrane. The values of the apparent diffusion coefficient ($\bar{D}_{app}$) increased as the external concentration was increased. Using the Donnan relation $\bar{D}\bar{C} = \bar{D}_{app} \cdot C$, true diffusion coefficients ($\bar{D}$) were calculated. These values decreased with increase in external concentration (Table V). The $\bar{D}_{app}$ values have been used in the equation

$$L_{22} = (C\bar{D}_{app})/(RTd) \qquad \text{(Eq. 77)}$$

(where L_{22} is the phenomenological coefficient and 1, 2, and 3 indicate counterion, co-ion, and water, respectively) to calculate L_{22} whose values are given in Table V. For the same membrane system values for the

TABLE VI

PHENOMENOLOGICAL COEFFICIENTS AND CHECK OF SPIEGLER'S MEMBRANE MODEL

External soln. concn., *m*	$L_{12} \times 10^{11}$	$L_{33} \times 10^{9}$	$L_{13} \times 10^{10}$	$L_{23} \times 10^{10}$ (Eq. 78)	L_{23} obsd.
1.00	0.59	11.2	5.68	1.16	Too small to be
1.50	0.37	8.3	5.60	0.55	measured;
1.75	0.32	8.0	6.00	0.43	about 10^{-11} [a]
2.25	0.12	6.0	5.44	0.13	
2.50		5.5	5.28		
3.42		4.5	5.36		

[a] 10^{-11} is the value at 0.7 salt concentration and decreased rapidly at other salt concentrations (73).

phenomenological coefficients, L_{12}, L_{13}, L_{23}, L_{33}, and L_{22} have been derived (Tables V and VI) by measuring the necessary parameters (conductance, transport number of 1 and 3, and permeability of water and solute) of the membrane phase (73). It is seen from Table V that the values of L_{22} coefficient calculated from Eq. 77 disagree considerably with the values derived from other experimental data (73). This was attributed to the inapplicability of the Spiegler's pore model (507) to describe the behavior of an ion-exchange membrane. The inadequateness of the model is further confirmed by the data of Table VI in which the relation

$$L_{23} = L_{12}L_{33}/L_{13} \qquad \text{(Eq. 78)}$$

derived by Spiegler on the basis of his model, is not satisfied.

Glueckauf and Watts (107) determined the diffusion coefficients of Na^+ co-ion in an anion-exchange membrane and found the diffusion coefficients to increase with increase in external concentration. Similar results were obtained for La^{3+} co-ion but the actual values were lower than the values obtained for Na^+ (55). These results which are straightforward are at variance with the results already discussed. This discrepancy is difficult to explain on ordinary grounds. However, in view of the heterogeneous structural character of the membranes and two different techniques of measurement used in the self-diffusion studies, what part the dead end pores play at different external concentrations is difficult to assess. The results of Schlögl and Stein (459, 460) emphasize the role the dead end cavities play in controlling diffusion. Through diffusion studies give low values whereas effusion technique which was employed by Watts, Crabtree, and Glueckauf (55, 106, 107) gives higher values. At very low concentrations, the Donnan principle should operate (unless the charge density of the pores is too low), and the $\bar{D}$ values should not depend very much on the method used in their determination. But as the concentration is increased effusion method will give higher values for $\bar{D}$. It is therefore possible that the wash out of electrolyte from the dead end pores is responsible for the discrepancy. Application of the two techniques to a single well-defined system is highly desirable to settle this point.

Wright (597, 598) determined the self-diffusion and permeability coefficients of Na^+ and Br^- ions in horn keratin, a material similar to wool. The values of these coefficients increased with increase in external concentration. The mobility values derived from Eq. 5 agreed with the results of his conductance studies. Na^+ and Br^- mobilities were of similar magnitude but 1000 times less than for diffusion in aqueous solution. For cellophane diffusion coefficient of KCl was about 1/10 of that in water (599). In ion exchangers the diffusion coefficients are about 1/5 of those in water.

The data for self-diffusion of water in various materials are given in Table VII. The decrease in the $\bar{D}$ values with increased cross linking is not as high as in the case of ions.

The self-diffusion coefficients of Na^+ ions (99) and of tritiated water (367) in agar gels (Table VIII) present a set of data illustrating the movement of different species in nonion-exchange materials, as agar gels have very few number of negative groups (99). The diffusion coefficients of Na^+ decrease as the per cent weight of agar is increased and also as the concentration of NaCl is increased. The latter parallel the behavior noticed in ordinary aqueous solutions. The diffusion values of tritiated water on extrapolation to zero agar concentra-

TABLE VII

SELF-DIFFUSION ($CM.^2$ $SEC.^{-1}$) OF WATER IN DIFFERENT MATERIALS

Material	Salt form	Cross linking, %	Temperature, °C. 3.4	16	25	Heavy water used	Ref.
			$\bar{D} \times 10^6$				
Water			15.4	22.0	26.6	H_2O^{18}	
				18.9	24.4	THO	576
					23.4	DHO	
PSSA–DVB cross linked	H^+	4	4.51		9.14		
	H^+	8	2.70		5.4	H_2O^{18}	30
	H^+	16	1.10		2.2		
	La^{3+}	8	0.82				
	K^+ (0.1 *N*)	12			21.4	DHO	545
	K^+ (0.001 *N*)	12			19.4		
Zeokarb 315 (PSA)	Na^+ (water)			10.8		3–5%	297
	H^+ (water)			10.6		Heavy water	
	H^+ (0.1 *N* HCl)			11.2			

TABLE VIII

SELF-DIFFUSION IN AGAR GELS

Agar, % weight	0.05 N NaCl, $\bar{D} \times 10^5$	0.10 N NaCl, $\bar{D} \times 10^5$	THO, $\bar{D} \times 10^5$
0.00 (water)	1.33	1.33	2.44
0.30			2.33
0.40	1.17	1.08	
0.50			2.29
0.75			2.22
1.00	1.13	1.03	2.18
3.00	1.06	0.95	
5.00	0.98	0.88	

TABLE IX

Br^{83} DIFFUSION IN DOWEX 1 AND CONCENTRATED ELECTROLYTE SOLUTIONS

External solution molality (LiCl)	Total Cl^- in resin	—Aqueous molality— LiCl same as free LiCl in resin	BCl	$\bar{D} \times 10^8$ (resin)	$D \times 10^8$ (solution)
1.02	6.6	0.3	6.3	82	272
3.20	9.5	2.4	7.1	48	172
6.86	13.7	6.5	7.2	21	78
11.1	18.9	11.2	7.7	6.5	23
16.1	25.8	(16.8)	(9.0)	1.6	—

tion gave a value of 2.41×10^{-5} agreeing with the value found in ordinary water.

Nelson (374) has presented a study where he has used very strong solutions of benzyltrimethylammonium chloride (BCl) as a model for resins of quaternary amine polystyrene–divinylbenzene type (Dowex 1).

The resin was equilibrated in different strong solutions of LiCl. Both the free LiCl and total Cl^- existing in the resin phase were estimated. Br^{83} diffusion was followed. Similarly, Br^{83} diffusion was studied in an aqueous concentrated solution system which was constructed from LiCl and BCl solutions by mixing them in such proportions as to have the same quantities that existed in the resin phase as free LiCl and total Cl^-. The results of Nelson are given in Table IX.

Both $\bar{D}_{Br}$ and D_{Br} values run parallel to each other, with $\bar{D}_{Br}$ values being lower. In this study, the resin system has been considered equivalent to a homogeneous phase similar to that of a strong electrolyte solution; whereas in other studies, it was considered as a porous medium consisting of two phases, the solid matrix and the interstitial pore liquid in which the diffusion took place. In the latter case three factors controlled the over-all diffusion: (1) Only the area unoccupied by the matrix was available for diffusion, (2) matrix obstructed diffusion and increased pore length, and (3) interaction of diffusing species with the pore walls. The last two do not affect the Nelson model which considered the resin similar to an aqueous solution of an organic electrolyte like benzyltrimethylammonium chloride. The retardation of the diffusing species was then entirely due to the reduction in total volume arising from the space occupied by the organic ions. The two models seem to present two extreme pictures, and the real one describing the behavior of cross-linked membranes probably lies somewhere between the two.

D. INTERDIFFUSION

When two electrolyte solutions of the same concentration are placed, one on either side of a membrane, diffusion of cations and anions through the membrane takes place. In dilute solutions, as the ionic activities are almost equal, each ion moves through the membrane following the relative order of their mobilities observed in dilute aqueous solutions. But their absolute values in the membrane will be lower. If the membrane is a charged one, the co-ions are excluded from the membrane phase and only the counterions diffuse through the membrane.

A quantitative description of the phenomena arising across an ion-exchange membrane when two different counterions (biionic) or more (multiionic) diffuse through the membrane is given by Helfferich (151) and Helfferich and Ocker (174). A summary of this appears also in Helfferich's book (163).

1. *Diffusion in Biionic Systems*

A membrane system, solution (AX)membrane| solution (BX), containing two dilute solutions of different counterions A and B and the same co-ion may be considered.

Applying Eq. 6 to the flow of two counterions

$$J_A = -\bar{D}_A\left[\frac{d\bar{C}_A}{dx} + z_A\bar{C}_A\frac{F}{RT}\frac{d\psi}{dx}\right] \quad \text{(Eq. 79)}$$

$$J_B = -\bar{D}_B\left[\frac{d\bar{C}_B}{dx} + z_B\bar{C}_B\frac{F}{RT}\frac{d\psi}{dx}\right] \quad \text{(Eq. 80)}$$

Convection and gradients of pressure and activity coefficients are neglected.

The system is subject to the following conditions.

$$z_A\bar{C}_A + z_B\bar{C}_B + \omega\bar{C} = 0 \text{ (electroneutrality)}$$

(It is assumed that $\omega\bar{C}$ is a constant.)

$$z_AJ_A + z_BJ_B = 0$$

This follows from the equivalence of fluxes, as otherwise there will be net transference of charge. The diffusion potential maintains the equality of fluxes J_A and J_B which are constant in the steady state.

Combination of Eq. 79 and 80 using the two conditions given above gives (152, 175)

$$J_A = -\left[\frac{\bar{D}_A\bar{D}_B(z_A^2\bar{C} + z_B^2\bar{C}_B)}{z_A^2\bar{C}_A\bar{D}_A + z_B^2\bar{C}_B\bar{D}_B}\right]\frac{d\bar{C}_A}{dx} \quad \text{(Eq. 81)}$$

Comparing it with Eq. 3, Eq. 81 describes coupled interdiffusion by one diffusion coefficient $\bar{D}_{AB}$ and is equal to

TABLE X

DIFFUSION COEFFICIENT OF Sr IN INTERDIFFUSION OF Sr–H IN AMBERPLEX C-1 MEMBRANES

		$\bar{D}_{Sr} \times 10^8$ Temp., °C.				
Pile 1	Pile 2	64	32	16	8	4
100% H ⇌	22.5% Sr + 77.5% H	7.17	4.08	1.60	1.01	0.88
100% H ⇌	45.0% Sr + 55.0% H	9.59	2.80	2.37	1.28	0.86
100% H ⇌	90.0% Sr + 10.0% H	7.97	3.47	2.63	2.17	1.81

$$\bar{D}_{AB} = \frac{\bar{D}_A \bar{D}_B (z_A{}^2 \bar{C}_A + z_B{}^2 \bar{C}_B)}{z_A{}^2 \bar{C}_A \bar{D}_A + z_B{}^2 \bar{C}_B \bar{D}_B} \qquad \text{(Eq. 82)}$$

$\bar{D}_{AB}$ will not be constant but will depend on the relative concentrations of A and B in the membrane phase. When $\bar{C}_A \ll \bar{C}_B$

$$\bar{D}_{AB} = \bar{D}_A$$

and when $C_B \ll C_A$

$$\bar{D}_{AB} = \bar{D}_B$$

This establishes the general rule that in coupled interdiffusion of two species, the one species whose membrane concentration is small controls the interdiffusional flux (151, 174).

The work of de Lopez-Gonzalez and Jenny (289) is in agreement with this rule (153).

Amberplex C-1 membranes in two piles, each pile containing five identical membranes, were used. Pile 1 and pile 2 were in the initial ionic form shown in Table X. They were pressed together by a 1-kg. weight under water, and interdiffusion was allowed to occur. The interdiffusion coefficient of Sr increased as the concentration of Sr increased, approaching the value of the ion that was present in small proportion, *i.e.*, H^+ ion.

Using the flux Eq. 79 and 80 but with the activity coefficient terms, *i.e.*, Eq. 7, Helfferich and Ocker (151, 174) calculated the fluxes of ions and their concentration profiles. The concentration profiles were governed by the ratio $\bar{D}_A/\bar{D}_B$ in the membrane which accumulated the slower ion.

The interdiffusional flux was found proportional to the total concentration of counterions which was approximately the same as the concentration of fixed charges in the membrane and inversely proportional to the membrane thickness. The absolute flux values were of the same order as in self-diffusion.

Similar theoretical work based on the application of Nernst–Planck Eq. 7 has been carried out by Mackay and Meares (300), who considered the effect of convection through the membrane. They have also extended the treatment to concentrated solutions (301). Their experimental flux results for the interchange of Na^+ and H^+ ions agreed with the conclusions already presented, but, when compared with the values calculated using their flux equations, agreement was within 10%. Both in dilute and concentrated solutions, membranes containing higher fraction of hydrogen ions produced fluxes 30% larger than the calculated values. However, in concentrated solutions the observed anion and solvent fluxes agreed with the theoretical fluxes.

TABLE XI

MEMBRANE INTERDIFFUSION COEFFICIENTS

	Cation-exchange membrane				Anion-exchange membrane $\bar{D} \times 10^7$, cm.^{2} sec.$^{-1}$	
	$\bar{D} \times 10^7$, cm.^{2} sec.$^{-1}$					
Solution concn., equiv./l.	$NaNO_3$–HCl		KCl–NH_4NO_3		KCl–NH_4NO_3	
	$\bar{D}_{Na}$ (515)	$\bar{D}_{Na}$ (552)	$\bar{D}_k$ (414)	$\bar{D}_{Cl}$ (414)	$\bar{D}_k$ (414)	$\bar{D}_{Cl}$ (414)
0.001			1.09			
0.01			1.44			
0.10	8.9	13.9	1.70	3.24	2.41	0.78
0.50	9.0	16.0	1.72	3.00		0.85
1.0		16.0	1.75	2.91		
2.0		16.2				
4.0		15.8				

Peterson and Gregor (414) estimated the interdiffusion coefficients of K^+ counterion in the system KCl solution (C)|PSSA membrane|NH_4NO_3 solution (C) by measuring the K^+ ion fluxes. They found $\bar{D}_K$ to increase with increase in external concentration. The values of $\bar{D}_K$ and $\bar{D}_{Cl}$ are given in Table XI.

When the external concentration was increased, the co-ion was no longer prevented from diffusing through the membrane. The co-ion diffusion coefficient although larger than that of the counterion decreased slightly with the increase in concentration. For an anion permeable membrane similar trend is apparent (Table XI).

Apparent interdiffusion coefficients for a series of PSSA membranes have been determined by Stewart and Graydon and Ciric (46, 515) and also by Tombalkian, Yey, and Graydon (552). The monovalent Na^+ has an apparent interdiffusion coefficient $\bar{D}_{Na^+-H^+} = 6.5 \times 10^{-5}$ and divalent Ca^{2+} has a lower value 4.6×10^{-5} when the external concentration was 0.1 *N* (515). At this concentration the co-ion is almost absent from the membrane phase; its coefficient, however, has been estimated at 5×10^{-7}. Although Peterson and Gregor's values for the co-ion, compared with those of Stewart and Graydon, the counterion values differed almost by a factor of 300. This discrepancy will be considerably reduced when the membrane concentration gradient is taken into account. These corrected diffusion coefficients are given in Table XI. These values are higher than the values of Peterson and Gregor. This should be so, as the system contained highly mobile H^+ ions whereas the other system had NH_4^+ ions.

The apparent interdiffusion coefficients of cations against hydrogen decrease in the order Cs > Na > Ba > Sr > Ca > Mg > Al (552). In this work volume changes due to water transfer have also been measured. It was found that net water transfer increased in the same order. The apparent interdiffusion coefficient for any given cation decreased with increase in the external concentration whereas the membrane values, calculated as the product of the apparent value and the ratio of the solution concentration to the membrane concentration (Donnan relation) are almost independent of the external concentration (Table XI), thus agreeing with the trend exhibited by the values of Peterson and Gregor in the range 0.1–1 *M*. It was also found in accordance with expectations that $\bar{D}$ (interdiffusion) values decreased with decreasing membrane capacity and increasing membrane cross linking.

Ciric and Graydon (46) calculated single ion diffusion coefficients for H^+, NH_4^+, Li^+, Na^+, and K^+ ions from interdiffusion data obtained for combinations of two ions in various PSSA membranes using (509)

$$D = (2D_{i1}D_{i2})/(D_{i1} + D_{i2})$$

Applying the Donnan relation to these values they derived the diffusion coefficients referred to the membrane phase from which the specific conductance values were calculated using Nernst–Einstein Eq. 5. These values were found to be larger than the values measured directly. This discrepancy was attributed to water transfer.

Cases of interdiffusion where liquid films only or membrane liquid films controlled the flux in biionic systems have been treated by Helfferich (151, 164). Very little experimental work is reported about complete film controlled interdiffusion, but partial film control which might exist may be corrected for by following the procedures described by Mackay and Meares (299).

2. Biionic Potentials

Membrane potential of a biionic cell containing two electrolytes AX and BX separated by a membrane is called the biionic potential (B.I.P.) (587).

Interdiffusion of A and B through the membrane gives rise to the potential which will be more positive in the solution containing the counterion of lower mobility, lower valence, or lower affinity for the membrane. This is true of a cation-exchange membrane, and the reverse is true of an anion-exchange membrane. A nonselective membrane will be effective only if it is able to exert some sieve effects thereby excluding one of the ions from the membrane phase.

The total B.I.P. may be considered in accordance with the concepts of Teorell (531–534) and Meyer and Sievers (342) (TMS) as being made up of three potentials—two Donnan potentials and one diffusion potential. Assuming absence of co-ions and convection in the membrane, Helfferich (151, 167) has given a complete mathematical discussion of biionic potentials under conditions of (1) membrane diffusion control, (2) film diffusion control, and (3) coupled membrane–film diffusion control.

For the case of complete membrane diffusion control there exist two Donnan potentials and a diffusion potential. For a general case, the potential is given by

$$E = \frac{RT}{F}\left[\frac{\bar{D}_B - \bar{D}_A}{\bar{D}_A z_A - \bar{D}_B z_B} \ln \frac{\bar{D}_B z_B}{D_A z_A} + \frac{1}{z_A z_B} \ln K_B{}^A + \frac{z_A - z_B}{z_A z_B} \ln \frac{\bar{C}}{C'} + \frac{1}{z_B} \ln \frac{C'}{C''} + \ln \frac{\gamma_A{}'^{1/z_A}}{\gamma_B{}''^{1/z_B}}\right] \quad \text{(Eq. 83)}$$

It is assumed that $\bar{D}_A/\bar{D}_B$, $\ln K_B{}^A$, and $\bar{C}$ are constants. $\bar{C}$ is the total counterion concentration and $K_B{}^A = (\bar{\gamma}_B)^{z_A}/(\bar{\gamma}_A)^{z_B}$, the ratio of activity coefficients in the membrane.

For counterions of equal valence ($z_A = z_B$)

$$E = \frac{RT}{z_A F} \ln \frac{\bar{D}_A a_A' \bar{\lambda}_B}{\bar{D}_B a_B'' \bar{\lambda}_A} \quad \text{(Eq. 84)}$$

Michaelis (345, 346) was the first investigator who derived a relation between B.I.P. and selectivity, and he wrote for the potential

$$E = \frac{RT}{F} \ln \frac{\bar{u}_A}{\bar{u}_B} \quad \text{(Eq. 85)}$$

where $\bar{u}_A$ and $\bar{u}_B$ are the mobilities of the permeating ions.

Sollner (491) and others (50, 74, 491, 495, 496) replaced mobilities by transference numbers. Marshall and Krinbill (318) expressed the potential as a function of the products of mobilities and activities (*cf.* Eq. 84)

$$E = \frac{RT}{F} \ln \frac{a_A' \bar{u}_A}{a_B'' \bar{u}_B} \quad \text{(Eq. 86)}$$

Wyllie (600) considered the selectivity the membrane would exert on ions and derived for the B.I.P. an equation similar to Eq. 86. His expression for the B.I.P. was (398, 600)

$$E = \frac{RT}{F} \ln \frac{a_A'}{a_B''} (\bar{u}_A/\bar{u}_B) \quad \text{(Eq. 87)}$$

but the intramembrane mobility ratio was expressed by

$$\bar{u}_A/\bar{u}_B = \bar{l}_A/\bar{l}_B = (\bar{m}_A/\bar{m}_B)(\bar{\kappa}_A/\bar{\kappa}_B) \quad \text{(Eq. 88)}$$

where $\bar{l}_A/\bar{l}_B$ is the intramembrane transference ratio and $\bar{m}_A$ is the steady-state equilibrium concentration of A in the junction zone. $\bar{\kappa}_A$ is the conductivity of the membrane when wholly in A form and $\bar{\kappa}_B$ when wholly in B form. Further $\bar{m}_A/\bar{m}_B$ was shown to be approximately related to $K_B{}^A$. Thus $\bar{u}_A/\bar{u}_B$ was related to the chemical and electrical properties of the membrane by

$$\bar{u}_A/\bar{u}_B \cong K_B{}^A(\bar{\kappa}_A/\bar{\kappa}_B) \quad \text{(Eq. 89)}$$

($K_B{}^A$ = selectivity constant of the membrane for the exchange of B in membrane and A in solution.)

Using a variety of membranes, Wyllie and Kanaan (601) tested Eq. 87 and 89. They derived intramembrane mobility ratio $\bar{u}_A/\bar{u}_B$ by B.I.P. measurements. This they did by a graphical technique. The potentials were measured by keeping the concentration of AX constant at 0.01 *m* and by varying the molality of BX from 0.01 to 4.0 *m*, and again by keeping BX constant at 0.01 *m* and varying AX from 0.01 to 4.0 *m*. The B.I.P.'s for these two sets of measurements were plotted against the logarithm of the mean molal activities. Excellent straight-line plots were obtained. These straight lines were extended to cut the activity axis at zero potential. Thus two sets of a_A and a_B values for which E was zero were obtained. The ratio a_A/a_B was equal to $\bar{u}_B/\bar{u}_A$. For the membranes used, $K_B{}^A$ values were known and thus $\bar{\kappa}_A/\bar{\kappa}_B$ could be calculated from Eq. 89. These calculated values agreed with the ratio of the directly measured $\bar{\kappa}_A$ and $\bar{\kappa}_B$ values.

Bergsma and Staverman (20) used a variety of membranes and four combinations of ions, H^+–Na^+, K^+–Na^+, H^+–Ag^+, and Na^+–Ag^+ and measured not only the B.I.P.'s but also transport numbers. Using the graphical technique of Wyllie and Kanaan (601), they derived the intramembrane mobility ratios. These ratios were checked directly against transport number ratios (Eq. 84). As

$$\frac{\bar{t}_A}{\bar{t}_B} = \frac{\bar{D}_A\bar{C}_A}{\bar{D}_B\bar{C}_B} = \frac{\bar{D}_A\bar{a}_A\bar{\gamma}_B}{\bar{D}_B\bar{a}_B\bar{\gamma}_A}$$

by the Donnan relation

$$\bar{a}_A/\bar{a}_B = a_A{}'/a_B{}''$$

and so

$$\bar{t}_A/\bar{t}_B = (\bar{D}_A/\bar{D}_B)(a_A{}'/a_B{}'')(\bar{\gamma}_B/\bar{\gamma}_A)$$

$\bar{t}_A/\bar{t}_B$ was measured for each system using a multicompartment cell. They observed definite discrepancies between transport ratios determined by the two measurements. B.I.P. measurements gave lower values except for the system (Na^+–Ag^+). They also noticed that the slope of the straight line plot of B.I.P. against log (activity) was too low in some cases. These deviations from theory were attributed to the neglect of the effects of certain factors in the theory—possibly the effects due to anion and solvent transports.

Dray and Sollner (74) investigated also the concentration dependence of B.I.P.'s. They found B.I.P.'s to be low at concentrations less than 0.05 *N*. This they attributed to diffusion layers controlling part of the diffusion process. Mackay and Meares (300, 301) observed satisfactory agreement, according to their theory, between measured and calculated potentials.

The cases of film diffusion- or partial film diffusion-controlled biionic systems have been discussed by Helfferich (151, 168). In case of complete film diffusion control, the biionic potential which is composed of two Donnan potentials and two interdiffusion potentials in films (no concentration gradient in the membrane) is given by

$$E = \frac{RT}{F}\ln\left(\frac{C'}{C''}\right)\left(\frac{D_A}{D_B}\right) \qquad \text{(Eq. 90)}$$

where C' and C'' are bulk concentrations.

As co-ion transfer across membrane is forbidden in these considerations, these biionic potentials could be very large compared to liquid junction potentials where co-ions are transferred.

For counterions of different valence, the potential is given by (168)

$$E = \frac{RT}{F}\left[\frac{(D_AC' - D_BC'')}{(z_AD_AC' - z_BD_BC'')}\ln\frac{z_AD_AC'}{z_BD_BC''}\right] \qquad \text{(Eq. 91)}$$

For counterions of different valences, it is observed from Eq. 83 and 91 that in case of membrane diffusion control E is dependent on concentration with equal concentrations on either side of the membrane; whereas with film diffusion control, E is independent of concentration. A consequence of this is that the potential may vary greatly (120) and may even have the opposite sign (168, 450).

In the case of partial film control, besides the four potentials controlling complete film diffusion already mentioned, interdiffusion potential across the membrane will have to be taken into account (301).

3. Diffusion in Multiionic Systems

Two solutions containing electrolytes AX, BX, CX, . . . and PX, QX, RX . . . and separated by a membrane constitute a multi (or poly) ionic system. These systems are very interesting in that the situation is similar to conditions existing in a physiological membrane system. A review of salt transport through some physiological membrane systems has been recently presented by Hendricks (177).

Making some simplifying assumptions (counterion valences equal, co-ion flux negligible, no convection, no gradient of activity coefficient) and considering diffusion coefficients and fixed charge density to be constant, Helfferich (165, 176) calculated the fluxes and concentration profiles using the Nernst–Planck flux equations.

The flux equation for the species A was expressed as

$$J_A = \frac{\bar{D}_A(-\omega\bar{C})a_A}{z_i\bar{\gamma}_Ad}\,\frac{M_k}{(L_kM_j - L_jM_k)}\ln\frac{L_kM_j}{L_jM_k} \qquad \text{(Eq. 92)}$$

where a_A is the activity of A in solution, j refers to counterions A, B, C,. . . (originally on the left-hand side of membrane), k refers to P, Q, R,. . . (originally on the right-hand side of membrane), and L and M are defined by $L_i = \sum_i(a_i/\bar{\gamma}_i)$ and $M_i = \sum_i(\bar{D}_ia_i/\bar{\gamma}_i)$.

Considering only two counterions A and B present on the same side of a membrane, Eq. 92 reduces to

$$\frac{J_{\mathrm{A}}}{J_{\mathrm{B}}} = \frac{\bar{D}_{\mathrm{A}} a_{\mathrm{A}} \bar{\gamma}_{\mathrm{B}}}{\bar{D}_{\mathrm{B}} a_{\mathrm{B}} \bar{\gamma}_{\mathrm{A}}} \qquad \text{(Eq. 93)}$$

Neihof and Sollner (372) derived this equation without the activity coefficient terms on qualitative considerations.

From Eq. 93, it follows that the flux of a species depends on the ratio $\bar{\gamma}_{\mathrm{A}}/\bar{\gamma}_{\mathrm{B}}$ and thus on the relative attraction of the membrane for the particular species. Membrane becomes more permeable to the species for which it has the highest attraction, *i.e.*, a low value of $\bar{\gamma}$. But higher attraction results in lower mobility and so the value of the ratio $\bar{D}_{\mathrm{i}}/\bar{\gamma}_{\mathrm{i}}$ may not change very much.

Further the flux ratio is independent of the concentration of the species on the other side of the membrane. This flux ratio $J_{\mathrm{A}}/J_{\mathrm{B}}$ may be derived from the biionic potential data (372).

Equation 92 may be applied to one or several particular counterions present on both sides of a membrane. If a counterion A is present on side (′)(A′) and also on side (″)(A″), the fluxes of A′ and A″ are given by Eq. 92. The net flux of A is given by

$$J_{\mathrm{A}} = J_{\mathrm{A}'} - J_{\mathrm{A}''} = \frac{\bar{D}_{\mathrm{A}}(-\omega\bar{C})(a_{\mathrm{A}'}M_{\mathrm{k}} - a_{\mathrm{A}''}M_{\mathrm{j}})}{z_{\mathrm{i}}\bar{\gamma}_{\mathrm{A}} d(L_{\mathrm{k}}M_{\mathrm{j}} - L_{\mathrm{j}}M_{\mathrm{k}})} \ln \frac{L_{\mathrm{k}}M_{\mathrm{j}}}{L_{\mathrm{j}}M_{\mathrm{k}}} \qquad \text{(Eq. 94)}$$

J_{A} will be positive if $a_{\mathrm{A}'}M_{\mathrm{k}} > a_{\mathrm{A}''}M_{\mathrm{j}}$. This may happen even if $a_{\mathrm{A}'} < a_{\mathrm{A}''}$. The ion will move against its own activity gradient if $M_{\mathrm{j}} < M_{\mathrm{k}}$. That is, provided A ions on side (′) receive less competition from other ions on side (′) in passing through the membrane than A ions on side (″), where the other ions present offer greater competition to A ions to get through the membrane. In effect the diffusion potential due to highly diffusing ions present on side (″) drive the A ion from side (′) to side (″).

4. Multiionic Potentials

The total membrane potential, composed of two Donnan potentials and one interdiffusional potential, is given by (176, 600)

$$E = \frac{kT}{z_{\mathrm{i}}F} \ln \frac{\sum\limits_{\mathrm{i}} \bar{D}_{\mathrm{i}}(a_{\mathrm{i}}'/\bar{\gamma}_{\mathrm{i}})}{\sum\limits_{\mathrm{j}} \bar{D}_{\mathrm{j}}(a_{\mathrm{j}}''/\bar{\gamma}_{\mathrm{j}})} \qquad \text{(Eq. 95)}$$

(i refers to counterions A, B, C, … and j refers to P, Q, R, …).

Equation 95 may be applied to the following membrane system (LX)′|membrane|(LX, MX, NX, …)″ (LX′ is reference solution and LX on side (″) is unknown) to determine the unknown activity of LX in the mixture. If the membrane is ideal and permeable only to L, measurement of the concentration potential would give the activity of a_{L}'' as $E = (RT/z_{\mathrm{L}}F) \ln (a_{\mathrm{L}}'/a_{\mathrm{L}}'')$. But if the membrane is nonideal (permeable to M, N, …, but not to X) assuming valences of counterions to be equal, Eq. 95 may be written as

$$E = \frac{RT}{z_{\mathrm{i}}F} \ln \frac{a_{\mathrm{L}}'}{a_{\mathrm{L}}'' + \left(\dfrac{\bar{D}_{\mathrm{M}}\bar{\gamma}_{\mathrm{L}}}{\bar{D}_{\mathrm{L}}\bar{\gamma}_{\mathrm{M}}}\right)a_{\mathrm{M}}'' + \left(\dfrac{\bar{D}_{\mathrm{N}}\bar{\gamma}_{\mathrm{L}}}{\bar{D}_{\mathrm{L}}\bar{\gamma}_{\mathrm{N}}}\right)a_{\mathrm{N}}'' + \cdots}$$

But $\bar{D}_{\mathrm{M}}\bar{\gamma}_{\mathrm{L}}/\bar{D}_{\mathrm{L}}\bar{\gamma}_{\mathrm{M}}$, etc., may be evaluated by measuring the B.I.P.'s of the respective systems, *viz.*, MX |LX, NX| LX, etc., with equal activities in both solutions. Hence the membrane electrode may be made specific (593). Similarly, Bagg and Gregor (12) used calcium stearate membrane electrode in the system

$$\text{Ag–AgCl} \left| \begin{array}{c} \text{CaCl}_2 \\ (C_1) \end{array} \right| \text{membrane} \left| \begin{array}{l} \text{CaCl}_2\ (C_1) \\ \text{NaCl}\ \ (C_2) \end{array} \right| \text{AgCl–Ag}$$

and measured the B.I.P.'s as a function of the Na^+ ion concentration. Assuming that the potential is due to the diffusion of Na^+ ions through the membrane, they have given an analysis based on Nernst–Planck flux equations which enabled them to estimate the activity of the calcium ions in unknown solutions.

Dray and Sollner (75) have developed a general equation for a multiionic system with a transition zone of ideal selectivity and two solutions containing any number of univalent (permeable) "critical" ions which are cations in case of cation-selective membrane (anions impermeable) and anions in case of anion-selective membrane (cations impermeable). The potential for the system

$$\begin{array}{c|l|c} \text{solution (′)} & \text{diffusion} & \text{solution (″)} \\ C_{\mathrm{A}}' & \quad\text{zone of} & C_{\mathrm{A}}'' \\ C_{\mathrm{B}}' & \quad\text{ideal} & C_{\mathrm{B}}'' \\ C_{\mathrm{C}}' & \quad\text{ionic} & C_{\mathrm{C}}'' \\ & \quad\text{selectivity} & \end{array} \qquad \text{(Type 96)}$$

is expressed by

$$E = \pm \frac{RT}{F} \ln \frac{\bar{U}_{\mathrm{i}}'}{\bar{U}_{\mathrm{i}}''}, \qquad \text{(Eq. 97)}$$

where

$$\bar{U}_{\mathrm{i}}' = \bar{C}_{\mathrm{A}}'\bar{u}_{\mathrm{A}} + \bar{C}_{\mathrm{B}}'\bar{u}_{\mathrm{B}} + \cdots \text{ and } \bar{U}_{\mathrm{i}}'' = \bar{C}_{\mathrm{A}}''\bar{u}_{\mathrm{A}} + \bar{C}_{\mathrm{B}}''\bar{u}_{\mathrm{B}} + \cdots$$

The mobilities are replaced by transport numbers; thus

$$\bar{U}_{\mathrm{i}}'/\bar{U}_{\mathrm{i}}'' = \bar{T}_{\mathrm{i}}'/\bar{T}_{\mathrm{i}}'' \text{ and } \bar{T}_{\mathrm{i}}' + \bar{T}_{\mathrm{i}}'' = 1$$

where

$$\bar{T}_{\mathrm{i}}' = \bar{t}_{\mathrm{A}}' + \bar{t}_{\mathrm{B}}' + \cdots \text{ and } \bar{T}_{\mathrm{i}}'' = \bar{t}_{\mathrm{A}}'' + \bar{t}_{\mathrm{B}}'' + \cdots$$

Equation 97 is therefore written as

$$E = \pm \frac{RT}{F} \ln \frac{\bar{t}_{\mathrm{A}}' + \bar{t}_{\mathrm{B}}' + \ldots}{\bar{t}_{\mathrm{A}}'' + \bar{t}_{\mathrm{B}}'' + \ldots} \qquad \text{(Eq. 98)}$$

The $\bar{t}_i$ values were next referred to a standard state in the polyionic system where $a_A = a_B = a_C = \ldots$, and * indicates the standard values in the polyionic system and ° indicates the same in biionic system. It was shown that

$$\bar{t}_A = \frac{a_A\bar{t}_A^*}{a_A\bar{t}_A^* + a_B\bar{t}_B^* + a_C\bar{t}_C^* + \ldots}, \text{ etc.} \qquad \text{(Eq. 99)}$$

and

$$\bar{t}_A = \bar{t}_A' + \bar{t}_A'',\ \bar{t}_B = \bar{t}_B' + \bar{t}_B'', \text{ etc.}$$

and

$$a_A = a_A' + a_A'',\ a_B = a_B' + a_B''$$

Therefore the transference number in one direction may be written as

$$\bar{t}_A' = (a_A'\bar{t}_A^*/\sum_i a_i\bar{t}_i^*) \text{ and } \bar{t}_A'' = (a_A''\bar{t}_A^*/\sum_i a_i\bar{t}_i^*) \qquad \text{(Eq. 100)}$$

Substituting Eq. 100 into Eq. 98 gives

$$E = \pm\frac{RT}{F}\ln\frac{a_A'\bar{t}_A^* + a_B'\bar{t}_B^* + \cdots}{a_A''\bar{t}_A^* + a_B''\bar{t}_B^* + \cdots} \qquad \text{(Eq. 101)}$$

Particular cases for the potential of the two ionic or three ionic or four ionic system follow from Eq. 101.

For a two ionic system, KCl (a_1)|membrane|LiCl (a_2)

$$E_{2\text{-ionic}} = \frac{RT}{F}\ln\frac{a_1\bar{t}^\circ_K}{a_2\bar{t}^\circ_{Li}}$$

where the ratio of $\bar{t}^\circ_K$ and $\bar{t}^\circ_{Li}$ were evaluated by measuring the B.I.P.'s of the cell KCl (a_1)|membrane|LiCl (a_1). Good agreement between directly measured $E_{2\text{-ionic}}$ values and those calculated using the $\bar{t}^\circ_K/\bar{t}^\circ_{Li}$ ratio was recorded (76, 494). Even mixtures of KCl and LiCl may be used on either side of the membrane. The equation for this case will be

$$E_{2\text{-ionic}} = \frac{RT}{F}\ln\frac{a_K'\bar{t}^\circ_K + a_{Li}'\bar{t}^\circ_{Li}}{a_K''\bar{t}^\circ_K + a_{Li}''\bar{t}^\circ_{Li}}$$

Experimental results agreed with the theory (76).

For testing Eq. 101 for any multiionic system, potentiometric measurements of biionic systems A||B, A||C, A||D, etc., were carried out to derive $\bar{t}^\circ$ values. From $\bar{t}^\circ$ ratios of each system $\bar{t}^*$ values were calculated from the equation

$$\bar{t}_A^* = \frac{1}{1 + (\bar{t}^\circ_B/\bar{t}^\circ_A) + (\bar{t}^\circ_C/\bar{t}^\circ_A) + \cdots}$$

The measured values of potentials were found to agree with the calculated values within the reproducibility of the measurements (77, 494).

Utilizing the assumptions on which the multiionic potential theory is based, Neihof and Sollner (372) derived a general expression for the ratio of the rates of exchange of two co-existing species across a membrane in the system

$$\begin{array}{l|c|l} a_1\ \text{AX} & & \\ a_2\ \text{BX} & \text{membrane} & a_n\ \text{PX} \end{array}$$

The flux ratio equation was

$$J_A/J_B = (a_A'/a_B')(\bar{t}^\circ_A/\bar{t}^\circ_B) \qquad \text{(Eq. 102)}$$

and independent of the nature of the activity of P on the other side. This equation is similar to Eq. 93 but without the activity coefficient terms. The flux ratios calculated from Eq. 102 agreed with the measured fluxes for a number of systems (372).

These flux ratios may become very high. In the course of time, systems of type 96 will drift to Gibbs–Donnan membrane equilibrium. In the final state $a_A'/a_A'' = a_B'/a_B'' = a_C'/a_C'' = \ldots$ In the shift to this state, if the penetrating rates are too different, the faster ion for a short time may reach a concentration on the other side which will be in excess of that of the final equilibrium. Similarly, the concentration of a species in solution ('') may be lowered (373).

E. DIFFUSION OF ELECTROLYTE

When a membrane separates two solutions of the same electrolyte of different concentration, transfer of electrolyte from the concentrated solution side to the dilute solution side takes place. Further, if cations move faster than anions, separation of charges takes place setting up an electric field (diffusion potential) which slows down the faster ion and accelerates the slower ion. This mechanism maintains electroneutrality. Even though no electric field is imposed, an electric potential exists regulating the flow of ions through the membrane.

The fluxes of cations and anions are given by Eq. 7. These may be coupled with the equations of electroneutrality and equality of fluxes.

$$z_+\bar{C}_+ + z_-\bar{C}_- + \omega X = 0$$

$$z_+J_+ + z_-J_- = 0$$

$$J_+, J_- = \text{constant (steady state)}$$

1. Electrolyte Flux

Helfferich (161) has given a detailed mathematical treatment to calculate the steady-state flux of electrolyte and concentration profiles of ions across the membrane. The convection is not taken into account, whereas Schlögl (453), Mackie and Meares (303, 304), and Meares and Ussing (336) have taken convection into account and have given simplified solutions.

Oel (392) solved the flux equations introducing many simplifications. Activity coefficients and convection were omitted, and constancy of mobility and of fixed charge were assumed. The main conclusion of this study is that the rate of diffusion of electrolyte is governed by the diffusion coefficient of the co-ion; with high concentration of active groups and dilute solutions, the membrane acted as a complete barrier to salt diffusion.

Mackie and Meares (303), assuming constancy of fixed groups and of mobility of ions in the membrane, integrated the flux equation using an empirical formula for activity coefficients (302) and obtained for the steady state of diffusion of a 1:1 salt in a cation-exchange membrane, the equation

$$J_+ = \frac{\bar{D}}{d}\left[(C_+{}' - C_+{}'') - \frac{X(\bar{u} - \bar{v})}{2(\bar{u} + \bar{v})}L\right] + \frac{A^*\bar{D}}{d}\left[(2C_+{}' - C_+{}'') - \frac{\mathrm{X}(\bar{u} - \bar{v})}{(\bar{u} + \bar{v})}L\right] - \left[\frac{\bar{D}}{d}(C_+{}' - C_+{}'') + \frac{V^*(C'_-M - C_-{}'')}{1 - M}\right] \quad \text{(Eq. 103)}$$

where $\bar{D} = [(2RT\bar{u}\bar{v})/(\bar{u} + \bar{v})]$, $\bar{u}$ and $\bar{v}$ being the mobilities of cation and anion, respectively. $C_+{}'$ and $C_+{}''$, $C_-{}'$ and $C_-{}''$ are the concentrations (moles/cm.^{3}) of cation and anion at faces (′) and (″) in the membrane. $L = \ln[(\bar{u}C_+{}' + \bar{v}C_-{}')/(\bar{u}C_+{}'' + \bar{v}C_-{}'')]$ and $M = \exp(V^*d/\bar{D})$. X is expressed as moles/cm.^{3} of imbibed solution; A^* is a constant relating the activity coefficients of the ions in the membrane with their concentrations (302); V^* is the rate in cm./sec. of osmotic or hydrostatic flow and is calculated from the equation $V^* = -(d{\cdot}ml)/(1 - V_r)$ where ml is measured in ml./sec. flowing through the hydrogen form of the membrane separating 1 M HCl and conductivity water; and the minus sign appears to indicate that the flow is in the opposite direction to salt flow. Ionic mobilities were obtained using the relation

$$\bar{u} = u\left[\frac{1 - V_r}{1 + V_r}\right]^2 \quad \text{(Eq. 104)}$$

The three terms on the right-hand side of Eq. 103 are due to total ionic gradient, the activity coefficient gradient, and the convection, respectively.

Equation 103 has been tested for the diffusion of five different salts at three different temperatures through Zeokarb 315 disk (304). Calculated fluxes were found to be larger than observed fluxes, the discrepancy being greater at low concentrations. These differences were attributed to ionic immobilization by the fixed charges in dilute solutions and to the neglect of electrophoretic effect in concentrated solutions.

The flux ratio equation of Ussing (566) derived in connection with studies of biological interest and used to distinguish between active and passive transport through biological membranes (567) has been presented by Meares and Ussing (336) in the form

$$\ln\left(-\frac{J_a}{J_b}\right) = \ln\frac{C_a{}'}{C_b{}''} + \ln\frac{\gamma_a{}'}{\gamma_b{}''} + \frac{V\Delta P}{RT} + \frac{zF\Delta\psi}{RT} + \frac{V^*d}{\bar{D}_b} \quad \text{(Eq. 105)}$$

where $C_a{}'$ and $C_b{}''$ are the concentrations of solutions containing isotopes a and b on the two sides (′) and (″). The other terms have their usual significance. Hoshiko and Lindley (194) have derived this from the phenomenological equations of irreversible thermodynamics.

Using Zeokarb 315 and three concentration steps from 0.1, 0.5, and 1.0 M NaCl solutions, the flux of cations was measured in each direction by labeling in turn the concentrated and the dilute solution with $\mathrm{Na^{24}}$. Similarly, the fluxes of anions were also measured using $\mathrm{Cl^{36}}$. The flux ratios thus obtained by measurement were compared with values calculated using Eq. 105. Throughout ΔP was maintained at zero. Observed values were found to be larger but omission of the activity coefficient term made the agreement between observed and calculated flux ratio values better.

From the measured values of J_a and J_b for $\mathrm{Na^+}$, the net flux values were computed. These values were compared with the values calculated using the diffusion Eq. 103 assuming the applicability of the Nernst–Einstein equation. The experimental values were about 8% larger than those predicted by Eq. 103.

Calculation of net Na flux also enabled chloride flux ratios to be calculated from one side experiment with chloride ions. If $J_{\mathrm{Cl^-}}$ was measured, the flux ratio was given by $J_{\mathrm{Cl^-}}/(J_{\mathrm{Cl^-}} + J_{\mathrm{net}})$ where J_{net} was the net Na flux at the appropriate concentrations. The agreement between calculated and observed flux ratios was considered good.

Sethu (479) measured $\mathrm{NH_4Cl}$ diffusion through Permplex C-10 and C-20 cation-exchange membranes and obtained a value of 3.9×10^{-7} cm.^{2} sec.$^{-1}$ for the diffusion coefficient of the electrolyte. NaCl permeability through a sulfonated polythene-type membrane has been measured as a function of external concentration (73). The permeability decreased with increase in external concentration above 1 N.

Electrolyte transfer through uncharged membranes should occur in the same way as it is observed in charged membranes except for the differences that are due to the presence of fixed charges. In any case, diffusion in uncharged membrane should parallel co-ion transfer through ion-exchange membranes at moderate concentrations. As a consequence it is reasonable to expect the Meares function (Eq. 104) relating membrane phase mobility to aqueous phase value to give good agreement. But no such data for nonselective membranes exist.

Peterson and Livingston (415) measured the apparent rates of diffusion of KCl through untreated cellophane and cellophane treated with dialdehyde starch and found the diffusion coefficients to be 2.81×10^{-7} and 0.43×10^{-7} cm.^{2} sec.$^{-1}$, respectively. Treated cellophane showed decreased solubility to KCl. In general, the values of electrolyte diffusion through nonexchange membranes seem to be lower than in selective membranes. The values are determined by the membrane pore size and water content. Selective membranes invariably contain more water than nonselective membranes. It is therefore to be expected on the basis of the presence of some extra groups which are usually polar and possibly hydrated that the diffusion coefficients in selective membranes will be larger. These particular properties are of considerable industrial importance, as they determine the ultimate usefulness of the membrane in industrial dialysis and electrodialysis. These aspects are discussed by Tuwiner (559).

Other aspects of dialysis as an industrial process for effecting separation of an acid and electrolytes or nonelectrolytes are described in a recent paper by Japanese investigators (387). They have used a new weakly basic anion-exchange membrane of high capacity to separate sulfuric acid from its mixture with nickel sulfate.

A class of membranes which present interesting permeability characteristics has been investigated by a group of Indian workers. These membranes, whose preparation is described in part B, are formed from inorganic precipitates. Ferricyanide membranes of Co, Ni, and Ag (146) were found permeable to electrolytes KCl, K_2SO_4, and $K_3Fe(CN)_6$, following the order KCl > K_2SO_4 > $K_3Fe(CN)_6$. This order was reversed when electrolyte adsorption was studied. An isotonic sucrose method credited to Weiser (581) was employed to measure electrolyte transfer. This method was later replaced by a constant flow technique (10, 145, 584), and using thorium tungstate membranes, the permeability of a number of electrolytes were measured (307). The order of permeability was KCl > NaCl > K_2SO_4 > Na_2SO_4 > Na_2WO_4. The membranes were also used after a pretreatment with either Na_2WO_4 or thorium nitrate. Pretreatment with the former did not show any change, whereas with the latter, the rates of diffusion of the electrolytes increased and the order of permeability remained the same. The increase was attributed to the peptizing action of thorium nitrate on the thorium tungstate gel membrane. The order of electrolyte adsorption was again in the reverse order. These studies were extended to cobalt and manganese ferrocyanide membranes (308) and to chromic ferro- and ferricyanide membranes (309).

The valence effect on the permeability of various electrolytes was well defined, being in the order univalent > bivalent > tervalent. The permeability of various anions (with a common cation) were in the order $Cl^- > Br^- > NO_3^- > CNS^- > CH_3COO^- > SO_4^{2-} > Fe(CN)_6^{3-} > Fe(CN)_6^{4-}$. This is the reverse of the order found in ordinary aqueous solutions. These inorganic precipitates being of a colloidal nature exhibited very strong adsorption characteristics. The order of adsorbability was again the reverse of the above order. Membrane potentials arising across these membranes were also measured and related to permeability parameters by a Freundlich adsorption-type equation

$$E = aP^{1/n}$$

where E is the membrane potential, P is the permeability, and a and n are constants characterizing the membrane and were evaluated graphically.

Transport of material, through a barrier, *e.g.*, glass frit, when it separated a 1:1 electrolyte of different concentration and also when it separated a 1:1 electrolyte of the same concentration has been measured and analyzed (261, 280). A general theoretical description of electrolyte and solvent transport across charged membranes has also been given (280, 282, 344).

Using cellulose membranes, Woermann and Spei (594) investigated the transport of halogen ions which were initially the same on either side of the membrane. But they were mixed with other electrolytes to maintain a diffusion potential and convection. In the steady state an increase in concentration up to 70% was observed on one side of the membrane compared with the starting quantity. The diffusion potential, volume flux, and halogen concentration difference in the steady state were related by

$$E = \frac{RT}{F}\ln\frac{C'}{C''} + \left(\frac{RT}{F}\right)\left(\frac{V^*d}{\bar{D}_{\text{halogen}}}\right)$$

The results were discussed from the standpoint of this equation.

2. Osmosis

When there is transfer of electrolyte from the more concentrated solution side to the dilute solution side, there is also transfer of solvent in the opposite direction. In case of nonionic membranes which are completely impermeable to solutes (semipermeable) the solvent flow is from the dilute to the concentrated solution and is proportional to the osmotic pressure difference between the two solutions. If solutions on either side of the membrane are confined to closed chambers with capillary tubing attached, the level of liquid in the capillary of the concentrated solution chamber rises until the hydrostatic counterpressure balanced the osmotic pressure difference which is given entirely by the total concentrations of the dissolved species (electrolytes or nonelectrolytes). Osmosis is said to be normal if the simple Van't Hoff's law was obeyed (351).

With charged membranes and electrolytes as solutes, the osmotic behavior may become anomalous. If the rise in the height of the level of liquid in the capillary of the chamber containing stronger solutions is higher than the theoretical height, the flow is called anomalous positive osmosis. On the other hand, if there is a fall, it is called anomalous negative osmosis. Even with cellophane and glass membranes using polyethylene oxides in different solvents, both positive and negative anomalous osmosis have been observed (85).

Grim and Sollner (121, 122) have carried out exact measurements of anomalous osmosis across charged membranes using different electrolyte and nonelectrolyte solutions. The total osmotic flow is composed of two parts, one the normal component and the other the abnormal component. The normal flow was estimated by use of the electrolyte as its own reference under conditions of zero net charge on the membrane. They used both protamine– and oxyhemaglobin–collodion membranes which had clearly defined isoelectric points. A membrane maintained at its isoelectric point gave only the normal osmotic flow, but when it was put into a charged state by changing the pH, it gave a total flow which had the abnormal component. The difference between the two flows was called anomalous osmosis. Both positive and negative anomalous osmosis were observed.

Anomalous osmosis was considered to be due to electroosmosis brought about spontaneously by the electrolyte diffusion. The mechanism for the maintenance of a continuous flow was worked out on the basis that membrane pores were grossly heterogeneous. A brief summary is given by Sollner (488).

In contrast, without making any assumption about the pore structure, Schlögl (453) has developed a quantitative theory based on Nernst–Planck flux equations. He solved the flux equation for 1:1 electrolyte assuming constancy of activity coefficients, diffusion coefficients, fixed charge concentration, specific flow resistance, and fractional pore volume. The final result is very complicated. Profiles of ion concentration, of potential, and of pressure have been calculated. A summary appears elsewhere (589).

The liquid in the pores of a membrane is subject to two forces when an electrolyte diffuses through the membrane in the direction of the gradient. One is the internal gradient of pressure and the other is the gradient of electric field.

Effect of pressure alone is to allow solvent to move from dilute solution (high swelling pressure in the membrane) to concentrated solution. The strength of the electric field set up by electrolyte diffusion depends on the mobilities of the diffusing ions. Strong fields will be set up if there is a large difference in the mobilities of the counterion and co-ion. If the counterion moved faster, it would create a space charge on the dilute solution side, and the electric field, besides bringing about the equality of fluxes, would drive the pore liquid towards the concentrated solution. Electric field thus adds to the effect of the pressure creating positive osmosis. On the contrary, if the co-ion moved faster, an electric field of opposite sign would be created which would drive the pore liquid in the opposite direction. If the effect of the electric force is greater than that of the pressure force, negative osmosis is obtained. The other factor controlling the relative effects of electric field and pressure is the resistance of the membrane material to solvent flow.

If the membrane offers the least resistance to solvent flow and there are ions of low mobility, pressure gradient alone can generate an electric field in a highly charged membrane to produce a positive osmosis strong enough to provide enough energy to carry the electrolyte from the dilute solution side to the concentrated solution side.

Kobatake (233, 234) has derived the equation

$$J_v = (\text{constant})\left[-A(C_2 - C_1) + \ln\frac{C_2}{C_1} - B\ln\left(\frac{C_2+\beta}{C_1+\beta}\right)\right] \quad \text{(Eq. 106)}$$

where J_v is the volume flow and A, B, and β are constants. C_1 and C_2 are solution concentrations on the two sides of the membrane. The first term gives the contribution to volume flow of pressure difference and the last two terms give the contribution of electric potential difference. When the latter quantity becomes greater than the former, abnormal positive or negative osmosis occurs. Analytical curves of osmotic flow rate have been drawn assuming reasonable values for the constants. These constants are functions of k_2 and k_3, which are not directly measurable for the membrane.

In another paper Kobatake and Fujita (235) have developed a theory of anomalous osmosis based on the thermodynamics of irreversible processes assuming a capillary model for the charged membrane. The theory has some concepts expounded by Sollner, although the approach is completely different. Its predictions agree satisfactorily with the experimental results of Grim and Sollner (121, 122).

Kedem and Katchalsky (218, 221) have also worked out a set of equations based on the thermodynamics of irreversible processes but employing the frictional coefficients of the membrane theory of Spiegler (507).

Membrane is characterized by two constants ω_s and σ whose interrelationship is derived in terms of the frictional coefficients, *viz.*

$$\sigma = 1 - \frac{\omega_s \bar{V}_s}{L_p} - \frac{K f_{sw}}{\varphi_w(f_{sw} + f_{sm})} \quad \text{(Eq. 107)}$$

where the partition coefficient $K = (C_s\varphi_w{}^2)/X$ and L_p is the filtration coefficient of the membrane.

As $\omega_s \rightarrow 0$, $\sigma = 1$ (complete impermeability to solute) and $\sigma = 0$ (membrane nonselective). If both water and solute permeate through different routes, $f_{sw} = 0$.

$$\sigma = 1 - \frac{\omega_s \bar{V}_s}{L_p} \quad \text{(Eq. 108)}$$

In the case of electrolyte permeation the number of frictional coefficients instead of being only f_{sw}, f_{sm}, and f_{wm} (*i.e.*, in the case of nonelectrolytes) becomes f_{12}, f_{1w},

f_{1m}, f_{2w}, f_{2m}, and f_{wm} (1 and 2 indicate cation and anion, respectively).

Assuming $f_{sw} = f_{1w} + f_{2w}$, Eq. 107 becomes

$$\sigma = 1 - \frac{\omega_s \bar{V}_s}{L_p} - \frac{K(f_{1w} + f_{2w})}{\varphi_w(f_{1w} + f_{2w} + f_{1m} + f_{2m})} \tag{Eq. 109}$$

For a membrane of high charge density, counterion concentration being high f_{1w} and f_{1m} may be neglected, in comparison to f_{2w} and f_{2m}. As co-ion concentration is very small, being repelled by the membrane, it will be more attached to water and so f_{2m} may be neglected compared to f_{2w}. Therefore

$$\sigma = 1 - \frac{\omega_s \bar{V}_s}{L_p} = \frac{K(f_{1w} + f_{2w})}{\varphi_w f_{2w}} \tag{Eq. 110}$$

As the model chosen is such that friction is uninfluenced by the membrane

$$\frac{f_{1w} + f_{2w}}{f_{2w}} = \frac{f^{\circ}_{1w} + f^{\circ}_{2w}}{f^{\circ}_{2w}}$$

where f°_{1w} and f°_{2w} are the friction coefficients in water. As the frictional coefficients are inversely proportional to ionic mobilities in solution

$$\frac{f^{\circ}_{1w} + f^{\circ}_{2w}}{f^{\circ}_{2w}} = \frac{u + v}{u} = \frac{1}{t_1}$$

Equation 110 becomes

$$\sigma = 1 - \frac{\omega_s \bar{V}_s}{L_p} - \frac{C_s \varphi_w}{X} \frac{1}{t_1} \tag{Eq. 111}$$

At low salt concentration $\frac{\omega_s \bar{V}_s}{L_p}$ and $\frac{C_s \varphi_w}{X t_1}$ are negligible and $\sigma \rightarrow 1$, and as salt increases σ decreases. At low salt concentration σ will decrease if t_1 is lower. If t_1 is very small, there will be a certain concentration at which σ will vanish and, beyond that concentration, assume negative values. As $\sigma = (\Delta P)/(\Delta \pi_S)$, ΔP becomes negative. That is, in Schlögl terminology (453) the pressure force becomes less than the electric field force created by the diffusion process. Theoretical curves according to Eq. 111 presented for 1:1, 1:2, and 2:1 salts (218, 221) show that divalent co-ion increases selectivity of the membrane while a divalent counterion, which by virtue of its charge decreases more effectively the effect of the fixed charges of the membrane matrix, diminishes σ. So divalent counterions of low mobility (t_1 small) should increase negative osmosis. For positive membranes (protamine–collodion membranes) with solutions of acids, anomalous osmosis is in the order $H_3PO_4 > H_2SO_4 > HCl$ (489).

Kedem and Katchalsky (218, 221) have used this theoretical approach to test the experimental results of Loeb (284) and of Grim and Sollner (121, 122) and find satisfactory agreement.

Similar theoretical reasoning has been applied (218, 223) to the consideration of flows through complex membranes which may be formed by simple combination of homogeneous membrane elements. The two simplest combinations are a parallel and a series arrangement. With these two configurations, other very complex structures may be obtained. In a parallel array, the same total force operates on each element but the flows passing through the elements differ according to their ω_s and σ characteristics. In series combination forces acting on each element will be different whereas the flows will be the same passing through each element.

Kedem and Katchalsky (218, 223) have shown in case of nonelectrolytes that in a parallel array, the solute permeability at zero volume flow is not given by

$$\omega_s = x_1\omega_{s1} + x_2\omega_{s2}$$

but by

$$\omega_s = x_1\omega_{s1} + x_2\omega_{s2} + C_s\frac{(\sigma_1 - \sigma_2)^2}{R_1 + R_2}$$

where $R_i = 1/L_p$ and x_i is the fraction of area occupied by an element i. The term $C_s(\sigma_1 - \sigma_2)^2/(R_1 + R_2)$ is due to circulation of solvent through the elements. To keep over-all flow zero, the flow through one element is compensated by an opposite flow passing through the other. When $\sigma_1 = \sigma_2$, circulation disappears. As circulation increases entropy production, higher values are obtained for ω_s.

Similarly, circulation effect has been shown to be more pronounced in case of permeation of ions through charged membranes. In case of salt gradient, flow of cations through the cation-selective element and an equivalent flow of anions through the other element, gave over-all zero flow of current, although there was increased solute permeability due to circulation of current arising from circulation of ions.

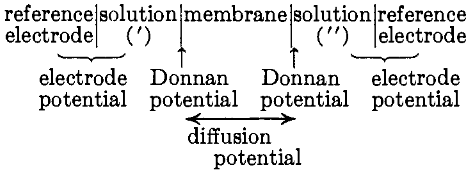
Neihof and Sollner in a number of neatly conceived experiments have observed this circulation effect (370) and the results obtained (370, 371) have been unambiguously analyzed. The salt permeability in these cases may increase to such an extent that extremely large anomalous osmosis may be obtained.

In a recent paper, Carr and Sollner (42) have described electroosmotic effects produced by local electrical circuits arising when cation-selective and anion-selective membranes are interposed between electrolyte solutions of different concentration. The membranes were so chosen in regard to their porosity and pore geometry as to exhibit maximum effects. A system with an electropositive membrane 50 cm.^{2} and electronegative membrane 120 cm.^{2} gave internal currents up to 20 ma. Even biionic systems were shown to exhibit electroosmosis. These results seem to substantiate the contention of Sollner that anomalous osmosis is due to heteroporous character of the membrane. If heteroporosity is regarded as a parallel array of elements of differing pore radii, according to the theoretical considerations already presented, the flows should so interact as to give negative values for σ to cause anomalous osmosis.

3. Membrane Potentials

It was observed that when a membrane separated two electrolyte solutions, an electric field (diffusion potential) maintained electroneutrality and brought about the balance of fluxes. The magnitude and sign of the potential depended on the nature of the membrane and the permeating species. If the membrane carried no fixed charge, the potential was the same as the liquid junction potential. Whereas if the membrane carried some fixed charges, the magnitude of the potential was determined by the concentration of the external solution and its sign by the nature of the fixed charge. However, it is found that many membranes considered completely inert, because of the absence of measurable quantity of fixed charge, have a tendency to generate an electric potential. This was attributed to adsorption of cations or anions to make them anion or cation selective. The work of Sollner and of others has shown that in the of case nitrocellulose, the electromotive activity was due to the end and stray carboxyl groups of the nitrocellulose (277, 492–496). Membranes like these can be made cation selective (369) or anion selective (112) by making them adsorb large anions or large cations which may be held loosely or firmly. This property is very typical of many uncharged polymer membranes.

The electrical potentials arising across an ionic membrane separating different salt solutions are usually measured by constructing cells of the type



(Type 112)

The reference electrode may be reversible electrodes of the type Ag–AgCl standing in chloride solutions or calomel connected to the solutions *via* KCl–agar bridges. In the former case the total potential measured is made up of two components, one the electrode potential and the other the membrane potential. In the case of the latter, the cell potential gives directly the membrane potential. These measurements to evaluate membrane potentials are not unambiguous (510). They involve all the extra nonthermodynamic assumptions about single ion activity coefficients, diffusion potential at KCl bridges, etc., typical of transport cells of classical electrochemistry. These types of measurements have become almost routine procedures to characterize the selectivity of membranes.

The theoretical approaches made to calculate the e.m.f.'s of cells of Type 112 fall under three groups already described. They are, however, treated under the following heads: (a) the idealized theory of TMS (342, 531–534) and its refinements (451, 452), (b) pseudothermodynamic approach due to Scatchard (446–448) and the treatments based on the thermodynamics of irreversible processes (180, 225, 232, 290, 513), and (c) a kinetic approach based on the theory of absolute reaction rates (365, 366).

a. The TMS Theory

The total membrane potential is considered to be composed of two Donnan potentials ψ_{Don}' and ψ_{Don}'' at the two solution–membrane interfaces (′) and (″) and a diffusion potential ϕ arising from unequal concentrations of the two membrane faces. The membrane surfaces were assumed to be in a state of equilibrium instantaneously established, although this seemed less true as the concentration gradient and consequent steady diffusion of electrolyte and solvent became appreciable.

The Donnan equilibrium governed the distribution of solute and osmotic forces determined the distribution of water between the two phases. The activity of the mobile ions in the two phases is given by the Donnan relation (178, 180, 273, 302)

$$RT \ln \frac{a_{\mathrm{i}}}{\bar{a}_{\mathrm{i}}} + zF(\psi - \bar{\psi}) = (\bar{P} - P)\bar{V}_{\mathrm{i}} \qquad \text{(Eq. 113)}$$

where $\psi - \bar{\psi}$ is the Donnan potential difference and $\bar{P} - P = \pi$ is the difference between swelling pressure in the membrane and the hydrostatic pressure in the outside solution.

Evaluation of $\psi - \bar{\psi}$ depends on the assignment of values for single ion activity coefficients for the ions in the membrane phase and in the solution. γ_{i} can be computed for dilute solutions using the usual formulas but no such calculation is possible for $\bar{\gamma}_{\mathrm{i}}$.

For any electrolyte, ij, in contact with a charged membrane, the condition of equilibrium is $\mu_{\mathrm{ij}} = \bar{\mu}_{\mathrm{ij}}$ and the $\psi - \bar{\psi}$ term in Eq. 113 disappears giving the relation (178, 180, 273)

$$\ln \frac{a_{\mathrm{ij}}}{\bar{a}_{\mathrm{ij}}} = \pi \bar{V}_{\mathrm{ij}}/RT \qquad \text{(Eq. 114)}$$

If the electrolyte dissociates into ν_{i} and ν_{j} ions and remembering that $\gamma_{\pm} = (\gamma_{\mathrm{i}}^{\nu_{\mathrm{i}}}\gamma_{\mathrm{j}}^{\nu_{\mathrm{j}}})^{1/\nu}$ where $\nu = \nu_{\mathrm{i}} + \nu_{\mathrm{j}}$, Eq. 114 becomes

$$\ln \frac{m_{\mathrm{i}}^{\nu_{\mathrm{i}}}\, m_{\mathrm{j}}^{\nu}\ \gamma_{\pm}^{\nu}}{\bar{m}_{\mathrm{i}}^{\nu}\ \bar{m}_{\mathrm{j}}^{\nu_{\mathrm{j}}}\ \bar{\gamma}^{\nu}_{\pm}} = \frac{\pi \bar{V}_{\mathrm{ij}}}{RT} \qquad \text{(Eq. 115)}$$

Equation 115 combined with the equation of electroneutrality gives the expression for $\bar{a}_{+}$ or $\bar{a}_{-}$ within the membrane. For a cation-selective membrane and 1:1 electrolyte, $\bar{a}_{+}$ and $\bar{a}_{-}$ are given by (178, 180)

$$\bar{a}_{+} = \frac{X\bar{\gamma}_{+}}{2} + \left[\frac{(X\bar{\gamma}_{+})^{2}}{4} + \frac{a_{\pm}^{2}\ \bar{\gamma}_{+}^{2}}{\bar{\gamma}_{+}^{2}e^{\pi \bar{V}/RT}}\right]^{1/2}$$

$$\bar{a}_- = -\frac{X\bar{\gamma}_-}{2} + \left[\frac{(X\bar{\gamma}_-)^2}{4} + \frac{\bar{a}_\pm{}^2\bar{\gamma}_-{}^2}{\bar{\gamma}_\pm{}^2 e^{\pi V/RT}}\right]^{1/2} \quad \text{(Eq. 116)}$$

Equation 116 may be rewritten as

$$\bar{a}_+ = \frac{X\bar{\gamma}_+}{2}\left[1 + \{1 + \xi^2\}^{1/2}\right]$$

$$\bar{a}_- = \frac{X\bar{\gamma}_-}{2}\left[-1 + \{1 + \xi^2\}^{1/2}\right] \quad \text{(Eq. 117)}$$

where

$$\xi = \frac{2a_\pm}{X\bar{\gamma}_\pm e^{\pi V/2RT}} \quad \text{(Eq. 118)}$$

The Donnan potentials at the two interfaces (′) and (″) are given by Eq. 113. Thus

$$\psi_{\text{Don}}' = \psi' - \bar{\psi}' = \frac{RT}{F}\ln\frac{a_+'}{\bar{a}_+'} + \frac{1}{F}\pi' V_+' = \frac{RT}{F}\ln\frac{\bar{a}_-'}{a_-'} + \frac{1}{F}\pi' V_-'$$

$$\psi_{\text{Don}}'' = \psi'' - \bar{\psi}'' = \frac{RT}{F}\ln\frac{\bar{a}_+''}{a_+''} - \frac{1}{F}\pi'' V_+'' = \frac{RT}{F}\ln\frac{a_-''}{\bar{a}_-''} - \frac{1}{F}\pi'' V_-'' \quad \text{(Eq. 119)}$$

$$\psi_{\text{Don}}' + \psi_{\text{Don}}'' = \frac{RT}{F}\ln\frac{a_+'}{\bar{a}_+'} + \frac{RT}{F}\ln\frac{\bar{a}_+''}{a_+''} + \frac{1}{F}(\pi' V_+' - \pi'' V_+'') = \frac{RT}{F}\ln\frac{\bar{a}_-'}{a_-'} + \frac{RT}{F}\ln\frac{a_-''}{\bar{a}_-''} + \frac{1}{F}(\pi' V_-' - \pi'' V_-'') \quad \text{(Eq. 120)}$$

The diffusion potential $\phi = \bar{\psi}'' - \bar{\psi}'$ within the membrane was equated to that of a constrained liquid junction. Teorell for 1:1 electrolyte used the expression

$$\phi = \left(\frac{\bar{u} - \bar{v}}{\bar{u} + \bar{v}}\right)\left(\frac{RT}{F}\right)\ln\frac{\bar{u}\bar{m}'_+ + \bar{v}\bar{m}'_-}{\bar{u}\bar{m}''_+ + \bar{v}\bar{m}''_-} \quad \text{(Eq. 121)}$$

Substituting for $\bar{m}_+$ and $\bar{m}_-$ from Eq. 117, Eq. 121 becomes

$$\phi = \bar{U}\frac{RT}{F}\ln\left[\frac{X'\{\bar{U} + (1 + \xi'^2)^{1/2}\}}{X''\{\bar{U} + (1 + \xi''^2)^{1/2}\}}\right] \quad \text{(Eq. 122)}$$

where $\bar{U} = (\bar{u} - \bar{v})/(\bar{u} + \bar{v})$.

The total membrane potential (sum of Eq. 120 and 122) combined with the electrode potential of the reference electrode given by

$$E_{\text{ref}} = \frac{RT}{F}\ln\frac{a_-'}{a_-''} \quad \text{(Eq. 123)}$$

gave the e.m.f. of the membrane cell (Type 112). Hence

$$E = \frac{RT}{F}\ln\frac{\bar{a}_-'}{\bar{a}_-''} + \frac{1}{F}(\pi' V_-' - \pi'' V_-'') + \bar{U}\left(\frac{RT}{F}\right)\ln\left[\frac{X'\{\bar{U} + (1 + \xi'^2)^{1/2}\}}{X''\{\bar{U} + (1 + \xi''^2)^{1/2}\}}\right] \quad \text{(Eq. 124)}$$

Substituting for $\bar{a}_-'$ and $\bar{a}_-''$ from Eq. 117, Eq. 124 becomes

$$E = \frac{RT}{F}\ln\left[\frac{\bar{\gamma}_-'X'\{-1 + (1 + \xi'^2)^{1/2}\}}{\bar{\gamma}_-''X''\{-1 + (1 + \xi''^2)^{1/2}\}}\right] + \frac{1}{F}(\pi' V_-' - \pi'' V_-'') + \bar{U}\left(\frac{RT}{F}\right)\ln\left[\frac{X'\{\bar{U} + (1 + \xi'^2)^{1/2}\}}{X''\{\bar{U} + (1 + \xi''^2)^{1/2}\}}\right] \quad \text{(Eq. 125)}$$

Experimentally measurable quantities in Eq. 125 are X and ξ. Even then X' and X'' as measured in separate equilibrium experiments may not be related to actual values at the interfaces of the membrane. Further $\bar{\gamma}_-$ and $e^{\pi V/RT}$ are indeterminable without making some assumptions.

Teorell, Meyer, and Sievers (342, 531–534) assumed all single ion activity coefficients to be unity, the pressure–volume term to be negligible, and X to remain constant at all values of external electrolyte concentrations. The implications of these assumptions have been discussed by Hills, Jacobs, and Lakshminarayanaiah (180).

Introducing these assumptions, TMS Eq. 125 suitable for a highly idealized system becomes

$$E = \frac{RT}{F}\left[\bar{U}\ln\frac{\sqrt{(4a'^2 + X^2)} + \bar{U}X}{\sqrt{(4a''^2 + X^2)} + \bar{U}X} + \ln\frac{a''}{a'}\,\frac{\sqrt{(4a'^2 + X^2)} + X}{\sqrt{(4a''^2 + X^2)} + X}\right] \quad \text{(Eq. 126)}$$

Three special cases arise. (1) When the outside concentration is large compared to the fixed ion concentration, *i.e.*, $a \gg X/2$, Eq. 126 reduces to

$$E = \frac{RT}{F}(t_+ - t_-)\ln\frac{a'}{a''} \quad \text{(Eq. 127)}$$

(2) When $a \ll X/2$, Eq. 126 reduces to the Nernst equation

$$E_{\max} = -\frac{RT}{F}\ln\frac{a'}{a''} \quad \text{(Eq. 128)}$$

corresponding to the maximum potential across a permselective membrane. (3) When $a \cong X/2$, a simplification is difficult. But if the approximations made in case 1 are carried through, Eq. 126 reduces to

$$E = \frac{RT}{F}(\bar{t}_+ - \bar{t}_-) \ln \frac{a'}{a''}, \qquad \text{(Eq. 129)}$$

where $\bar{t}_+$ and $\bar{t}_-$ are the transport numbers in the membrane phase. This equation may be rearranged to

$$E/E_{\max} = 2\bar{t}_+ - 1$$

$$\bar{t}_+ = (E/2E_{\max}) + 0.5 \qquad \text{(Eq. 130)}$$

Equation 130 has often been used to calculate transport numbers in the membrane phase from membrane potential measurements (86, 440). The transport number so calculated is used to evaluate the permselectivity P_s of a membrane which is given by (590)

$$P_s = \frac{\bar{t}_+ - t_+}{1 - t_+} \qquad \text{(Eq. 131)}$$

The earliest systematic measurements of membrane potential were made by Michaelis (345) and were later considerably added to by Sollner and Gregor (497) and by Marshall and Ayers (316, 317) who used collodion and zeolite membranes, respectively. Wyllie and Patnode (602) used heterogeneous membranes made by imbedding ion-exchange resin beads in inert binders. Hills, Kitchener, and Ovenden (182) used PMA membranes and measured membrane potentials with KOH solutions using reversible Hg–HgO electrodes. Mauro and Finkelstein (325) have used a multicompartment cell formed by partitioning a cylindrical Lucite tubing with cellophane sheets. Each compartment had either gelatin or PSA solution to provide the fixed charge. Both the concentration profiles and potentials were determined. It was shown for KCl that as the fixed charge concentration was increased, the potential also increased. The results were considered to support, though in a very crude way, the main tenets of the TMS theory.

In nearly every one of the cases considered above, the solution concentrations and concentration differences used were small and the observed potentials approached the Nernst values. Some instances of lower values were ascribed to diffusion through uncharged pores (490). Most of the important work carried out using collodion or modified collodion membranes is contained in the reviews by Sollner (492–496).

The main result of all these investigations was that membrane potentials can be determined with reasonable accuracy and that for dilute external solution, the membrane potential is close to the maximum value. With more concentrated solution this is not so; the membrane potential is progressively smaller than the maximum value. This is readily explained by decrease in selectivity of the membrane, the increasing concentration of co-ions, and the diffusion of electrolyte through the membrane. It is possible to express this decreasing selectivity by a transport number calculated using Eq. 130. But in no case has a convincing evaluation of membrane potential been made from first principles other than when it has attained its maximum thermodynamic value.

The principal defects of the TMS theory are the neglect of activity coefficients (182, 587) and transport of water through the membrane (505, 587).

Graydon and Stewart (113) using cross-linked PSSA membranes examined the observed membrane potentials from the standpoint of co-ion and water transfer, both of which diminish the membrane potential. They concluded that the deviations from the ideal values were due more to the transfer of water than to transfer of co-ion. Assuming that the mobilities of the ions were equal to those in water and that the activity coefficients were unity, they estimated not only the magnitude of the co-ion contribution but also calculated the number of moles of water transferred through the membranes. These values were indeed considered very approximate.

For the first time, Hills, Jacobs, and Lakshminarayanaiah (181) have put the TMS theory to a rigorous test by taking all the neglected factors into account. They measured the electrolyte uptake and calculated the activity coefficients in the membrane phase using Donnan Eq. 115. They measured also counterion and water transport numbers. $\bar{U}$ was evaluated from the equation

$$\bar{U} = \frac{\bar{t}_+\bar{m}_- - \bar{t}_-\bar{m}_+}{\bar{t}_+\bar{m}_- + \bar{t}_-\bar{m}_+}$$

where $\bar{t}_+$ and $\bar{t}_-$, $\bar{m}_+$ and $\bar{m}_-$ were determined as functions of external concentration. As all the quantities in Eq. 125 are known, E was calculated. The contribution of water transfer ψ_w to the total membrane potential was evaluated from the equation

$$\psi_w = -\frac{RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} \bar{t}_w d \ln a_w \qquad \text{(Eq. 132)}$$

using a constant average value for t_w determined directly from separate experiments as a function of external concentration. The results of these calculations are given in Table XII along with observed e.m.f.'s. The agreement is very unsatisfactory. This type of work was repeated by Lakshminarayanaiah and Subrahmanyan (278) for another membrane system containing PSA membranes. Here again the agreement was very poor (Table XIII).

In spite of these rigorous tests indicating its limitations, the TMS theory has a simplicity and an appeal to the unsophisticated. It has been used in the way illustrated by Meyers and Bernfeld (341) to determine the fixed charge capacity of membranes, the values of which are too low and hence very difficult to determine by the usual exchange reactions.

Theoretical concentration potentials for a cation-exchange membrane–1:1 electrolyte and a concentration ratio kept constant, $(C'/C'') = 2$, were calculated as a function of log (X/C'') for different mobility ratios $(\bar{u}/\bar{v})$ and plotted as shown in Figure 5. The experimental potential values were plotted in the same graph as a function of $-\log C''$. The experimental curve was shifted horizontally until it coincided with one of the theoretical curves. The shift gave log X and the coinciding theoretical curve gave $(\bar{u}/\bar{v})$. This technique has been used by Kumins and London (262) to estimate the capacity of thin polymer membranes of polyvinyl chloride and vinyl acetate, of purified polyvinyl acetate, and of polyvinyl acetate. It has also been used by Baxter (17) to determine the charge on keratin and by Lakshminarayanaiah (275) to evaluate the fixed charge on thin parlodion membranes.

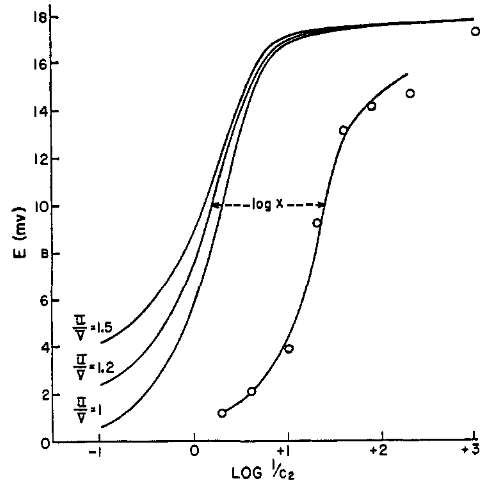


Figure 5.—Evaluation of membrane fixed charge capacity by Meyer-Sievers method. The smooth curves on the left are the theoretical concentration potentials for a cation-exchanger membrane, 1:1 electrolyte, and constant solution concentration ratio $C'/C'' = 2$, as a function of log $(1/C'')$. The curves are for different mobility ratios $\bar{u}/\bar{v}$. The experimental values for a thin parlodion membrane are plotted in the same graph *vs.* $-\log C''$. Shift of the experimental curve coinciding with one of the theoretical curves gave log X and the coinciding curve gave the mobility ratio.

TABLE XII

E.M.F.'S OF MEMBRANE CELL OF TYPE 112 CALCULATED FROM INTRAMEMBRANE ACTIVITY COEFFICIENTS AND OBSERVED TRANSPORT NUMBERS

(Membrane System: KOH-Cross-Linked Polymethacrylate)

Molality, m	ξ	Donnan p.d., mv.	Diffusion ϕ, mv.	Ref. electrode p.d. $\frac{RT}{F}\ln a_{\pm}$, mv.	ψ_w, mv.	Membrane cell e.m.f. Calcd., mv.	Membrane cell e.m.f. Obsd., mv.
0.001125	0.22	−70.68	−2.82	−144.52	−0.08	58.9	114.5
0.01125	0.26	−59.14	−6.25	−93.63	−0.71	58.3	108.8
0.1127	0.31	−49.79	−7.11	−43.11			
0.1005	0.30	−50.44	−7.11	−45.44	−0.63	23.6	31.4
0.2010	0.34	−38.84	−7.14	−32.80	−1.28	15.3	31.7
0.4025	0.43	−30.89	−7.96	−23.36	−2.53	22.0	31.0
0.8078	0.65	−9.17	−11.20	−17.33			
1.013	0.76	−1.57	−12.70	−15.43	−4.94	10.6	32.5
2.109	1.27	+1.31	−14.75	−0.68			

TABLE XIII

E.M.F.'S OF THE CELL Ag–AgCl/NaCl (m')/PSA MEMBRANE/NaCl (m'')/AgCl–Ag AND TESTS OF TMS THEORY AND OF EQ. 134

Molality, m	ξ	Donnan p.d. + diffusion ϕ, mv.	Ref. electrode p.d. $\frac{RT}{F}\ln a_{\pm}$. mv.	ψ_w, mv.	Membrane cell e.m.f. Calcd. (TMS), mv.	Membrane cell e.m.f. Obsd.. mv.	Membrane cell e.m.f. Calcd. (Eq. 134). mv.
0.001	0.14	−57.37	−181.30	−0.32	17.43	34.79	35.29
0.002	0.16	−57.32	−163.60	−0.50	21.36	45.85	46.14
0.005	0.17	−58.66	−140.40	−0.54	19.31	34.57	34.43
0.01	0.18	−56.41	−122.80	−0.99	14.25	33.80	33.36
0.02	0.22	−58.27	−105.70	−1.56	31.12	42.00	41.51
0.05	0.30	−47.90	−83.39	−1.94	22.25	30.00	29.06
0.10	0.32	−40.52	−66.58	−2.86	18.66	28.00	27.03
0.20	0.57	−35.68	−49.90	−6.77	28.99	32.30	31.77
0.51	1.08	−21.94	−27.88	−6.86	21.90	22.19	21.92
1.02	1.71	−10.74	−10.32	−7.80	19.38	20.74	20.65
2.09	2.98	−2.93	+9.05	−16.34	20.08	32.00	32.56
5.70	7.98	−1.73	+44.27				

The TMS theory is developed on the applicability of Donnan Eq. 113 to the electrolyte uptake by the ion-exchange membranes. This has been questioned by Glueckauf and Watts (104, 106, 107) who measured electrolyte uptake by ion-exchanger membranes by an elegant technique using radioactive Na. The diffusion coefficient values showed an abnormally high dependence on concentration, and from this they concluded that the ion-exchanger phase cannot be treated as a single homogeneous phase. Further, the amount of co-ion uptake plotted against external activity of the electrolyte gave a slope of 1.42, which should be 2 theoretically to agree with Donnan Eq. 115 applied to 1:1 electrolyte system.

Gustafson (125, 126) has adduced evidence based on (a) proton magnetic resonance studies (110, 111), (b) studies of electrolyte sorption by zeolites (15), and (c) activity coefficient studies of polyelectrolytes in aqueous solution (3, 219, 364, 517) to contest the conclusions of Glueckauf and Watts. His own studies of equilibria in cross-linked polymethacrylic acid–NaCl systems (125, 126) lend further support to the popular belief in the applicability of the Donnan equation to membrane systems.

b. Thermodynamic Theories of Isothermal Membrane Potentials

Disregarding considerations of membrane properties or structure, Scatchard (446–448) expressed the membrane potential as

$$E = -\frac{RT}{F}\sum_{i}\int_{a_i'}^{a_i''} \bar{t}_i \mathrm{d} \ln a_i \qquad \text{(Eq. 133)}$$

where a_i' and a_i'' solutions extend up to each interface. Taking the case of 1:1 electrolyte solution and applying Eq. 133 to all the four components, *i.e.*, counterion, co-ion, water, and fixed charges of the membrane phase, Hills, Jacobs, and Lakshminarayanaiah (180) showed that the total e.m.f. of a membrane cell (Type 112) is given by

$$E = -\frac{2RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} (\bar{t}_+ - 10^{-3}\, m_\pm M \bar{t}_\mathrm{w})\mathrm{d}\ln a_\pm \qquad \text{(Eq. 134)}$$

where M is the molecular weight of the solvent.

This equation is identical with the one derived by Lorimer, Boterenbrood, and Hermans (290) applying the principles of thermodynamics of irreversible process to diffusive processes in the membrane.

Lorimer, Boterenbrood, and Hermans subjected Eq. 134 to an experimental test. They measured the e.m.f.'s, $\bar{t}_+$, and $\bar{t}_\mathrm{w}$ using a cellulose membrane containing dissolved polyelectrolyte. By differentiating an empirical equation fitted to the e.m.f. data, they evaluated the quantity $(\bar{t}_+ - 10^{-3}m_\pm M\bar{t}_\mathrm{w})$. As $m_\pm$, M, and $\bar{t}_\mathrm{w}$ were known, $\bar{t}_+$ was thus evaluated and compared with the values measured directly. In one case out of only three cases considered, there was agreement. The concentration range used in their work was too small and barely adequate for a critical check of Eq. 134.

Hills, Jacobs, and Lakshminarayanaiah (181) also measured $\bar{t}_+$ and $\bar{t}_\mathrm{w}$ and the e.m.f.'s of membrane cells using cross-linked PMA membranes. They covered a concentration range up to 2 N KOH.

For the interfaces involved in the limits I and II (Eq. 134) $\bar{t}_+$ and $\bar{t}_\mathrm{w}$ were interpolated from the experimental data and, assuming them to vary linearly through the membrane, Eq. 134 was integrated numerically using Simpson's rule. The calculated e.m.f.'s were very much lower than the observed values. The values of $\bar{t}_+$ and $\bar{t}_\mathrm{w}$ used in their study were not unambiguous, as they were subject to systematic errors arising from back-diffusion during an electrolysis experiment. These errors have been eliminated by Lakshminarayanaiah and Subrahmanyan (278) in their studies using PSA membrane cells. Their results of numerical integration of Eq. 134 using unambiguous values of $\bar{t}_+$ and $\bar{t}_\mathrm{w}$ gave cell e.m.f.'s which agreed satisfactorily with the observed values (Table XIII) and thereby established the ability of the equation to describe satisfactorily (provided unambiguous values of $\bar{t}_+$ and $\bar{t}_\mathrm{w}$ are available) the electrical potentials of membrane cells even in high concentration ranges in which there is incomplete ionic selectivity of the membrane.

c. Kinetic Approach to Membrane Potentials

An attempt has been made to approach the problem of membrane potentials from the standpoint of the theory of rate processes. Nagasawa and Kobatake (366) have taken the structure of the membrane into account and, by the application of the Poisson–Boltzmann equation, have computed ionic concentrations in the membrane phase. The theoretical equation for the membrane potential is given by

$$E = \frac{RT}{F}\left[\alpha\ln\frac{C_1}{C_2} - \alpha\ln\left(\frac{C_1+\beta}{C_2+\beta}\right) + \frac{\bar{u}-\bar{v}}{\bar{u}+\bar{v}}\ln\left(\frac{C_1+\beta}{C_2+\beta}\right)\right. \qquad \text{(Eq. 135)}$$

where

$$\alpha = \frac{k_2(\bar{u}-\bar{v}) + k_3\bar{u}}{k_2(\bar{u}+\bar{v}) + k_3\bar{u}}$$

and

$$\beta = \frac{k_2(\bar{u}+\bar{v}) + k_3\bar{u}}{k_1(\bar{u}+\bar{v})}$$

k_1, k_2, and k_3 are complex functions involving the radius of the pores in the membrane, electrical potential due to the fixed charge, and the fixed charge of the membrane. It is difficult to express in precise terms what these constants mean. However, according to Tuwiner (557) α characterized membrane selectivity for ions and β measured the effect of adsorption of ions upon the membrane material.

The applicability of Eq. 135 to selective, nonselective, and glass membranes and the evaluation of the constant β have been discussed by Tuwiner (557).

Nagasawa and Kagawa (365) have written Eq. 135 replacing concentrations by activities. The cationic and anionic activities in the membrane phase were expressed by

$$\begin{aligned} \bar{a}_+ &= k_1 a + k_2 + k_3 \\ \bar{a}_- &= k_1 a + k_2 \\ a_+ &= a_- = a \end{aligned} \qquad \text{(Eq. 136)}$$

They measured both ionic activities and membrane potentials for an ion-exchange membrane, Nepton CR-51, using simple electrolytes (NaCl, Na_2SO_4) and polyelectrolyte (sodium polyvinyl sulfate) and found ionic activities better expressed by Eq. 136 than by the Donnan relation $\bar{a}_+\bar{a}_- = a^2$, and the observed membrane potentials agreed satisfactorily with the values calculated using Eq. 135.

Kobatake (232) has derived an equation similar to Eq. 135 using the methods of irreversible thermodynamics of continuous system based on hydrodynamics. His equation is the same as Eq. 135 except for the additional constant k_4 introduced to define α and β which are now given by

$$\alpha = \frac{(\bar{u}-\bar{v})k_2 + \bar{u}k_3}{(\bar{u}+\bar{v})k_2 + \bar{u}k_3 + k_4}$$

$$\beta = \frac{(\bar{u}+\bar{v})k_2 + \bar{u}k_3 + k_4}{(\bar{u}+\bar{v})k_1}$$

Equation 135 for the condition $\bar{\psi}_0 = 0$ (potential due to fixed charges), $\alpha = 1$, and β very small, *i.e.*, for a porous membrane like cellophane or parchment paper, became

$$E = \frac{RT}{F}\left[\ln\frac{C_1}{C_2} - \frac{2\bar{v}}{(\bar{u}+\bar{v})}\ln\frac{C_1+\beta}{C_2+\beta}\right] \quad \text{(Eq. 137)}$$

The effect of convection on membrane potential also has been considered by Kobatake (233) who introduced a correction factor into Eq. 137 to account for the osmotic flow. It is written as

$$E = \frac{RT}{F}\left[\ln\frac{C_1}{C_2} - \frac{2\bar{v} - k_3'}{(\bar{u}+\bar{v})}\ln\frac{C_1+\beta}{C_2+\beta}\right] \quad \text{(Eq. 138)}$$

where k_3' is a constant related to osmotic pressure coefficient.

Both anion- and cation-selective membranes have been used in membrane potential measurements. Good agreement was noted between observed and calculated e.m.f.'s. Cloos and Fripiat (49) found the theory to be applicable to paraffin membranes (pure paraffin holding calcium oxalate and trioleate of sorbic acid) which are porous and carry little charge.

In the calculations of membrane potentials, a value of β is required which was derived by an artifice whose meaning is not unambiguous. They equated Eq. 137 to Nernst Eq. 129 and from which a linear relationship between $1/\bar{t}_-$ and $1/C_1$ was obtained. From the slope of the plot of $1/\bar{t}_-$ against $1/C_1$, β was evaluated.

F. DIFFUSION OF NONELECTROLYTE

Unlike electrolyte diffusion where the flux of one ion influences the flux of the other ion, the flux of the nonelectrolyte species which are uncharged is not coupled electrically to other fluxes. The flux equation may be written as (166)

$$J_s = -\bar{D}_s\left[\frac{d\bar{C}_s}{dx} + \bar{C}_s\frac{d\ln\bar{\gamma}_s}{dx}\right] + \bar{C}_sV^* \quad \text{(Eq. 139)}$$

The convection velocity may be determined by following the rate of solvent transfer by osmosis. If $\bar{D}_s$ and $\bar{\gamma}_s$ are assumed constant and V^* negligible, Eq. 139 may be integrated. Thus

$$J_s = \frac{\bar{D}_s}{d}(\bar{C}_s' - \bar{C}_s'') \quad \text{(Eq. 140)}$$

As

$$K_s = (\bar{C}_s'/C') = (\bar{C}_s''/C'')$$

$$J_s = \frac{\bar{D}_sK_s}{d}(C' - C'') \quad \text{(Eq. 141)}$$

The flux is directly proportional to the diffusion coefficient in the membrane, concentration difference across the membrane, and the distribution coefficient and inversely proportional to membrane thickness. If the liquid film partially controlled diffusion, Helfferich (166) has shown that the flux is given by

$$J_s = \frac{\bar{D}_s}{d}\,\frac{K_s(C_0' - C_0'')}{1 + 2K_s\bar{D}_s\delta/D_sd} \quad \text{(Eq. 142)}$$

C_0' and C_0'' are bulk concentrations. As $D_sd/K_s\bar{D}_s\delta$ is very small, film diffusion control is very rare.

TABLE XIV

DIFFUSION OF NONELECTROLYTES THROUGH ION EXCHANGERS

G. of H_2O/g. of dry resin	Cs$^+$ form PSSA resin (267) $\bar{D}_s \times 10^6$ cm.^{2} sec.$^{-1}$ Glycerol	Glucose	Sucrose	K^+ form PSSA resin (414) $\bar{D}_s \times 10^3$ cm.^{2} sec.$^{-1}$ in 0.1 N KCl Urea	Acetic acid
0.19	0.07	0.05	0.008	4.11	3.76
0.30	0.35	0.23	0.02		
0.49	1.50	0.95	0.15		
Aq. soln.	9.4	6.8	4.9	1.36×10^{-5}	1.2×10^{-5}

The diffusion coefficients of urea and acetic acid have been determined by Peterson and Gregor (414) by measuring their fluxes in 0.1 N KCl across ion-exchange membranes. Similarly, Lagos and Kitchener (267) measured the diffusion coefficients of glycerol, glucose, and sucrose in Cs$^+$ form PSSA ribbon as a function of the resin water content. These results are given in Table XIV.

The diffusion of nonelectrolytes related to membrane porosity and structure (115) has been discussed by Tuwiner (560). A discussion of nonelectrolyte transfer in terms of frictional coefficients appears in section V of this article.

Mackie and Meares (305) measured the diffusion of ethanol in Zeokarb 315. From the sorption data, they showed that the activity coefficient of ethanol in the H$^+$ form of the resin phase can be expressed by $\ln\bar{\gamma} = 13.4\bar{C} - 0.183$. They also assumed a linear variation for $\bar{D}$ and wrote it as $\bar{D} = \bar{D}_0 + k\bar{C}$, where $\bar{D}_0$ and k are constants and integrated the flux equation

$$J_s = -\bar{D}\bar{C}\frac{d\ln\bar{a}}{dx} + \bar{C}V^*$$

For dilute solution, the result was expressed by

$$J_s = \frac{13.4\bar{D}_0 + k}{2d}(\bar{C}_s'^2 - \bar{C}_s''^2) + 13.4k\,\frac{(\bar{C}_s'^3 - \bar{C}_s''^3)}{3d} + \frac{\bar{C}_s'' - \bar{C}_s'\exp(V^*d/\bar{D}_0)V^*}{1 - \exp(V^*d/\bar{D}_0)} \quad \text{(Eq. 143)}$$

$\bar{D}_0$ was calculated using Eq. 76. V^* was evaluated by measuring the rate of osmotic flow. In the experiments $\bar{C}_s''$ was maintained at zero and $\bar{C}_s'$ was determined by sorption experiments. At three concentrations of external solution, *viz.*, 0.1, 0.5, and 1.0 M, the fluxes

TABLE XV

SOLUTE AND WATER FLOW ACROSS A COLLODION MEMBRANE

Solute	Mol. wt.	Semipermeability of membrane, σ Obsd.	Calcd.	Solute flow $\bar{\omega}_s \times 10^8$, ml./sec.	Water flow, ml./sec. ($\Delta C = 1$ osmolal)
H_2O^{18}	18	0	0	1.58	2.8
Urea	60	0	0	0.85	3.7
Glucose	180	0.009	0.01	0.40	18.0
Sucrose	342	0.0131	0.0126	0.27	24.8
Raffinose	504	0.0185	0.019	0.24	35.6
Dextran	52,000	1.0	1.0	—	1740

were calculated and found to be higher than observed values. The low observed fluxes were attributed to immobilization of part of the ethanol by dispersion forces and the rest of the free ethanol was transported.

Meschia and Setnikar (339), in a series of well-planned experiments executed to understand the nature of osmotic flow in membranes, measured the net flux of solute and water across a collodion membrane using different solutes (Table XV). $\bar{\omega}_s$ is an empirical proportionality constant, being proportional to the diffusion constant. The data indicate that the flux of solute decreased with increase in the molecular size of the solute and was zero for dextran ($\sigma \rightarrow 1$); whereas the flow of water increased and reached a maximum for the solute that did not pass through the membrane, thereby establishing a correlation between molecular size and flux of water determined by a given difference in osmolal concentration of solute. This suggested the possibility that if a membrane separated two solutions, one containing a diffusible solute (urea) and the other a nondiffusible solute (dextran), a flow of water by osmosis from higher osmolal solution to lower osmolal solution would take place. By choosing the proper concentrations, Meschia and Setnikar demonstrated the flow of water against its own gradient.

In a series of papers, Craig and his collaborators (56–59, 108) have discussed the membrane properties of cellophane like selectivity and porosity and their effects in controlling the rates of escape of polypeptides, proteins, and amino acids through the membrane. These studies have enabled them to perfect dialysis techniques for effecting separations and fractionations of various proteins and amino acids.

Similar studies were carried out by Fuchs and Gorin (98) with millipore filter membranes of larger pore size; whereas Ackers and Steere (1) evolved a technique for pore-size calibration of membranes based on the diffusion data of two roughly spherical macromolecules of known radii. They have also carried out diffusion measurements on other proteins. This work and that of Polson (419) have established the agar–gel filtration method for fractionating protein mixtures.

Hoch and Turner (187, 190) have investigated quantitatively the factors controlling the rate of flow of proteins through nitrocellulose membrane. Vink (571–573) and Almin (4) have discussed membrane diffusion as a tool for fractionating high polymers.

G. DIFFUSION OF ELECTROLYTE AND NONELECTROLYTE

The quantitative relations already discussed for electrolyte and nonelectrolyte transfer should describe, at least in an approximate way, the diffusion phenomena in systems containing both electrolyte and nonelectrolyte. Electrolyte transfer in presence of a nonelectrolyte or *vice versa* should still give a diffusion potential despite some changes in activity coefficients and swelling which may not be significant to bring about drastic changes in the expected fluxes.

Equation 141 described the flux of nonelectrolyte. The flux equation for a multivalent electrolyte is written as (162), ignoring activity coefficients

$$J_{+z+} = \frac{\bar{D}_-C'}{d}\left(\frac{C'}{\bar{X}}\right)^{-(z_-/z_+)} \text{ for a cation-exchange membrane}$$

$$J_{+z+} = \frac{\bar{D}_+C'}{d}\left(\frac{C'}{\bar{X}}\right)^{-(z_+/z_-)} \text{ for an anion-exchange membrane} \qquad \text{(Eq. 144)}$$

C' is concentration on side ($'$), and C'' on side ($''$) is zero. Dividing Eq. 141 by Eq. 144

$$\frac{J_s}{J_{+z+}} = \frac{\bar{D}_s}{\bar{D}_-}\left(\frac{\bar{X}}{C'}\right)^{-(z_-/z_+)} \text{ for a cation-exchange membrane}$$

$$\frac{J_s}{J_{+z+}} = \frac{\bar{D}_s}{\bar{D}_+}\left(\frac{\bar{X}}{C'}\right)^{-(z_+/z_-)} \text{ for an anion-exchange membrane} \qquad \text{(Eq. 145)}$$

The flux ratio may become very large (enrichment of nonelectrolyte) if $C' \ll X$, *i.e.*, highly charged membrane and dilute solutions, and very small for uncharged membranes.

When $z_+ < z_-$, *i.e.*, valence of counterion smaller than that of co-ion, the flux ratio is large. Acetone in 0.5 *M* HCl has an enrichment factor of 2.6 (314, 315) through PSA membrane compared to 9.25 in 0.5 *M* H_2SO_4. Steric factors like size of the nonelectrolyte, the swollen state of the resin play an important part. For example, the enrichment factor for acetic acid increased from 2.6 to 3.5 when the anion of the electrolyte was made bigger (HCl to CCl_3COOH); formaldehyde in β-naphthalenesulfonic acid had the highest enrichment factor of 12.8 (314).

The penetration of dyestuffs into textile fibers present another interesting study of considerable industrial importance about which volumes have been written. All the work described in those volumes presents studies designed to make the dye stay longer fixed to the fibers and make the fabric look attractive. Little of the work is amenable for a theoretical analysis of the mechanism controlling diffusion of dyes into textile fibers. Some papers of interest specific to the purpose of this article have appeared in recent years. Exact measurements of diffusion coefficients of Chlorazol Sky Blue FF (327) and of Chrysophenine G (577) into viscose sheet as a function of dye concentration and also as a function of salt concentration have been presented. Similarly, Naphthalene Scarlet 4R diffusion into nylon 6:6 has been studied under a variety of conditions (328).

IV. PHENOMENA DUE TO AN APPLIED ELECTRIC FIELD

When an electric field is applied to a membrane system

anode|solution (C)|membrane|solution (C)|cathode
(Type 146)

the current is carried through the membrane by the ions whose movement will be facilitated if the membrane is highly conducting (high fixed charge density). The movement may not take place if the membrane is nonconducting (dielectric), but, in general, nonselective membranes which are mostly porous are not completely nonconducting. Both cations and anions are transferred across it, whereas selective membranes transfer only counterions provided the external solutions are dilute.

Meares and Ussing (337) tested the flux ratio Eq. 105 for the movement of ions during the passage of an electric current. Zeokarb 315 membrane was used to separate the two solutions of identical chemical composition and concentration. The individual flux of cations and anions in each direction was measured for different values of electric current through the membrane using radioactive tracers.

The Nernst–Planck flux Eq. 6 and 8 were written for the flux of isotope a as

$$J_a = -\bar{u}_a RT \frac{d\bar{C}_a}{dx} - z_a \bar{C}_a \bar{u}_a F \frac{d\psi}{dx} + \bar{C}_a V^* \quad \text{(Eq. 147)}$$

where V^* was given by Eq. 9 but was written as

$$V^* = \bar{u}_0' F\omega X(\Delta\psi/d)$$

For the conditions of the experiments, *viz.*, $z_a = z_b$, $\bar{C}_a + \bar{C}_b = \bar{C}$, $\bar{u}_a = \bar{u}_b$, $d\bar{\gamma}_a/dx = d\bar{\gamma}_b/dx = 0$, and no pressure gradient, the fluxes for the isotopes a and b are given by

$$J_a = -\bar{u}_a RT \frac{d\bar{C}_a}{dx} + \bar{C}_a F(\bar{u}_0'\omega X - z_a \bar{u}_a) \frac{\Delta\psi}{d} \quad \text{(Eq. 148)}$$

$$J_b = +\bar{u}_a RT \frac{d\bar{C}_a}{dx} + (\bar{C} - \bar{C}_a) F(\bar{u}_0'\omega X - z_a \bar{u}_a) \frac{\Delta\psi}{d}$$

The flux equation was integrated in the steady state, $(dJ_a/dx) = 0$, and using the appropriate boundary conditions, the individual fluxes were obtained.

$$J_a = \frac{(z_a \bar{u}_a - \bar{u}_\theta'\omega X)F\Delta\psi\bar{C}\bar{L}}{d(1 - L)} \quad \text{(Eq. 149)}$$

$$-J_b = \frac{(z_a \bar{u}_a - \bar{u}_0'\omega X)F\Delta\psi\bar{C}}{d(1 - \bar{L})} \quad \text{(Eq. 150)}$$

where

$$\bar{L} = \exp\left[\frac{F(\bar{u}_0'\omega X - z_a \bar{u}_a)}{\bar{u}_a RT} \Delta\psi\right]$$

Equations 149 and 150 give on division

$$-\frac{J_a}{J_b} = \exp\left[\frac{-F\Delta\psi(z_a \bar{u}_a - \bar{u}_0'\omega X)}{\bar{u}_a RT}\right]$$

Replacing $\bar{u}_a RT$ by $\bar{D}_a$ and $\bar{u}_0'\omega X$ by $dV^*/F\Delta\psi$

$$\ln\left[-\frac{J_a}{J_b}\right] = \frac{z_a F(\psi^\circ - \psi^d)}{RT} + \frac{dV^*}{\bar{D}_a} \quad \text{(Eq. 151)}$$

J_a and $-J_b$ were measured. They were also calculated by estimating the potential from measured currents, area, thickness, and specific conductance of the membrane at the appropriate concentration. Convection was evaluated by measuring the volume of flow due to electroosmosis. The calculated fluxes were compared with the observed fluxes. Only with 0.01 *N* solution there was agreement. At 0.02 and 0.05 *N* solutions, the agreement was bad. But when the conductance term which was evaluated from the measurement of equivalent conductance of the membrane was introduced into the flux equation, *viz.*

$$\bar{\lambda}_a = z_a F^2(z_a \bar{u}_a - \bar{u}_0'\omega X)/|z_a| \quad \text{(Eq. 152)}$$

and corresponding fluxes were

$$J_a = \frac{|z_a|\bar{\lambda}_a \Delta\psi\bar{C}\bar{L}}{z_a F d(1 - \bar{L})}, \textit{ et seq.} \quad \text{(Eq. 153)}$$

where

$$\bar{L} = \exp[-\bar{\lambda}_a |z_a| \Delta\psi/z_a F\bar{D}_a]$$

the agreement was good.

Similar disparities were noticed for the chloride fluxes which could be measured only at 0.05 *N*. The conductance for the Cl^- could not be measured directly as the Na^+ ions carried most of the current but was estimated in an indirect way using observed net Cl^- flux and potential differences according to

$$\bar{\lambda}_{Cl^-} = Fd(J_a + J_b)/\bar{C}\Delta\psi$$

The significance of the conductance term, introduction of which into the flux ratio equation gave good agreement between calculated and observed flux ratios for both sodium and chloride ions, has been discussed by Meares and Ussing (337).

If the membrane system (Type 146) contained 1:1 electrolyte of different concentration, ionic diffusion will also occur in presence of the electric current which brought about electrical transference of ions and convection. The calculations of ion fluxes, concentration

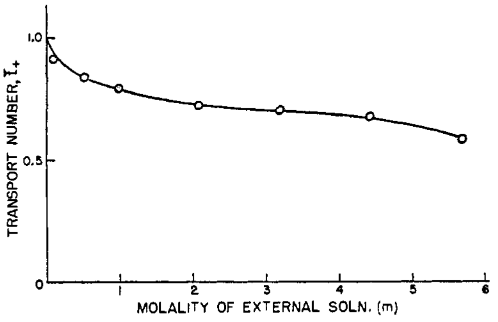


Figure 6.—Variation of counterion transport number $\bar{t}_+$ as a function of the external electrolyte concentration.

profiles, and convection, a difficult undertaking, have been accomplished by Schlögl and Schodel under some simplifying conditions (458). A summary of this is given by Helfferich (172) and by Bergsma and Kruissink (19).

A. MEASUREMENT OF TRANSPORT NUMBER

The efficiency with which a membrane transports selectively any particular ionic species may be inferred by measuring the transference number of the species in the membrane. Two methods are normally used to determine the membrane transport number (388–390, 440). They are (a) the e.m.f. method (262, 440) and (b) the Hittorf's method (440).

Membrane potentials measured using concentrations C' and C'' on either side of the membrane may be used in Eq. 130 to derive an average transport number (262); or, if Ag–AgCl electrodes immersed in two chloride solutions are used, $\bar{t}_+$ is derived from (86, 132, 440)

$$E = 2\bar{t}_{+(\text{app})}\frac{RT}{F}\ln\frac{a'}{a''} \qquad \text{(Eq. 154)}$$

The transport number value derived has been called the apparent transport number because in this type of measurement water transport has not been taken into account. This apparent value will be close to the true value when very dilute solutions are used.

In the Hittorf's method (440) a known quantity of electricity was passed through the membrane cell containing two chambers filled with the same electrolyte solution and separated by a membrane. Cations migrate to the cathode and anions migrate to the anode. The concentration change, which was not more than about 10%, brought about in the two chambers, was estimated by the usual analytical methods. The transport number was calculated from Eq. 14.

In most of the transport number measurements (20, 26, 120, 181, 182, 270, 290, 389, 390, 440, 518, 591), the same electrolyte solution was used on either side of the membrane and electricity was passed using reversible Ag–AgCl electrodes or irreversible platinum or stainless steel electrodes. When very dilute solutions were used, concentration changes up to 15% gave constant values which were independent of the electrolyte concentration donating (anode chamber) or receiving (cathode chamber) the counterions. This is so when the co-ion presence in the membrane phase is negligible. But when the external concentration was increased, $\bar{t}_+$ values depended very much on the concentration of either the donating side or the receiving side. Which side-controlled $\bar{t}_+$ values depended on the nature of the membrane–electrolyte system (249, 254)? In the systems investigated by Kressman and Tye (254) and Lewis and Tye (283) $\bar{t}_+$ values depended on the concentration of the solution receiving the ions and independent of the donating concentration. A theoretical discussion of this aspect is also given by them (254). They have predicted that, for a system where there is considerable convection at high concentrations, the transport number will decrease with increase in concentration, reach a minimum, and then increase on further increase in external concentration. So far, decrease in counterion transport number only with increase in external concentration has been reported (250, 254, 278, 283). Figure 6 indicates the variation of $\bar{t}_{\text{Na}^+}$ as a function of external concentration for a PSA–NaCl system obtained by Lakshminarayanaiah and Subrahmanyan (278).

In all of the transport experiments, the same electrolyte solution was used on either side of the membrane. Kressman, Stanbridge, and Tye (251) have used different electrolytes but with a common anion and determined the transport number for the cation in the donating solution for the following systems.

Donating solution ⇌	membrane ⇌	receiving solution
KOH	Permplex	NaOH
KOH	C-20	LiOH
NaOH	Permplex	KOH
NaOH	C-20	LiOH
LiOH	Permplex	KOH
LiOH	C-20	NaOH
	Permplex	
LiCl	C-20	KCl
LiOH	T.N.O. C-60	KOH

They found that the counterion transport number was controlled by the mean activity and not the concentration of the receiving solution for the alkali metal hydroxides with both Permplex C-20 and T.N.O. C-60 membranes. But for chlorides, it was found that the concentration and not the mean activity controlled the transference number. This behavior was attributed to the way the co-ion concentration inside the membrane was controlled by the mean activity of the external solution. In the case of the hydroxyl co-ion, its concentration was controlled by the mean activity of the outside electrolyte whereas, in case of the chloride ion, the counterion and not the co-ion dominated the mean activity.

Determination of meaningful transport numbers for any membrane–electrolyte system calls for careful control of a number of factors. The important factors,

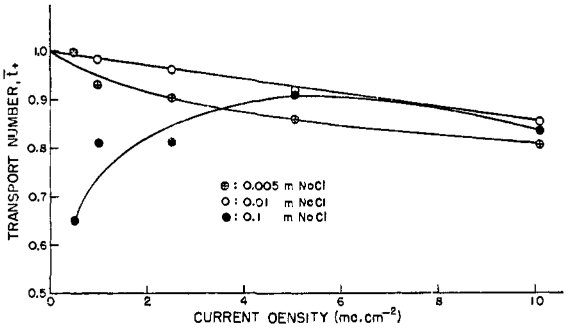


Figure 7.—Effect of current density on the counterion transport number $\bar{t}_+$ at "constant" external concentration.

besides the control of concentration of donating or receiving side already referred to, are (a) external concentration, (b) current density, and (c) difference in concentration on either side of the membrane.

Preliminary experiments are recommended to determine which side controlled the $\bar{t}$ values (249, 254). By keeping the concentration of the concentration-dependent side constant, transport number may be determined by analysis of the solution on the other side after electrolysis. By this technique, values for $\bar{t}$ have been determined at various external concentrations (250, 251, 278, 521).

The effect of current density on the values of $\bar{t}$ has been demonstrated by Kressman and Tye (253) using multicompartment cells and by Lakshminarayanaiah and Subrahmanyan (278, 521) using simple cells. The data of Figure 7 (278) illustrate a number of points.

When external concentrations are small (<0.1 N), increase of current density gives decreasing $\bar{t}$ values. This is attributed to polarization effects at the membrane–solution interface facing the anode. These effects, whose theoretical interpretation based on Nernst–Planck flux equation has been recently given by Gregor and Peterson (119), were noticed as early as 1914 by Bethe and Toropoff (21).

The amount of polarization decreases as the concentration is increased. When the external concentration is 0.1 N, $\bar{t}$ exhibits a maximum at a certain current density below which the $\bar{t}$ values decrease as the current density is decreased and above which $\bar{t}$ values decrease as the current density is increased. The reasons for the latter case have already been noted. The decrease as the current density is lowered is attributed to back-diffusion (132, 253, 278, 521).

When external concentrations >0.1 N are used, polarization effects are negligible but back-diffusion becomes dominant. As the quantity of back-flux due to diffusion is determined by the concentration differences allowed to build up during electrolysis, it should be made as small as possible or the Kressman–Tye technique (254) may be used to derive meaningful values for $\bar{t}$.

Besides, other techniques have been used to overcome these back-diffusion effects. Three approaches are suggested (278): (a) circulating during electrolysis on the anode side a solution whose concentration will be close to that on the cathode side. The concentrations of the solution circulated and that allowed to build up are kept within certain limits, *i.e.*, $C + \Delta C$, C is the concentration at which $\bar{t}$ is to be determined and ΔC is the limit of concentration change permitted which is about 5% of C. (b) A high current is passed for a very short time to bring about a concentration change amenable for accurate estimation (278). (c) The initial concentrations in the two chambers are such that on completing the experiment, the concentration in the two compartments are reversed. The mean concentration difference between the two compartments during the course of the experiment would be close to zero, and the effect of diffusion through the membrane might be expected to be eliminated (132, 591).

The first two techniques were used by Lakshminarayanaiah and Subrahmanyan (278, 521), and the third has been developed into a useful technique by Hale and McCauley (132). They used the steady-state cation flux equation derived by Patridge and Peers (409) for 1:1 electrolyte and rearranged to get

$$\frac{FJ_+}{i} = t_+ + \frac{D}{\delta}\left[\frac{\Delta t}{(D/\delta) + 2P}\right] - \frac{DF}{\delta i}\left[\frac{P}{(D/\delta) + 2P}\right](C' - C'') \quad \text{(Eq. 155)}$$

where $\Delta t = \bar{t}_+ - t_+$, P = permeability constant, and FJ_+/i is the total amount of cation (g.-ion/faraday) transferred across the membrane which was measured and plotted against a mean concentration difference between the chambers during the course of the experiment. This mean concentration difference was calculated from the initial concentration difference started with and the amounts of ions and water transferred across the membrane.

According to Eq. 155, FJ_+/i *vs.* $C' - C''$ plot should be a straight line whose intercept when $C' - C'' = 0$ will be

$$t_+ + \frac{D}{\delta}\left[\frac{\Delta t}{(D/\delta) + 2P}\right]$$

For $D/\delta \gg 2P$, intercept will give $t_+ + \Delta t = \bar{t}_+$.

Similarly, a plot of FJ_+/i against $1/i$ should give a straight line. This has been established by Kressman and Tye for Permplex C-10 membrane (253). Even here the intercept should be the same.

If $(D/\delta) \not\gg 2P$, $\bar{t}_+$ cannot be obtained from linear plots. In such a case, Hale and McCauley (132) carried out experiments in such a way that allowance for the effects of back-diffusion could be made in both the membrane and the solutions contacting the membrane faces. This they did by using two membranes having different permeabilities to NaCl but having the same value for $\bar{t}_+$. These membranes they prepared using the same ion-exchange material (PSSA, *i.e.*, same $\bar{t}_+$) embedded in different weights of the inert binder, polythene (*i.e.*, different P values).

For these two membranes, plots of FJ_+/i against $C' - C''$ gave straight lines intersecting at a point where

$$C' - C'' = -\frac{2\Delta t i \delta}{DF} \qquad \text{(Eq. 156)}$$

and

$$FJ_+/i = \bar{t}_+$$

From the point of intersection $\bar{t}_+$ was derived, for a number of membranes. These values were plotted against $C' - C''$ and the straight line cut the zero concentration difference ($C' - C'' = 0$) axis at a point where $\bar{t}_+ = t_+$, *i.e.*, transport number of Na^+ ion in solution. From the slope of the line according to Eq. 156 a value of 150 μ was obtained for δ, the thickness of the diffusion layer. This value, although larger than most of the values presented in section IIIB, appears reasonable, compared to the values obtained by Stewart and Graydon (515).

This method described for measuring transport numbers in the membrane phase has a serious limitation in that the success depends on the availability of two membranes satisfying the requirements of identical $\bar{t}_+$ and different permeabilities.

A very elegant method in which the concentration difference built up on either side of the membrane may be eliminated, using ion-exchange resins as buffers in the system has been described by McKelvey, Spiegler, and Wyllie (330). In this method use of radioactive tracers allowed ion transport to be measured at constant concentration without interference from electrode reactions. The specific radioactivity of one of the chambers changed and this was determined after electrolysis. Current was passed from two platinum electrodes. Weakly acidic carboxylic cation-exchange resin (Amberlite IRC-50), a few grams, was used. For a cation-exchange membrane, cathode contained resin in H^+ form and anode contained resin in the appropriate metal form. $\bar{t}_+$ calculated by radioactive tracer transfer agreed with $\bar{t}_+$ obtained from estimation of change in chloride ion concentration. External concentrations in the range 0.1–0.3 N were used.

B. ELECTROOSMOSIS

Application of an electric field to cell of Type 146 causes not only transference of ions but also transference of liquid existing in the membrane pores. This solvent transport accompanying ion migration through a membrane has been called electroosmosis. Usually this transference takes place in the direction in which the counterions move. As counterions experience less resistance due to solvent movement also in the same direction, they move faster than co-ions. True transference numbers of counterions account for increased ion transfer due to convection.

Virtually all types of membrane exhibit electroosmosis which arises (1) by the existence of charged groups by adsorption of one or more ionic species in solution on to the walls of the pores of the membrane or (2) by the existence of charged groups in the structure of the membrane itself.

Preferential adsorption of one species of ion leads to the type of ionic distribution associated with the electrical double layer. A slip plane in the double layer is usually envisaged dividing the fixed charges and the diffuse part of the double layer of opposite total charge density (402). The electrical potential in this plane is identified with the ζ-potential, and it has been shown that the electroosmotic velocity, V_E, of the solution is given by

$$V_E = \frac{\epsilon \zeta E}{4\pi\eta} \qquad \text{(Eq. 157)}$$

where ϵ and η are the dielectric constant and viscosity of the solution, respectively. E is the applied potential gradient and ζ is the ζ-potential. The volume of solution transported per sec. per cm.^{2} is given by

$$V = \frac{\epsilon \zeta i}{4\pi\eta\kappa} \qquad \text{(Eq. 158)}$$

These equations are ideal and only apply to uncharged membranes of relatively large pore radius in contact with dilute solutions. Under these conditions the volume of solvent transported per faraday of current is very large. In considering it, three factors are generally neglected: (a) volume of ions transported, (b) volume of water transported as ionic hydration if not included in (a), and (c) the migration of ions in the close-packed part of the double layer, *i.e.*, surface current. As the concentration of adsorbed or fixed charges is increased and/or the pore size is decreased, the volume of solvent transported per faraday will decrease and the three factors become progressively important. In ion-exchange membranes, it is possible that all of the current is similar to surface current and the three factors completely determine V_E or V.

In dilute solutions with ion-exchange membranes, only counterions flow in one direction giving rise to flow of solvent also in that direction. This flow of solvent thus enables counterions to move faster than they would otherwise in the absence of solvent flow. So, for any given applied voltage, the net current flow i will be greater than i' flowing in absence of solvent flow. Schmid and Schwarz (461–463, 465–468) have derived an expression relating i and i' to the radius of the membrane capillaries.

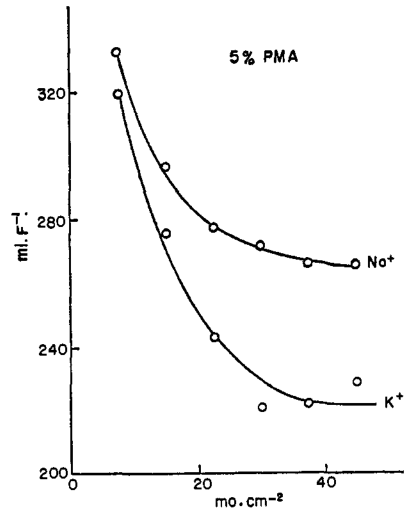


Figure 8.—Electroosmotic flow (ml. f.$^{-1}$) through a 5% PMA membrane (Na$^+$ or K$^+$ form) as a function of current density.

$$\frac{i - i'}{i} = \frac{F^2X^2r^2}{8\eta\kappa} \qquad \text{(Eq. 159)}$$

Despic and Hills (68) have put it in the form

$$\lambda - \lambda' = \frac{10^3F^2Xr^2}{8\eta}$$

and find it to be inapplicable to charged membranes. A summary of the other aspects of the theory appears elsewhere (171, 588).

The total volume of solvent transported electroosmotically per faraday of current (ml. f.$^{-1}$) has been measured by a number of investigators (26, 40, 67, 132, 249, 252, 270–272, 278, 290, 298, 330, 388–390, 422, 440, 472, 516, 518–520, 551, 591).

The main noncontroversial results are as follows: Water transported, (ml. f.$^{-1}$), decreases as the external concentration is increased and also as the water content of the membrane is decreased. The effect of cross linking on (ml. f.$^{-1}$) depended on the way cross linking affected the water content of the membrane; (ml. f.$^{-1}$) decreased in the order Cs = Rb < K < Na < Li. The transfer also decreased as the charge of the ion permeating the membrane increased. The specific binding of the ion to the fixed groups of the membrane became very important as the ionic charge increased. Rosenberg, George, and Potter (440) found, in case of thorium counterion, negative transport of water. The ion was so strongly adsorbed that it conferred anion selectivity to the membrane and thus water was transported in the opposite direction (to anode instead of to cathode). Similarly, Schulz (472) found in case of sodium diphosphate, adsorption of the diphosphate anion on the surface of the anion-exchange diaphragm Permplex A-10, reversing the charge on the membrane and the direction of transfer of water.

Oda and Yawataya (388) introduced the idea of bound water existing in the membrane phase to explain their results and found about 10–15 moles of water fixed per equivalent of fixed ion in the membrane phase.

Winger, Ferguson, and Kunin (591) assumed the net transfer of water to be given by

$$\bar{t}_w = \frac{\bar{t}_+n_+}{z_+} - \frac{\bar{t}_-n_-}{z_-} = \bar{t}_+\left[\frac{n_+}{z_+} + \frac{n_-}{z_-}\right] - \frac{n_-}{z_-} \qquad \text{(Eq. 160)}$$

n_+ and n_- are the number of moles of water associated with cation and anion, respectively, and $\bar{t}_w$ = (ml. f.$^{-1}$)/18. Accordingly, they found a linear variation between $\bar{t}_w$ and $\bar{t}_+$. This straight line was extended in either direction. It was found that for $\bar{t}_+ = 1$, n_+ was 14.1, 8.6, and 7.3 for Li$^+$, Na$^+$, and K$^+$, respectively, and for $\bar{t}_w = 0$, n_- for the OH ion was about 5 and $\bar{t}_+$ for the different species were LiOH = 0.24, NaOH = 0.38, and KOH = 0.45. These values were probably the solution transport numbers for the concentrated alkali solutions (~6 *M*).

Kressman, Stanbridge, Tye, and Wilson (252) found, on the other hand, the plots of $\bar{t}_w$ against $\bar{t}_+$ to be curved and so also were the results of Oda and Yawataya (388–390). For $\bar{t}_+ = 0$, they found 1 mole of water associated with the OH$^-$ group. For $\bar{t}_+ = 1$, they obtained n_+ to be 12.5, 10.7, and 9.0, respectively, for Li$^+$, Na$^+$, and K$^+$ form of Permplex C-20 membrane and about 28 for leached form of T.N.O. C-60 membrane. These values corresponded very well with the water contents of the membrane which were 11.9, 10.4, 9.1, and 27.6 for Li$^+$, Na$^+$, and K$^+$ form of C-20 and Li$^+$ form of C-60, respectively. From these results it was concluded that water moved at the same linear velocity as the ion, whereas Stewart and Graydon (516) found only half of water per ion-exchange group per faraday transported.

Kressman, Stanbridge, Tye, and Wilson (252) related water transport to the transport number of the counterion by the expression

$$\bar{t}_w = \bar{t}_+(\bar{m}_w + 1) - 1 \qquad \text{(Eq. 161)}$$

where $\bar{m}_w$ is the moles of water per equivalent of counterion in the membrane and -1 is the 1 mole associated with OH$^-$ group. The curvature of the simple plot of $\bar{t}_w$ against $\bar{t}_+$ was ascribed to the variation of $\bar{m}_w$. They found $\bar{t}_w$ calculated according to Eq. 161 to agree with the $\bar{t}_w$ values measured.

The dependence of $\bar{t}_w$ on current density has been considered by a number of workers. Only Tombalkian, Barton, and Graydon (551) and Lakshminarayanaiah and Subrahmanyan (270–272, 278, 518–520) report dependence of $\bar{t}_w$ on current density. Tombalkian, Barton, and Graydon found $\bar{t}_w$ values to decrease at high current densities. This they ascribed to membrane polarization. The work of Lakshminarayanaiah (270–272) was mostly concerned with dilute solutions of KOH (*i.e.*, $\bar{t}_+ \sim 1$). Using the alkali metal ions and

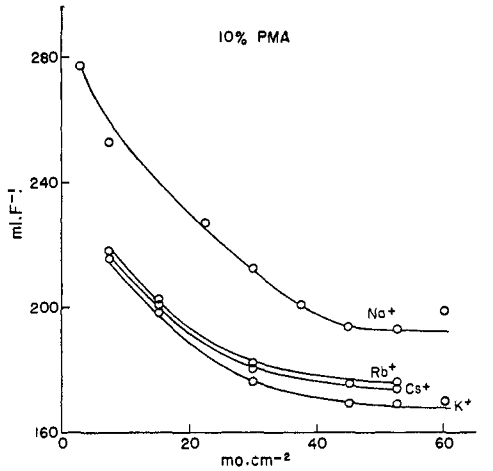


Figure 9.—Electroosmotic flow (ml. f.$^{-1}$) through a 10% PMA membrane (Na$^+$, K$^+$, Rb$^+$, or Cs$^+$ form) as a function of current density.

differently cross-linked PMA membranes, total transport (ml. f.$^{-1}$), and also rate of transport (272) have been measured. The results (Figures 8–10) indicate strong dependence of (ml. f.$^{-1}$) on current density. At low current densities, $\bar{t}_w$ values are high and decrease with increase in current density and reach a limiting value. This behavior was noticed also by Subrahmanyan (518) for his PSA-NaCl system when the external electrolyte concentration was <0.1 *N* (Figure 11).

A simple explanation for the variation of (ml. f.$^{-1}$) with current density is that electrolysis induced some chemical change in the membrane. This change can only be membrane polarization (replacement of metal ion by H$^+$) considered by Tombalkian, Barton, and Graydon (551). Such polarization undoubtedly increases with increase in current density and in the PMA system leads to deionization of the membrane. But with the PSA system, membrane polarization simply changes the ionic form of the membrane from Na$^+$ to H$^+$. So, if membrane polarization is responsible for decreasing (ml. f.$^{-1}$) with increasing current density, the two systems should be affected in opposite directions as the H$^+$ form of PSA is more conducting than the Na$^+$ form. But the observed dependence is the same in both the systems.

It was shown also by both Lakshminarayanaiah (270, 272) and Subrahmanyan (518) by employing manual stirring at high currents, that the concentration polarization decreased (ml. f.$^{-1}$) only to the extent of about 17%. At very low current densities where there was little concentration polarization (253, 278) rise of (ml. f.$^{-1}$) with decrease in current density was very high.

Lakshminarayanaiah (272) has derived an expression relating electroosmotic permeability ω_p (volume of solvent flowing per sec. through unit area of membrane for a potential gradient of 1 v./cm.) to space-charge density and the radius of the pores considering the membrane to be made up of a bundle of capillaries. On the basis of the expression

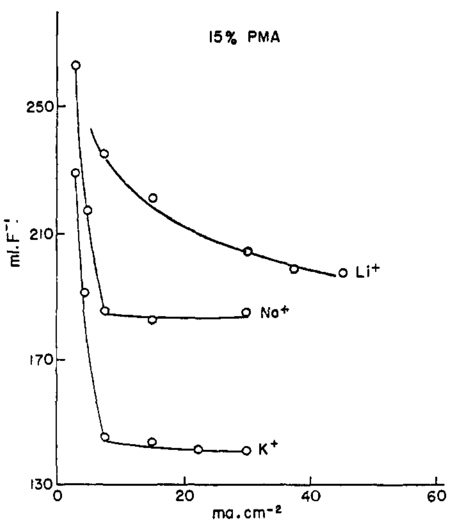


Figure 10.—Electroosmotic flow (ml. f.$^{-1}$) through 15% PMA membrane (Li$^+$, Na$^+$, or K$^+$ form) as a function of current density.

$$\omega_p = \frac{r}{2\sigma^s}\bar{\kappa} = \frac{(\text{ml. f.}^{-1})}{F}\bar{\kappa} \qquad \text{(Eq. 162)}$$

he explained the variation of ω_p with current density to be due to variation of σ^s and r in a manner governed by the peculiar ion distribution in the membrane. Low current densities affected ion distribution and mobilization in such a way that effective r was high and effective σ^s was low; or rather transport through only large pores of low charge density took place. At high current densities, average values of r and σ^s operated to produce limiting values for ω_p.

As the external concentration is increased, co-ion uptake increases and the membrane loses its selectivity.

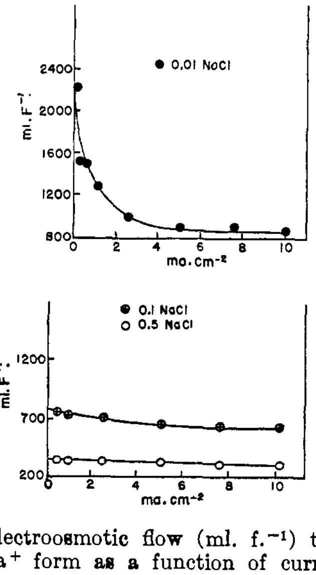


Figure 11.—Electroosmotic flow (ml. f.$^{-1}$) through a PSA membrane in Na$^+$ form as a function of current density at external electrolyte NaCl concentrations, <0.1 *N* (upper curve) and >0.01 *N* (lower curve).

Each pore of the membrane gets filled uniformly with the solution and as a result transport becomes independent of current density. In agreement with the results of other workers, Lakshminarayanaiah and Subrahmanyan (278) observed (ml. $f.^{-1}$) to decrease with increase in external concentration. Mackay and Meares (298) ascribed this decrease to nonuniform distribution of space-charge density. According to Eq. 162, (ml. $f.^{-1}$) goes down with increased electrolyte concentration due to decrease in pore size resulting from contraction in membrane volume (less water content). The decrease will be further enhanced by surface charge increase.

The above discussion was concerned with the parameters r and σ^s which are not measurable for the membrane. Both Spiegler (507) and Mackay and Meares (298), in their treatments of transport processes in ion-exchange membranes based on irreversible thermodynamics, have arrived at some interesting conclusions regarding electroosmosis.

For a membrane in equilibrium with dilute solutions (0.01 N), the concentration of co-ion is practically zero (*i.e.*, $C_2 = 0$ according to Spiegler's symbols). Total water transport per faraday will depend on the concentration of counterion and of water (C_1 and C_3) and on the frictional interaction between counterions and water and between water and the membrane matrix. In a porous membrane, if the interaction between water and membrane matrix is negligible compared to that between counterion and water, counterions and water would move through the membrane with the same linear (average) velocity; (ml. $f.^{-1}$) should therefore be equal to the concentration of water in the membrane expressed as ml. per g.-equiv. of exchangeable counterion. In Spiegler's symbol (ml. $f.^{-1}$)/18 $= C_3/C_1$.

In terms of the expressions worked out by Lakshminarayanaiah (272)

$$(\text{ml. f.}^{-1}) = VF/I \qquad \text{(Eq. 163)}$$

where V is the ml. of solvent flowing per sec. But

$$V = \pi r^2 U' \qquad \text{(Eq. 164)}$$

and

$$I = (E/l) r^2 \bar{\kappa} \qquad \text{(Eq. 165)}$$

where U' is the uniform velocity of the mobile layer when a potential of E volts acts along length l cm. of capillary.

Substitution of Eq. 164 and 165 into Eq. 163 gives

$$(\text{ml. f.}^{-1}) = \frac{U'F}{(E/l)\bar{\kappa}} \qquad \text{(Eq. 166)}$$

But $U'F/(E/l) = \bar{\lambda}$, the equivalent conductance of the membrane

$$(\text{ml. f.}^{-1}) = \frac{\bar{\lambda}}{\bar{\kappa}} \approx \frac{10^3}{\bar{m}_1} \qquad \text{(Eq. 167)}$$

TABLE XVI

THEORETICAL AND LIMITING VALUES OF (ML. F.$^{-1}$)

Membrane system	$\bar{m}_1$	(ml. f.$^{-1}$)	Limiting values
1. 5% PMA (Na$^+$ form)	1.225	816	265
2. 10% PMA (Na$^+$ form)	2.748	364	195
3. 15% PMA (Na$^+$ form)	2.345	426	185
4. PSA (Na$^+$ form)	0.824	1213	880

At least for dilute solutions ($C_2 = 0$), (ml. $f.^{-1}$) is expressed in terms of a measurable quantity $\bar{m}_1$, which is the interstitial concentration of counterions associated with 1000 g. of water in the membrane phase.

The theoretical values of (ml. $f.^{-1}$) for some of the systems used by Lakshminarayanaiah and Subrahmanyan are given in Table XVI.

It is seen from the data of Table XVI that ~31, ~9, ≃13, and ~19 moles of water are trapped in the systems 1, 2, 3, and 4. The number of moles of water trapped per equivalent of the fixed group will be 25.3, 3.2, 5.5, and 23. In contrast Oda and Yawataya (388–390), Glueckauf (103), and Boyd and Soldano (29) found 1.5–3.5, 0.9, and 1 mole of water, respectively. In column 4 of Table XVI, the limiting values only are listed. If some of the values obtained at low current densities are considered, the moles of water associated per equivalent of counterion will become less and even negative in the case of the PSA system. This is possible only when there is ion association or when transport is confined to pores where $\bar{m}_1$ values are less than the measured average values. As these systems have high electrical conductance, ion association is least probable. Consequently, transport is thought to take place selectively through slightly charged or uncharged pores.

Explanation in terms of Eq. 167 of the results (Figure 11) obtained with stronger solutions is not possible as the condition for its application, *viz.*, $C_2 = 0$ does not exist. As a consequence some of the results compiled by Spiegler (507) using the measurements of Winger, Ferguson, and Kunin (591) who used concentration of 0.5 N NaCl (*i.e.*, $C_2 \neq 0$) must be viewed with caution, as also the values presented by Hale and McCauley (132) for the ratio (ml. $f.^{-1}$)/(C_3/C_1) for different cross-linked heterogeneous membranes owing to use of 1.0 N NaCl solution.

Observed flow when the membrane is in contact with strong solutions is better explained by Eq. 160. The volume of transport is thus governed by the transport number and the relative hydration of the counter- and the co-ions. Assuming hydration of ions to be concentration independent, it is seen from Eq. 160 that $\bar{t}_w$ will decrease with increase in external concentration if $\bar{t}_+$ goes down. For the many systems already considered, $\bar{t}_+$ goes down with increase in concentration. Unfortunately Eq. 160 is completely inadequate to explain the current dependence of $\bar{t}_w$ in the case of dilute

TABLE XVII

TRANSPORT DATA FOR A PSA–NaCl SYSTEM AND CHECK OF EQ. 161

Molality of external soln., m	Equiv./ 1000 g. of water, $\bar{m}_+$	$\bar{m}_w$	$\bar{t}_+$	$\bar{t}_+ (\bar{m}_w + 1)$	$\bar{t}_w$ (calcu.)	$\bar{t}_w$ (obsd.)
0.005	1.29	43.1	0.997	44.0	35.0	90.0
0.010	1.30	42.7	0.997	43.5	34.5	86.2
0.10	1.41	39.4	0.910	36.8	27.8	37.3
0.51	1.70	32.7	0.830	28.0	19.0	18.2
1.02	2.05	27.1	0.800	22.5	13.5	11.1
2.09	2.86	19.4	0.721	14.7	5.7	6.1
5.70	6.69	8.3	0.574	5.3	(−3.7)	2.1

TABLE XVIII

TRANSPORT DATA FOR A PMA–KOH SYSTEM AND CHECK OF EQ. 161

Molality of external soln., m	Equiv./ 1000 g. of water, $\bar{m}_+$	$\bar{m}_w$	$\bar{t}_+$	$\bar{t}_+ (\bar{m}_w + 1)$	$\bar{t}_w$ (calcd.)	$\bar{t}_w$ (obsd.)
0.005	2.88	19.3	0.954	19.4	14.4	9.2
0.010	3.00	18.5	0.941	18.3	13.3	8.1
0.10	3.16	17.6	0.914	17.0	12.0	7.8
0.48	3.65	15.2	0.807	13.1	8.0	6.9
1.00	4.10	13.5	0.708	10.3	5.3	4.9
1.70	4.50	12.3	0.666	8.9	3.9	3.8

solution even though $\bar{t}_+$ is current dependent; it is not so to that degree as to account for the observed variation of $\bar{t}_w$, and n_+ cannot be assumed to be current dependent unless a chameleon-like property can be ascribed to it. Further on the basis of Eq. 160 it should be expected that a stage will be reached when $\bar{t}_w$ is zero. In the systems studied so far, this zero transport or reversal of direction of flow has not been reported.

The experimental values of Subrahmanyan (518) and Lakshminarayanaiah (270) are examined from the standpoint of Eq. 161. The results are presented in Tables XVII and XVIII.

Equation 161 may be written as

$$\bar{t}_w = \bar{t}_+(\bar{m}_w + 1) - n_- \qquad \text{(Eq. 168)}$$

where n_- is introduced to substitute the required value for the anion concerned. The results using $n_{Cl^-} = 9$ are given in Table XVII. The agreement between observed and calculated $\bar{t}_w$ is very bad at the extremes of the concentration scale and tolerable in between (0.5 to 2 N NaCl). In the case of PMA–KOH system $n_{OH^-} = 5$ was substituted into Eq. 168. Even here the agreement is poor, and the calculated values are all higher than the observed values.

These discrepancies cannot be attributed to any errors in measurement, as the generalizations valid for a set of measurements seem to be inapplicable to another set of equally good measurements. Equation 161, although found applicable to a set of data presented by Kressman, Stanbridge, Tye, and Wilson (252), has an inconsistency in that the value of n_{OH^-} was taken to be unity whereas Winger, Ferguson, and Kunin (591) found n_{OH^-} to be about 5. These variations illustrate the futility of attempts to find generalizations to predict membrane behavior as far as electroosmosis is concerned.

TABLE XIX

HYDRATION AND MOBILITY RATIOS IN THE MEMBRANE PHASE

Metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Co^{2+}	Ni^{2+}
n_+ (591)	13.5	9.5	7.0	7.2	6.9	28	26
n_+ (270)	12.5	11.0	9.5	9.7	9.7		
n_{Li^+}/n_+ (591)	1.0	1.5	1.93	1.87	1.95	0.97	1.04
$\bar{U}/\bar{U}_{Li^+}$	1.0	1.4	1.83	1.78	1.82	1.11	1.09

Winger, Ferguson, and Kunin (591) using a large quaternary ammonium cation in Amberplex A-1 membrane system (exclusion of cation from membrane phase) measured the total transport which was attributed entirely to Cl^-. In this way a value of 9 was derived for n_{Cl^-}. Using this value in the electroosmotic transport measurements involving other cations, they computed n_+ values for a number of cations. These values are given in Table XIX.

Employing the Wyllie–Kanaan technique (601), they also derived values for the mobility ratios for a number of ions using Li^+ as the reference ion. The mobility was inversely proportional to the magnitude of interaction between ion and solvent. These relationships are brought out in the data presented in Table XIX.

The limiting $\bar{t}_w$ values (*i.e.*, n_+ values) obtained by Lakshminarayanaiah for various alkali metal ions with a 10% PMA membrane are also given in Table XIX. These values indicate the state of relative hydration in the membrane.

Despić and Hills (67) carried this approach to the problem of ionic hydration a stage further and divided the total water associated with an ion into two parts: (a) water firmly held by the ion (primary hydration) and (b) water transported electroconvectively (68). Schmid (464), however, considered this division improper on phenomenological grounds but accepted the necessity from a theoretical standpoint.

Despić and Hills (67) attempted to separate the total water transport into the two parts. This they did by measuring both the self-diffusion and equivalent conductance $\bar{\lambda}$ of the membrane material. From the self-diffusion coefficient, they derived a value for $\bar{\lambda}'$ from the equation

$$\bar{D} = \frac{RT}{F^2}\bar{\lambda}'$$

The difference between $\bar{\lambda}$ (in presence of electric field) and $\bar{\lambda}'$ (in absence of electric field) was attributed to electroosmosis or electroconvection. This $\Delta\bar{\lambda}$ was related to the number of moles of water transported electroconvectively by the equation

TABLE XX

DATA RELATING TO CALCULATION OF IONIC HYDRATION NUMBERS, n_+

Membrane ion system	λ	$\bar{\lambda}'$	$\bar{m}_+$	ΔV_E (Eq. 169)	Total hydration V, ml.	$V-\Delta V_E$, ml.	n_+ Eq. 169	n_+ Revised
5% PMA-Na^+	20.96	16.940	1.225	157	266	109	6.2	4.0
10% PMA-Na^+	12.51	9.684	2.748	82	193	111	6.0	4.8
15% PMA-Na^+	11.42	8.976	2.345	91	183	92	5.1	3.7
PSA-Na^+	15.37	9.966	1.303	270	507	237	13.2	5.0
5% PMA-K^+				157[a]	222	65	3.6	1.6
10% PMA-K^+				82[a]	169	87	4.8	3.5
15% PMA-K^+				91[a]	141	50	2.8	1.4
PSA-K^+				270[a]	438	168	9.3	1.2
10% PMA-Rb^+				82[a]	175	93	5.2	3.8
10% PMA-Cs^+	27.56	21.52	2.665	82	173	91	5.0	3.7
15% PMA-Li^+				91[a]	198	107	6.0	4.6

[a] The values are assumed, based on the fact that both Na^+ and and Cs^+ ions in 10% PMA membrane gave the same value for ΔV_E.

$$\Delta V_E = \frac{\Delta\bar{\lambda}}{\bar{\lambda}} \frac{10^3}{18\bar{m}_I} \qquad \text{(Eq. 169)}$$

They also measured by electrolysis experiments already described the total water transport using 0.01 N NaOH in which $\bar{t}_{Na^+} = 1.0$. They found total transport to be 13.6 moles and water transported electroconvectively to be 4.6 moles. The difference, 9, was taken as the hydration number of Na^+ ion. Lakshminarayanaiah (270) has investigated this method thoroughly using 0.01 N solutions of NaOH and CsOH with 5, 10, and 15% cross-linked PMA membranes. He has also used the PSA-NaCl system.

Total water transport through different membranes was measured at different current densities. Using the same membrane material and the metal ion, self-diffusion coefficients were determined. Using Eq. 169, electroconvection was evaluated. As the total transport is current dependent, it is difficult to choose one value for the total transport. The obvious choice, though not unambiguous was the limiting value using which the hydration numbers were computed for all the alkali metal ions. The complete data are given in Table XX.

The values are not unreasonable but they are not constants characteristic solely of the ion. They are dependent on the nature of the membrane.

A slight modification of Eq. 169, replacing $\bar{\lambda}$ by $\bar{\lambda}'$ in the denominator to derive ΔV_E, removes almost the membrane dependence of the hydration number. The values according to this calculation (Table XX, revised column) seem to be quite consistent and independent of the nature of the membrane material.

The method, although it seems to give reasonable values, is based on some unsound facts. These are (a) choosing the limiting value for total transport is quite arbitrary. It would be sound if a membrane system which gave no current dependence of total transport is used. Systems used by other investigators where no

TABLE XXI

IONIC HYDRATION NUMBERS, n_i

Method	Concn., N	Conventional value	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mg^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	F^-	Cl^-	Br^-	NO_3^-	SO_4^{2-}	Acetate$^-$	Ref.
Electrolytic water transport (e.w.t.)			0	150	70	20											20					375
E.w.t.	1.3	$H^+ = 0$															3.5					36
E.w.t.		$Cl^- = 0$	0.28	4.7	2.0	1.3		0.7														578, 579
	1.0	$Cl^- = 1$	0.46	7.0	3.6	2.3																
		$Cl^- = 4$	1.02	13.9	8.4	5.4		4.7														
E.w.t.	1.0	$Cl^- = 3$	1.0	12.6	8.4	4.0			10.0	8.3	4.1	13.3										429, 430
E.w.t.	1.0		1.0	13.0	7.9	5.0		10–11									4.0		4.5	1.35		14
	0.1		5.0	62.0	44.5	29.3											26.6					
E.w.t.	0.5	$Cl^- = 9$		13.5	9.5	7.0		6.9														591
E.w.t. (D_2O)				22.0	13.0	7.0		6.0	29.0	29.0	28.0	36.0	34.0	44.0	39.0	7.0	5.0	5.0	6.0	12.0	11.0	443
		PMA membrane		6.0	6.0	4.0	5.2	5.0														
		PSA			13.2	9.3																
E.w.t.	0.01	PMA		5.0	4.0	2.0	4.0	4.0														270
	(revised)	PSA			5.0	1.2																Table XX
E.w.t.		[$Li^+ = 7$	0.5	7.0	5.0	2.0		1.5		10.0	9.5				11.0		1.0					128
Ionic mobility		$Na^+ = 5$]							10.0			12.0		12.0								
Ionic mobility		$H^+ = 1$			10.8	6.2		5.5							5.6							362
Ionic mobility				3.5	2.0				7.5		5.0		10.5									564, 565
Ionic entropies			4.0	5.0	3.5	2.0			7.5		7.5	9.0	10.5	11.0	9.5		2.0					
Raoult's law		$Cl^- = 3$	13.0	13.0	8.0	4.0	2.5		10.5	10.0	9.0	15.0	24.0	21.0	15.0	8.0	3.0	3.0	0	12.0	4.0	444
Activity coefficient		$I^- = 0.9$	3.9	3.4	2.0	0.6	0	0	4.3	3.7	3.0	5.1		5.3			0.9	0.9	0		2.6	103
Adsorption by resin			3.9	3.3	1.6			0.4	5.2	4.7	2.0	7.0										105
X-Ray diffraction				4.0		4.0									8–9							33, 34
Probable values				5.0	5.0	4.0	3.0									4.0	1.0	1.0				53
Diffusion		$Cl^- = 0$		2.8	1.2	0.9												0.2				
		$NH_4^+ =$		2.3	0.7	0.4											0.5	0.7				437

TABLE XXII

CHECK OF EQ. 171 USING THE DATA OF LORIMER, BOTERENBROOD, AND HERMANS (290)

Mean molality, m	$\bar{t}_{+(\mathrm{app})}$	$\bar{t}_w$	$(0.018m_\pm \bar{t}_w)$	$\bar{t}_+$ Calcd.	Obsd.
0.0015	0.860	280	0.0076	0.868	0.80
0.0035	0.834	230	0.0145	0.848	0.74
0.0075	0.699	140	0.0189	0.718	0.69
0.015	0.665	120	0.0324	0.697	0.67

current dependence was found must be used with dilute solutions to measure the total transport. It should prove a worthwhile study to make. (b) Equation 169 probably requires some better basis for its existence and to prove its usefulness.

Recently Rutgers and Hendrikx (443) have used transport measurements of D_2O and H_2O using membranes both selective and nonselective to derive ionic hydration numbers. The values they derived and the values of others obtained by other methods are collected in Table XXI for comparison.

C. RELATIONSHIP BETWEEN TRUE AND APPARENT TRANSPORT NUMBERS

The e.m.f. of a cell of Type 112 is given by Eq. 134 which cannot be integrated without a knowledge of how $\bar{t}_+$ and $\bar{t}_w$ vary with external electrolyte concentration. $\bar{t}_+$ and $\bar{t}_w$ must be found by separate experiments and their values must be unambiguous without being influenced by factors like current density and back-diffusion. Even then what relation these experimental values bear to $\bar{t}_+$ and $\bar{t}_w$ of Eq. 134 is not clearly known.

However, an approximate approach can be made by integrating Eq. 134 within narrow limits $a_\pm'$ and$a$ $_\pm''$. On integration, Eq. 134 takes the form (522)

$$E = -\frac{2RT}{F}(\bar{t}_+ - 10^{-3}m_\pm M\bar{t}_w)\ln\frac{a_\pm'}{a_\pm''} \quad \text{(Eq. 170)}$$

The e.m.f. of cell of Type 112 can be calculated from the modified Nernst Eq. 154, which can be equated to Eq. 170 to give (132)

$$\bar{t}_+ = \bar{t}_{+(\mathrm{app})} + 0.018m_\pm \bar{t}_w \quad \text{(Eq. 171)}$$

Hale and McCauley (132) tested Eq. 171 using different heterogeneous membranes and found good agreement between true $\bar{t}^+$ measured directly and $\bar{t}_+$ calculated using Eq. 171. Their measurements, although confined to a number of different membranes, were made with one set of electrolyte solutions only (0.667 and 1.333 N NaCl). The data of Lorimer, Boterenbrood, and Hermans (290) and that of Lakshminarayanaiah and Subrahmanyan (278) covering a wider concentration range may be used to effect a critical check of Eq. 171. It is seen from the results collected in Table XXII that the agreement is poor and that the calculated values are all larger. The results presented in Table XXIII tell a similar story. The agreement between calculated and observed values of $\bar{t}_+$, although good in case of dilute solutions, is not very satisfactory in the case of strong solutions, calculated values being larger. It is interesting to record that the water transport correction term becomes larger with increase in external concentration. At a mean concentration of 3.895, the contribution of water transport to the total transport is as high as 35%.

TABLE XXIII

CHECK OF EQ. 171 USING THE DATA OF SUBRAHMANYAN AND LAKSHMINARAYANAIAH (522)

Mean molality, m	$\bar{t}_{+(\mathrm{app})}$	$\bar{t}_w$	$(0.018m_\pm \bar{t}_w)$	t_+ Calcd.	Obsd.
0.0015	0.964	91.0	0.003	0.967	1.000
0.0075	0.988	90.0	0.012	1.000	0.997
0.015	0.953	83.1	0.023	0.976	0.995
0.075	0.905	46.0	0.062	0.967	0.930
0.152	0.827	34.0	0.093	0.920	0.886
0.765	0.633	15.0	0.207	0.840	0.815
1.557	0.537	8.0	0.224	0.761	0.760
3.895	0.481	3.4	0.238	0.719	0.682

The discrepancies between observed and calculated $\bar{t}_+$ values reinforce the suspicion already expressed that the measured values of $\bar{t}_+$ and $\bar{t}_w$ may not be the values relevant to the respective terms in Eq. 134, although the check carried out elsewhere by Lakshminarayanaiah and Subrahmanyan (278) tend to discount this suspicion.

D. ELECTRODIALYSIS

Ion movement across membranes caused by the application of an electric field is called electrodialysis. In recent years following the development of mechanically strong and electrically conducting ion-exchange membranes, electrodialysis has become an important industrial operation employed very much in the desalting of brackish waters and also used in other operations involving recovery or removal of salts or other colloidal substances from industrial waste liquids. Physicochemical or electrochemical principles governing efficient operation include most of the transport phenomena presented in this article. Other principles governing successful operation of electrodialysis have been discussed at length elsewhere (54, 70, 71, 170, 192, 245, 257–259, 311, 441, 494, 508, 561, 585, 586).

The behavior of KCl solutions in a continuously operated electrodialysis cell using ion-exchange membranes has been described (409). Theoretical expressions have been derived for the current efficiency of the desalting process. The dependence of current efficiency on the ionic concentration in the desalting chamber has been assessed.

The coulomb efficiency of an electrodialytic demineralization process was found to vary in a peculiar manner with the electrolyte concentration in the dialysate, C. At $C < 0.1$ N, the coulomb efficiency increased with C. But at values of $C > 0.1\ N$, the coulomb efficiency went through an anomalous minimum and rose with increase in C (310). This effect was found to be strong at high mass transfer rates (in presence of applied field) and weak in a system with very low mass transfer rates (membrane potential). It was suggested by Mandersloot (310) that this anomaly may be used to prepare concentrated brine from sea water by electrodialysis.

McClintock, Neihof, and Sollner (326) have outlined the numerous factors which must be considered in electrodialysis experiments. The effect of polarization has been particularly emphasized. Assuming the membrane system

$$\text{anode}\left|\begin{array}{l} C_1\ \mathrm{A^+X^-}\ \text{soln.}\\ C_1\ \mathrm{B^+X^-}\end{array}\right|\begin{array}{c}\text{cation-exchange}\\ \text{membrane}\end{array}\left|\begin{array}{l} C_2\ \mathrm{L^+X^-}\ \text{soln.}\\ \ \end{array}\right|\text{cathode} \qquad \text{(Type 172)}$$

to behave ideally, they derived the relation

$$\left(\frac{J_{\mathrm{A^+}}}{J_{\mathrm{B^+}}}\right)_{\mathrm{elect}} = \frac{a_{\mathrm{A^+}}{}^{(1)}}{a_{\mathrm{B^+}}{}^{(1)}}\left(\frac{J^\circ{}_{\mathrm{A^+}}}{J^\circ{}_{\mathrm{B^+}}}\right)_{\mathrm{BIP}} = \frac{a_{\mathrm{A^+}}{}^{(1)}}{a_{\mathrm{B^+}}{}^{(1)}}\left(\frac{J^\circ{}_{\mathrm{A^+}}}{J^\circ{}_{\mathrm{B^+}}}\right)_{\mathrm{exchange}} \qquad \text{(Eq. 173)}$$

where $(J_{\mathrm{A^+}}/J_{\mathrm{B^+}})_{\mathrm{elect}}$ is the ratio of net flux of $\mathrm{A^+}$ and $\mathrm{B^+}$ in presence of an electric field. This ratio becomes equal to the ratio of the transport numbers, $\bar{t}_{\mathrm{A^+}}/\bar{t}_{\mathrm{B^+}}$. But $(J^\circ{}_{\mathrm{A^+}}/J^\circ{}_{\mathrm{B^+}})_{\mathrm{BIP}} = \bar{t}^\circ{}_{\mathrm{A^+}}/\bar{t}^\circ{}_{\mathrm{B^+}}$ according to Eq. 85. This has been shown to be equal to the ratio of exchange $(J^\circ{}_{\mathrm{A^+}}/J^\circ{}_{\mathrm{B^+}})_{\mathrm{exchange}}$. With solutions in the range 0.02–0.2 N and with current densities 0.3–1.0 ma. cm.$^{-2}$, agreement between theory and experiment was found. At high current densities, polarization caused experimental flux ratios to be lower than theoretical values. At lower current densities, the experimental flux ratios were again lower, the causes for which could not be assigned. Back electrolyte diffusion or water transfer by osmosis and electroosmosis both of which could cause lower flux ratio values (see Bergsma and Staverman (20)) were shown by carefully planned experiments to be not responsible for causing lower flux ratios.

Sethu (479) applied electrodialysis to decant natural rubber skim latex. During electrolysis, rubber particles migrated to the anion-selective membrane. Optimum conditions including current reversal have been recommended for efficient electrodecantation of rubber skim latex.

Blainey and Yardley (23) have described a three-compartment electrodialysis cell for desalting amino acids. An elementary theory has been worked out by Peers (412) to serve as a guide for efficient desalting of mixtures of amino acids. The effects of various factors like current density, anolyte and catholyte composition on the recovery of acidic (142), neutral, and basic amino acids have been discussed and demonstrated. Desalting of amino acids is shown to be improved by operating with relatively low current densities and a combination of acid anolyte and alkaline catholyte. This method of separation has been effectively used by Hara (143) to separate a complex mixture of amino acids into three broad groups, namely neutral, acidic, and basic. Other techniques based on electrodialysis have been worked out for the separation and characterization of proteins (416, 603) and amino acids (527).

Jarvis and Tye (211) studied the transport of nonelectrolytes through selective membranes during electrodialysis of brine solution. Passage of NaCl through membranes was accompanied by the transport of nonelectrolytes (D-glucose, glycerol). At current densities $\not<$ 10 ma. cm.$^{-2}$, the passage of nonelectrolyte was all by electroosmosis. At low current densities, the transport per faraday was larger due to increased nonelectrolyte transfer by diffusion.

A theoretical expression relating the total transport to the respective contributions from electroosmosis and diffusion was given. It was shown that (a) transport by electroosmosis and diffusion were not directly additive, (b) transport by electroosmosis depended only on the concentration of nonelectrolyte in solution donating the counterions to the membrane, and (c) the loss of nonelectrolyte during electrodialysis was independent of nonelectrolyte concentration but dependent on the reduction in salt concentration. Further it was shown that water was transported preferentially. When a pressure differential was applied against this flow, transport of glycerol was markedly reduced (212).

Ion sorting involving transport of ions against a concentration gradient may be also brought about by applying an electric field to a cell composed of closed compartments of constant volume and containing reversible electrodes and solutions of two counterions (173). Electric field drives the faster ion which is smaller at a higher rate. This produces a pressure difference which affects the larger and slow moving ion. The net result is that there will be accumulation of faster ion in the cathode. As the volume is fixed, in the steady state several smaller ions will have been exchanged for the larger ion.

Electrodialysis when reversed becomes similar to a membrane accumulator. A multicompartment cell containing concentrated and dilute solutions in alternate chambers can act as a source of e.m.f. The membrane potentials across each membrane (cation- and anion-exchange membranes alternate) add up to give the cell voltage (312, 343, 410).

1. Anomalous Conduction

It is generally believed that a steady state will be attained in an electrolytic demineralizer when an electric field is applied for a long time. Contrary to this expectation, Forgacs (94) obtained unharmonic oscillations of potential difference between the two sides of a homogeneous cation exchanger.

Seno and Yamabe (476) constructed a membrane system (Figure 12) to demonstrate some anomalous effects. The electrode chambers, E, contained 0.05 *N* NaCl solution and were separated from chambers A and B by cellophane membranes. Chambers A and B were separated by a cation-exchange membrane. Compartment B contained 0.05 *N* NaCl solution whereas A contained a mixture of agar and 0.05 *N* NaCl. When a d.c. voltage was applied, initially the current was ohmic. With time, the current decreased and reached a constant value. Further increase of voltage produced repeated pulses superimposed on the direct current. A mechanism based on the concentration changes in the Nernst diffusion layer was proposed. When the agar was replaced by the solution, no pulse was generated. It was surmised that the gel-like structure of agar stabilized the diffusion layer. Similarly concentrated glycerol–water solution of NaCl also produced pulses.

Membranes formed by joining anion-selective and cation-selective membranes in various configurations exhibit diverse electrical effects, some of which have been demonstrated and discussed by Friedlander (96).

Lovreček and Kunst (292) measured the rest potential at a junction of cation- and anion-exchange membranes. The potential was inversely proportional to the thickness of water layer between the two membranes. The effect was attributed to overlapping of double layers of both the membranes.

Lovreček, Despić, and Bockris (291) obtained rectification of alternating currents across a membrane system in which highly mobile protons were present on one side of the system and highly mobile hydroxyl ions were present on the other side. They attributed the rectifying property to the combination of H^+ and OH^- to form water in one phase of the cycle and to ionization of water in the other phase. The former had less resistance to current flow. Maslov and Ovodova (320) produced similar systems and the phenomenon has been described by Odynets (391) and by Kedem and Katchalsky (218, 224).

Mauro (323, 324) has presented theoretical discussions about some of these effects and showed that reactive effects could arise from close juxtaposition of anion- and cation-exchange membranes. The condition for the reactive effect (capacitative) was that the distance between the two membranes should be small compared to the Debye length of the solution (*i.e.*, thickness of ion atmosphere). The analysis has been explored by Schwartz and Case (473) who showed that at relatively high currents fused anion–cation membrane gave rectifying and reactive effects. As the frequency was increased, rectification became less pronounced (264). The effect was due to changes in concentration profiles of ions during positive and negative phases of the a.c. cycle. As the current was reduced, *I–V* response was linear. The reactive effect may be due either to the presence of transition regions of fixed charge (324) or to the diffusion mechanism of ions in an a.c. field. The former is frequency independent whereas the latter is frequency dependent. An approximate equivalent circuit composed of frequency-dependent element has been described. Similarly, Seno and Yamabe (477) and Läuger (281) have measured and analyzed the *I–V* characteristics of membrane systems and find the rectification mechanism to be similar to that of 'p' and 'n' semiconductor junction.

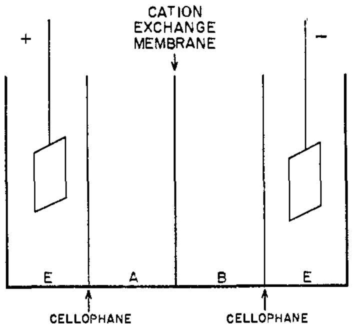


Figure 12.—Membrane electrolyte system to demonstrate anomalous conduction.

Amplification of current was observed in a system composed of two pairs of anion- and cation-exchange membranes (membrane rectifiers) connected to source of a.c. and a source of pulsating d.c. current (293). The mechanism of amplification was expressed in terms of ionization and deionization of water at the junction.

2. *Oscillatory Phenomena*

Theoretical treatments of Schlögl (452, 453, 458) and of Schmid (461–463, 465–468) have been successful in explaining a number of phenomena that arise across membranes separating different salt solutions and subjected to the action of an electric field. A special feature of these presentations is that the ζ-potential so often used in classical theories to characterize the charge on particles or membranes has been substituted by the fixed charge symbol ωX in units of concentration (536). In these considerations, actually three driving forces, *viz.*, potential difference, $\Delta\psi$, concentration difference, ΔC, and a hydrostatic pressure difference, ΔP, have been recognized. Simultaneous action of these forces lead to flow of solute (flux), flow of water (flow), and flow of electricity (current). These flows across membranes of fixed charge have been considered in detail by Teorell (535, 537–540, 543, 544). He has investigated both experimentally (539) and theoretically (540) the effects of introducing the third driving force (hydrostatic pressure difference) to the consideration of transport kinetics across fixed charge membranes separating different salt solutions. The simultaneous interaction of the three forces resulted in oscillatory transport processes of ions and of water across the membrane.

The oscillatory membrane unit was constructed according to the scheme: AgCl electrode|0.01 N NaCl| porous glass membrane|0.01 N NaCl|AgCl electrode. Constant currents were applied across the electrodes, and changes of membrane potential, electrical membrane resistance, and water pressure difference across the membrane were simultaneously recorded with respect to time. The important feature of these variables was the rhythmical variations with time. Two different responses, damped or undamped, could be observed. Below a certain threshold value of the current density, damped oscillations were observed and above the threshold, the oscillations became undamped. The effect of other factors like concentration and concentration ratio on these oscillatory phenomena have also been studied. The experimental results have also been mathematically analyzed (537, 540).

The results of these studies have been applied to explain the formation of action potentials and other excitability phenomena in living cells (538, 541, 542, 544).

In these studies, the results of which have been utilized to explain a number of electrophysiological phenomena, the concentration of the electrolytes bounding the membrane never approached the electrolyte concentrations prevailing in the physiological systems. In order to remove this particular deficiency at least partially, a membrane system, cathode solution (′)|filter paper|ion-exchange gel|filter paper|anode solution (″), was constructed. NaCl (or KCl) solution (0.02 N) was circulated through the two chambers holding the membrane which was a cation-exchange gel consisting of a mixture of 40% dry weight SE-Sephadex G50 and 60% Sephadex G75 (neutral gel filter powder) as a support. Thin hardened filter papers bounded the gel bed. In accordance with the results of rigid membranes (538, 539), this system also gave, as regards the three parameters, intramembrane potential, resistance and pressure damped oscillations at moderate current densities (a few ma. cm.$^{-2}$), continuous oscillations at high current densities, and only an overshoot at weak current densities (543). Experiments to obtain information about the current–resistance relationship were also performed. In these experiments, the pressure was kept constant at various preset levels (pressure clamps) and a kind of hysteresis loop behavior indicating the existence of an unstable system with inherent rhythmic properties was noticed. The relevance of these oscillations to excitability phenomena exhibited by living tissues such as nerve was also pointed out (543, 544).

Aranow (8) from first principles derived all of the theoretical equations of Teorell and showed that the periodic behavior was a consequence of the effect of boundary conditions on hydrodynamic stability. Franck (95) has shown that an ion-retaining porous membrane when subjected simultaneously to electric, pressure, and concentration gradients gave eight different types of current–voltage curves depending on the way these forces are superimposed. Applying the Nernst–Planck equation for ion transport, he further showed how the different curves arose and under what conditions periodic transport behavior became possible.

Kobatake and Fujita (237) have given a theoretical analysis of the phenomena described by Teorell and found relaxation oscillations of mass flow and of difference of potential and pressure across the membrane in accordance with Teorell's observations. The experiments of Teorell under clamped pressure when repeated to study the variation of transmembrane potential with current across a Pyrex glass filter containing NaCl, 0.05 and 0.5 N, on either side, a "flip-flop" type (N-shaped) current–voltage relation was obtained. A theoretical study of this phenomenon has been presented (236). The occurrence of a discontinuous change in current at a certain threshold has been attributed to the concentration dependence of the electroosmotic coefficient.

V. FLUX DUE TO A PRESSURE GRADIENT

In the preceding sections, although pressure differences incidental to maintenance of electrochemical potential gradient were considered, no external hydrostatic pressure gradients were applied. In this section, the phenomena arising out of application of an excess hydrostatic pressure on one of the solutions existing on either side of a membrane will be considered.

When an excess hydrostatic pressure is applied to the solution on one side, the liquid in the pores of the membrane is displaced leading to the development of a potential called the streaming potential which tends to oppose the effect of the pressure and thereby reduce the flow across the membrane. Further, the potential slows down the counterion and accelerates the co-ion and thus maintains electroneutrality. The applied pressure being stronger, both counterions and co-ions are carried along relative to the matrix. The streaming potential can be short circuited by using reversible electrodes attached to membrane surfaces and connected together. The pressure now produces an ion flow which results in a current flow called streaming current. Another important effect of pressure in a highly permselective membrane is the realization of the filtration of electrolyte brought about by the operation of the Donnan principle in excluding the co-ions from the membrane phase. In spite of the co-ion movement being facilitated by the streaming potential, the electrolyte flux across the membrane remains small, whereas the solvent will be forced out thus causing electrolyte filtration.

A. STREAMING POTENTIAL

Relatively little work exists about this phenomenon in ion-exchange membranes. The interesting work of Schmid (463) and Schwarz (468) has been reviewed by Helfferich (169). Their treatment of streaming potential, unlike the classical electrokinetic approach based on the concept of ζ-potential, discards the use of this concept and uses instead some directly measurable parameters of the membrane phase.

Assuming absence of concentration gradients within the membrane and of specific interactions between the mobile species and the fixed groups of the membrane, it is shown that the streaming potential, $\Delta\psi$, is related to the hydrostatic pressure difference, ΔP, by the equation

$$\Delta\psi = \frac{\omega XF}{\rho_0 \bar{\kappa}} \Delta P \qquad \text{(Eq. 174)}$$

$\Delta\psi$ is directly proportional to ΔP and to X, but the effect of X is annulled by the effect of $\bar{\kappa}$. Membrane thickness has no effect on the streaming potential whose magnitude is about a few millivolts for ΔP = 1 atm. across a typical ion exchanger ($X \approx 2\ N = 2 \times 10^{-3}$ mole/cm.^{3}, $\bar{\kappa} = 10^{-2}\ \Omega^{-1}$ cm.$^{-1}$, and $\rho_0 = 10^{13}$ g. cm.$^{-3}$ sec.$^{-1}$).

The variation of $\Delta\psi$ with time (35) was established by Schmid and Schwarz (468). When a pressure of 65.5 mm. was applied to one solution existing on either side of the membrane electrolyte system, 2×10^{-4} M KCl|membrane|2×10^{-4} M KCl, the streaming potential assumed a value given by Eq. 174. Due to concentration changes at the membrane solution interfaces (accumulation on high-pressure side and depletion on the low-pressure side), an additional concentration potential was added to the streaming potential and therefore a transient rise was noted. After a certain time, a steady-state value, always a little higher than the initial value, was reached. When the pressure was removed, the potential took some time before it reached its zero value. This type of behavior indicated some sort of filter action by the membrane.

1. *Effect of Pressure on Membrane Potential across a Simple Ion-Exchange Membrane*

Stewart and Graydon (516) studied e.m.f.'s of a concentration cell under conditions of constant pressure of 1 atm. on the dilute solution (0.05 M) and of varying pressures up to 3 atm. on the concentrated solution (0.1 M) and observed the e.m.f. across some membranes to go above the theoretical value. But this increase was not very much.

2. *Effect of Pressure on Membrane Potential across a Bipolar Membrane*

Ishibashi and Hirano (203) measured the effect of pressure on the membrane potentials arising across a bipolar membrane which was made by cementing together a cation-exchange membrane and an anion-exchange membrane. The 0.5 N solution side of the membrane cell

Ag–AgCl | 0.5 N NaCl | bipolar membrane (anion–cation) | 0.1 N NaCl | Ag–AgCl

was subject to pressures ranging from 0 to 400 mm. H_2O. Results of Table XXIV reveal that as the pressure was reversed, the membrane potential got reversed. This transition caused by the reversal of pressure difference of 200 mm. H_2O as a function of time is shown in Figure 13. The pressure head of 0.5 N solution is larger than 0.1 N solution in the interval PQ and the relation is reversed at RS. In the intervals $P'P$, QR, and ST, water heads were equal on both sides. The results of Figure 13 indicating the variation of $E_m^P - E_m$ (see also Table XXIV) against ΔP are very striking compared to the slight increase in potential observed by Stewart and Graydon (516) for simple membranes subjected to a pressure difference of nearly 3 atm. These large effects in the case of bipolar membranes were explained using the three-layer model depicted in Figure 14 as the basis. The construction of this model seems to be based on the

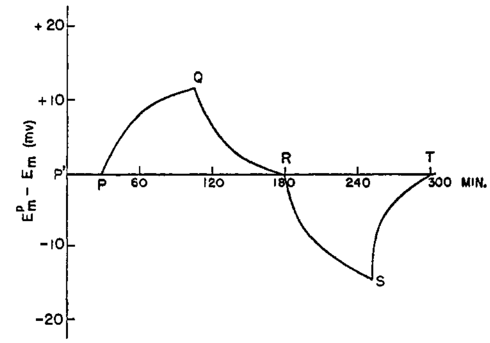


Figure 13.—Transition of membrane potential caused by pressure difference, ΔP = 200 mm. H_2O.

Table XXIV

The Effect of Pressure on Membrane Potential across a Bipolar Membrane

Membrane	Concn. of outer solutions, mole/l.	E,[a] mv.	E_m,[b] mv.	E_m^P,[c] mv.	$E_m^P - E_m$, mv.
1	0.5–0.1	50.28	13.36	17.74	4.38
	0.5–0.1	50.44	13.52	9.12	−4.40[e]
	0.1–0.02	51.98	14.49	16.14	1.65
	0.1–0.02	51.76	14.27	11.40	−2.87
2	0.5–0.1	43.23	6.31	17.71	10.40
	0.1–0.02	39.52	2.03	17.03	15.00
	0.1–0.02	39.18	1.69	−15.61	−17.30

[a] E = the observed total potential of the membrane cell under zero pressure difference (includes the potential due to electrodes). [b] E_m = membrane potential, *i.e.*, $E - E_{\text{electrodes}} = E - (RT/F) \ln C_2/C_1$. [c] E_m^P = membrane potential under given pressure difference. [d] $E_m^P - E_m$ = deviation of membrane potential due to application of pressure. [e] Negative values indicate application of pressure on dilute solution side.

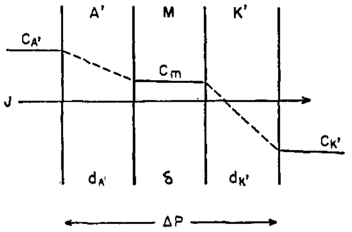


Figure 14.—Three-layer membrane model for a bipolar membrane.

measurement of membrane potentials across bipolar membranes at the same atmospheric pressure (202). Unlike Frilette's measurements (97) of potentials across bipolar membranes which were unstable and irreproducible, Ishibashi (202) measured reproducible potentials and found that the calculation of a transport number through a bipolar membrane regarding it as a single membrane by applying the Nernst equation was not valid; as the membrane potential was considered to be the sum of two such potentials. It was expressed by

$$E_m = \frac{RT}{F}(2\bar{t}_+^{A'} - 1)\ln\frac{C_A'}{C_m} + (2\bar{t}_+^{K'} - 1)\ln\frac{C_m}{C_K'} \quad \text{(Eq. 175)}$$

where C_A' and C_K' were the concentrations on either side and C_m was the concentration in the interlayer of free solution. It was expressed as

$$C_m = \frac{\bar{D}_A' C_A' + \bar{D}_A' C_K'}{\bar{D}_A' + \bar{D}_K'} \quad \text{(Eq. 176)}$$

where $\bar{D}_A' = D_A'/d_A'$, $\bar{D}_K' = D_K'/d_K'$, and D_A' *et seq.* are diffusion coefficients through A′ layer *et seq.*; d_A' and d_K' are the thickness of layers A′ and K′. δ is the thickness of interlayer solution.

When a pressure was applied, C_m changed and this change was assumed to be given by

$$C_m^{P'} = C_m^{P} + (C^{\circ}_m - C_m^{P})\exp[-(\bar{D}_A' + \bar{D}_K' + J)t/\delta] \quad \text{(Eq. 177)}$$

$$C_m^{P} = (\bar{D}_A' C_A' + \bar{D}_K' C_K' + J C_A')/(\bar{D}_A' + \bar{D}_K' + J) \quad \text{(Eq. 178)}$$

where $C_m^{P'}$ = concentration C_m, at some pressure difference; C_m^{P} = concentration C_m, in the stationary state; and $C^{\circ}_m = C_m$ when there is no pressure difference. J is the permeation velocity of solution through the membrane which was measured at various pressures, t is the transport number, and $\bar{D}_A'$, $\bar{D}_K'$, d_A', and d_K' were known for individual membranes. On the basis of these relations $E_m^{P} - E_m$ (E_m = 0.33 mv. for a membrane BP-3A′ (203)) was calculated at various pressures and compared with observed values. Satisfactory agreement was obtained (Table XXV).

TABLE XXV

DEVIATIONS OF MEMBRANE POTENTIALS (OBSERVED AND CALCULATED) AT VARIOUS PRESSURE DIFFERENCES

P (mm. H_2O)	0	50	100	200	300	400
$E_m^P - E_m$ (obsd.), mv.	—	1.71	3.33	6.21	8.64	10.58
$E_m^P - E_m$ (calcd.), mv.	—	1.74	—	6.31	8.67	10.58

B. STREAMING CURRENT

The ionic flux is given by

$$J_i = -z_i\bar{C}_i\bar{u}_i\frac{\Delta\psi}{d} + \bar{C}_i V^* \quad \text{(Eq. 179)}$$

but

$$V^* = \frac{\omega F X}{\rho_0 v_0}\frac{\Delta\psi}{d} = \omega\bar{u}_0\frac{\Delta\psi}{d} \quad \text{(Eq. 9)}$$

As the pressure gradient is opposed by the electrical gradient

$$V^* = -\frac{\Delta P}{d\rho_0} + \omega\bar{u}_0\frac{\Delta\psi}{d} \quad \text{(Eq. 180)}$$

and

$$\Sigma z_i\bar{C}_i + \omega X = 0 \quad \text{(Eq. 10)}$$

Combining Eq. 179, 180, and 10

$$J_i = (X\bar{u}_i + \bar{C}_i\bar{u}_0)\omega\frac{\Delta\psi}{d} - \bar{C}_i\frac{\Delta P}{\rho_0 d} \quad \text{(Eq. 181)}$$

Streaming current

$$I = (F\sum_i z_i J_i)_{\Delta\psi=0} \quad \text{(Eq. 12)}$$

$$I_{\Delta\psi=0} = -F\sum_i z_i\bar{C}_i\frac{\Delta P}{\rho_0 d}$$

Substituting for $\sum_i \bar{C}_i z_i = -\omega X$

$$I_{\Delta\psi=0} = \frac{\omega X F}{\rho_0 d}\Delta P \quad \text{(Eq. 182)}$$

The streaming current is directly proportional to ΔP and fixed charge and inversely proportional to ρ_0 and d. For a typical ion exchanger, streaming currents are of the order of 0.1 to 1.0 ma. cm.$^{-2}$ per atmospheric pressure difference.

C. SALT FILTRATION

The flux of an ionic species i is given by Eq. 181

$$J_i = \frac{\Delta\psi}{d}(\bar{C}_i\bar{u}_0\omega - z_i\bar{C}_i\bar{u}_i) - \bar{C}_i\frac{\Delta P}{\rho_0 d} \quad \text{(Eq. 183)}$$

Substituting for the streaming potential $\Delta\psi$ in Eq. 174

$$J_i = \frac{\omega X F}{\rho_0 d\bar{\kappa}}\Delta P\bar{C}_i(\omega\bar{u}_0 - z_i\bar{u}_i) - \bar{C}_i\frac{\Delta P}{\rho_0 d} \quad \text{(Eq. 184)}$$

transport number

$$\bar{t}_i = \frac{\bar{C}_i(z_i\bar{u}_i - \omega\bar{u}_0)}{\sum z_i^2\bar{u}_i\bar{C}_i + \bar{u}_0X} \qquad \text{(Eq. 185)}$$

and

$$\bar{\kappa} = F\sum_i z_i^2\bar{u}_i\bar{C}_i + \bar{u}_0X \qquad \text{(Eq. 186)}$$

Substituting Eq. 185 and 186 into Eq. 184, ionic flux is given by

$$J_i = -\frac{\Delta P}{\rho_0 d}(\bar{C}_i + \omega X\bar{t}_i) \qquad \text{(Eq. 187)}$$

In highly permselective membranes, co-ions are negligible and so their flux is very small. If only one counterion is present, the flux will be negligible. But if several counterions are present, application of a high pressure causes convection which establishes an opposing streaming potential. This potential will drive the counterion back towards the solution on the high-pressure side. The smaller and more mobile ion has high rate of transference, whereas the larger and less mobile ion has low rate of transference but high rate of convection. Thus the faster ion accumulates on the high-pressure side and the bigger and slower ion on the low-pressure side.

In the case of membranes of high fixed charge, it was stated that the electrolyte flux was negligible, whereas the solvent was forced out. This filtration was caused purely by the electrostatic effect which will be observed even if the membrane pores were larger than the ionic diameters (329, 468, 474).

It is found that even nonselective membranes like cellophane, cellulose acetate, etc., which have few fixed groups are also able to filter salt solutions and water will flow through the membrane when a pressure in excess of the osmotic pressure of the solution is applied (47, 400). This process which is the reverse of osmosis is not electrostatic in nature. Various theories like solubility, capillarity, etc., have been proposed (529) to explain the semipermeability of the membranes. Contrary to the action of ion-selective membranes, these membranes exclude ions by blocking their passage. Reid and Breton (425) argued that the presence of hydrophilic groups in the membrane material is a prerequisite for it to serve as a semipermeable membrane. Water will enter into hydrogen bonding with the carbonyl oxygen of the hydrophilic group and thus will be bound strongly. They proposed two types of mechanism for transport. Ions and molecules (no hydrogen bonding) will be transported by hole-type diffusion, and hydrogen-bonded molecules will be transported by alignment-type diffusion. Strong hydrogen bonding reduced considerably the probability of hole formation, and as a result solute diffusion which depended on pore size will be reduced. Cellulose acetate membrane, which showed high salt rejection, was shown to be due to bound water in the membrane. This prevented the passage of ions which did not fit into the quasi-crystalline bound water network. Measurements of dielectric constant and electrical resistance of these membranes tend to confirm these suggestions which were further supported by similar studies under a variety of conditions using a number of different membranes (427).

Further it was shown by measurements of activation entropy values which were negative (426) for diffusion of water through cellulose acetate that the water molecules were confined to states of high order as they were transferred across the membrane under high pressures.

Sourirajan (286, 499) proposed a mechanism based on the Gibbs adsorption equation. Due to negative adsorption of the dissolved salt at the air–water interface, the topmost layer of a solution of NaCl kept exposed to air, was only pure water. The thickness of this layer was estimated to be about 4 Å. in a solution of 110 g. of NaCl per liter. When an aqueous solution was brought in contact with a membrane surface of proper chemical nature, it was proposed that multilayers of demineralized water were formed at the interface. The proper adjustment of parameters involved for the success of this operation would enable production of potable water from brine solution. The parameters were: (1) nature of solution, (2) nature of membrane surface contacting the solution, (3) critical diameters of pores in the membrane, and (4) optimum pressure necessary to bring about the continuous flow of liquid through the pores at the required rate. For the success of the operation, membrane surface and pore size should conform to such a nature as to have preferential sorption for water. It was shown from the data acquired for a number of membranes (285, 286) that cellulose acetate and cellulose butyrate membranes had high sorption capacity for water due to hydrogen bonding. Silicone-treated cellophane also had a similar property. The effects of pressure and salt concentrations were also considered. The minimum pressure is of course the osmotic pressure at which the rate of permeation of water is zero. As the pressure was increased, the build-up of salt at the interface increased. To eliminate this build-up and to facilitate orientation of water only at the interface, good circulation of solution was necessary.

The ability of a cellulose acetate membrane to separate inorganic ions from their aqueous solutions was found to be in the order Mg, Ba, Sr, Ca, > Li, Na, K (500) for cations and citrate > tartrate = sulfate > acetate > Cl > Br > NO_3 > I > CNS for anions (286). This order is the same as the lyotropic series for both cations and anions. Hydration of ions (Table XXI) also follow the same order. Employing this technique, organic substances in aqueous solution also have been

TABLE XXVI

CALCULATED "DIFFUSION COEFFICIENTS" FOR THE PERMEATION OF WATER AND OF ALCOHOLS THROUGH CELLOPHANE MEMBRANES

Substance	Temp., °C.	$\bar{D} \times 10^5$, cm.^{2} sec.$^{-1}$ —Membrane swollen in— 60% ethanol	Water	3% NaOH	Self-diffusion $D \times 10^5$, cm.^{2} sec.$^{-1}$
Water	20		37		2.8 to 4.4 in the range 25–45°
	28		45		
	38		63		
	40		67		
Methanol	30	2.97	7.37	10.3	2.5
Ethanol	30	0.87	1.95	2.3	1.16
1-Propanol	30	0.33	0.70	1.06	0.73
1-Butanol	30	0.20	0.39	0.47	0.58

separated. For some substances the following orders were established: *n*-PrOH > EtOH, *i*-BuOH > *n*-BuOH, *i*-PrOH > *n*-PrOH, *t*-BuOH > sec-BuOH > *n*-BuOH, acetaldehyde > EtOH > acetone > acetic acid. The technique has been developed into a neat separation process for separating hydrocarbon liquids from their mixtures (332, 501).

1. Nature of the Flow through Membranes

On ordinary grounds, it is difficult to assess the nature of the flux occurring across a membrane subjected to an hydrostatic pressure difference. Both Ticknor (549) and Mauro (321, 322) have analyzed this problem. Ticknor found that the type of flow depended on the sizes of the permeating molecule and of the capillaries of the membrane and on the extent of bonding the permeating species had for the membrane material. He estimated that the rate of diffusional flow and the rate of viscous flow would be equal when the pore radius of the membrane capillaries was nearly twice the radius of the permeating molecules. It was surmised that when the pore radius became very much larger than the molecular radius, the flow would be viscous and when they are nearly equal the flow would be diffusional. Using the permeability data of Madras, McIntosh, and Mason (306), he calculated diffusion coefficients for the permeation of water and for the permeation of alcohols through swollen cellophane membranes. It is seen from his calculations (Table XXVI) that water diffusion coefficients are nearly ten times larger than self-diffusion coefficients of water. So a faster transport mechanism (viscous flow or hole-type diffusion of Reid and Breton (425)) must be involved.

In the case of methanol, the diffusion coefficients are larger than its self-diffusion and so again mass flow is involved. In other cases, the flow is diffusive. These two types of flow are illustrated by Reid and Spencer (428) who found convective permeability (viscous flow) decreased with increase in pressure whereas diffusive permeability was independent of pressure, emphasizing again the role of pore size in determining the type of flow.

TABLE XXVII

FLUX DATA (DIFFUSION AND TOTAL FLOW) FOR THREE TYPES OF COLLODION MEMBRANES

Membrane	DA/d	$(dn/dt)_{H_2O^{18}}$ diffusion, mole sec.$^{-1}$/dyne cm.$^{-2}$	Total flow due to ΔP, mole sec.$^{-1}$/dyne cm.$^{-2}$	Flux ratio, diffusion/total
M-1	30×10^{-4}	12×10^{-14}	8800×10^{-14}	1/733
M-2	14×10^{-4}	5.6×10^{-14}	310×10^{-14}	1/55
M-3	2.7×10^{-4}	1.1×10^{-14}	39×10^{-14}	1/36

Analysis by Mauro (321, 322) has shown that the solvent flow by osmosis is composed of both viscous and diffusion components. The relative importance of the two components depended on the nature of the membrane. It was shown that for most barriers, the predominant component was the viscous flux. Robbins and Mauro (435) using different types of collodion membranes and tracer H_2O^{18} showed that the flux due to diffusion was a small part of the total flux which was measured by applying different pressures. Flux varied linearly with applied hydrostatic pressure. The diffusion of H_2O^{18} across the membrane was also measured.

Fick's law may be written as

$$dn/dt = \frac{DA}{RT} C \frac{d\mu}{dx} \qquad \text{(Eq. 188)}$$

where dn/dt is the rate of transfer of n and $d\mu = \bar{V} dP$ and $C\bar{V} = 1$. Making the substitutions in Eq. 188

$$dn/dt = \frac{DA}{RT} \frac{dP}{dx} \qquad \text{(Eq. 189)}$$

As dP/dx can be maintained constant, it can be written as $\Delta P/d$

$$dn/dt = \frac{DA}{RT} \frac{\Delta P}{d} \qquad \text{(Eq. 190)}$$

DA/d was evaluated by observing the diffusion of H_2O^{18} across the membrane from the relation

$$(dn/dt)_{H_2O^{18}} = (DA/d) \Delta C_{H_2O^{18}} \qquad \text{(Eq. 191)}$$

as ΔP was equated to the osmotic pressure $RT\Delta C_{H_2O^{18}}$. Assuming linear gradients, integration of Eq. 191, gave

$$\frac{DA}{d} = \frac{2.303V}{2\Delta t} \log \frac{C' + C'' - 2C_{t_0}''}{C' + C'' - 2C_{t_0+\Delta t}''} \qquad \text{(Eq. 192)}$$

where V is the volume of the chambers (equal volumes), C' = initial concentration in chamber (′) at time $t = 0$, C'' = initial concentration in chamber (″) at time $t = 0$, C_{t_0}'' = concentration in chamber (″) at time $t = t_0$, and $C_{t_0+\Delta t}''$ = concentration in chamber (″) at time $t = t_0 + \Delta t$.

The values of DA/d obtained for different membranes are given in Table XXVII. From these values (d*n*/

$dt)_{H_2O^{18}}$ was worked out from Eq. 191 for $\Delta P = 1$ dyne/cm.^{2}.

TABLE XXVIII

WATER PERMEABILITY THROUGH ACRYLAMIDE GELS

Polymer. %	$K_s \times 10^{16}$, cm.^{2} sec.$^{-1}$	$\bar{D} \times 10^5$, cm.^{2} sec.$^{-1}$	Pore size, Å.
5	37.9	61.0	About 18
10	18.2	30.9	
15	14.0	25.2	
20	8.8	16.8	
25	3.5	7.1	About 5
30	4.3	9.4	
35	2.1	4.9	

As the membrane became tighter (M-2, M-3), the change in the diffusional component of the flux was less than the change in the nondiffusional component.

The studies of White (582) with acrylamide polymer gels further illustrate this change over from the viscous to the purely diffusional flux very neatly. In Table XXVIII are given his data for the diffusion of water through the gel as a function of the polymer concentration. The flow rate varied linearly with pressure, and from the slope of the line the permeability coefficient K_s was evaluated. From the values of K_s the diffusion coefficients were calculated. At polymer concentrations in the range 25–35%, the $\bar{D}$ values are close to the value of self-diffusion of water. Further using the Ferry equation relating permeability to membrane pore size, *viz.*

$$r = \sqrt{\frac{8K_s}{S}} \qquad \text{(Eq. 193)}$$

where r is the radius of the pore and S is the specific water content, the radius of the pores was estimated. For 25–35% gels a value of about 5 Å. was calculated. This is nearly twice the radius of a water molecule (1.5 Å.) and thus lends support to the calculations of Ticknor (549) for the condition to realize diffusional flow only.

2. Determination of Equivalent Pore Size

Having recognized the existence of two types of flow across the membranes, theories have been developed particularly by two groups of physiologists (239, 406, 407) to relate the two kinds of flow to the existence or absence of aqueous channels across cell membranes. These theories have been analyzed and shown to be equivalent to each other in their formulations in some limiting cases (79). Diffusion permeability (diffusional flow) and filtration permeability (viscous or volume flow) are two distinct measurements whose comparison gives useful information regarding the structure of the membrane. This is already evident from the somewhat approximate treatment of data given in the previous section. The following derivation due to Renkin (431), Robbins and Mauro (435), and Nevis (377) emphasize the usefulness of the two measurements in deriving a value for the average radius of the pores present in a membrane.

According to Fick's law

$$J_d = -D_w A_0 \frac{\Delta C_w}{d} = -P_d \Delta C_w \qquad \text{(Eq. 194)}$$

where J_d = flux of water (diffusional), A_0 = total area of pores ($n\pi r^2$). According to Poiseuille's law

$$J_f = \frac{n\pi r^4}{8\eta \bar{V}_w}\,\frac{\Delta P}{d} = P_f'\Delta C_s \quad (\Delta P = RT\Delta C_s) \qquad \text{(Eq. 195)}$$

P_f' includes the diffusional flux if any.

From Eq. 194 and 195, it follows

$$r^2 = \frac{8D_w \eta \bar{V}_w}{RT}\,\frac{P_f'}{P_d} \qquad \text{(Eq. 196)}$$

Substituting the literature values for the constants

$$r = 3.6\sqrt{\frac{P_f - P_d}{P_d}} = 3.6\sqrt{\frac{P_f}{P_d} - 1} \qquad \text{(Eq. 197)}$$

This equation has been utilized in connection with studies with natural systems. The data of Table XXVII may be used to calculate the pore radius for the three types of collodion membranes (435). The values obtained were 97 Å. for M-1, 25 Å. for M-2, and 21.4 Å. for M-3. The value of 97 Å. obtained for M-1 was found to be far removed from the true value as hemaglobin whose radius is about 35 Å. did not pass through the membrane. The other values were considered reasonable.

In a similar manner but ignoring the effect of diffusion, Peterson and Livingston (415) calculated the effective pore radius for both treated and untreated cellophane. The values were found to be 15.5 and 16 Å., respectively. These values indicate the ineffectiveness of the cross-linking treatment with dialdehyde starch in closing up the pores. However, it was found that KCl diffusion was lowered from 2.81×10^{-7} to 0.43×10^{-7} cm.^{2} sec.$^{-1}$ on treatment. This was attributed on X-ray evidence to decrease in crystallinity of the cellophane. This in turn emphasized the fact that the cross-linking treatment by increasing the tortuosity of the path traveled by the ions of KCl produced lower diffusion coefficients.

Equation 196 has been written by a number of investigators (83, 90, 124) in the form

$$r_e = 2\sqrt{\frac{2K_f \eta d}{S}} \qquad \text{(Eq. 198)}$$

K_f is called the filtration coefficient and is equal to $J_f/\Delta P$, volume flow per unit pressure difference. This is based on the consideration that pores run straight and perpendicular to the membrane surface. In a membrane, it is highly probable that they are oriented

TABLE XXIX

CHARACTERISTICS OF DIFFERENT MEMBRANES

Measurement	Visking cellulose	Dupont cellophane	Sylvania wet gel	Ref.
Thickness d, cm. × 10^3	5.47	7.86	8.43	431
	4.52		8.42	102
Water content, S	0.664	0.763	8.38	431
φ_w	0.68		0.77	102
Filtration coefficient, K_f	9.5	22.4	194	431
(cm.^{3}/dyne sec.) × 10^{12} L_p	34		100	102
	17	64	250	78
A/d, cm.^{a}				
H_3HO	19.0 (4)	16.6 (10.8)	23.6 (66)	431
D_2O	15.0 (9)	17.0 (30.0)	16.0 (125)	78
Urea	17.2	18.3	22.6	431
Glucose	9.6	14.7	23.7	
Antipyrine	11.9		24.6	
Sucrose	6.6	11.4	21.1	
Raffinose	5.1	9.9	20.1	
Hemaglobin	0	0	2.4	
Calculated pore radius, Å.				
1. r_e	7.5	12.6	37.3	Eq. 198
2. r_m	13.0	21.9	64.6	Eq. 199
3. (a) Diffusion of water, r_p	18.9	31.0	76.7	Eq. 200
	23	41	82	78
(b) Restricted diffusion, r_d	15	30	80–100	
(c) Ultrafiltration, r_f	15	35–40	~200	
(d) Distribution of pore radii	14	30	—	
(e) r using Eq. 211	18.3	31	79	431
	28	53	110	78
(f) Friction model	23		31	102

^{a} $\dot{K} \times 10^{14}$ values in parentheses.

randomly. Bjerrum and Manegold (22) therefore took the pore length to be equal to 3d and wrote

$$r_m = 2\sqrt{\frac{6K_f\eta d}{S}} = r_e\sqrt{3} \qquad \text{(Eq. 199)}$$

But Pappenheimer (406), Renkin, and Borrero (407) took a mean length between d and 3d and used A/d derived by direct measurement of diffusion of isotope labeled water (see Eq. 192).

$$r_p = 2\sqrt{\frac{2K_f\eta}{(A/d)_w}} \qquad \text{(Eq. 200)}$$

These equations have been tested by Renkin (431) for three different membranes, Visking cellulose, Dupont cellophane, and Sylvania wet gel. The data derived for these membranes are given in Table XXIX.

The values of pore radii, r_m and r_P, derived by the use of Eq. 199 and 200 are close whereas the values of r_e (Eq. 198) are too low. It was concluded by Renkin that r_e values were in error.

The data of Table XXIX show that A/d decreased with increasing molecular weight of the substance whose radii are given in Table XXX. These values are a little different from the values given by Durbin (78) which are also included in the table. The decrease of A/d is greater in membranes with smaller pores. This fall in apparent diffusion area was attributed to two factors: (1) steric hindrance at the entrance to the pores and (2) frictional resistance with the pores felt by the molecules. Pappenheimer (406, 407) proposed corrections for these factors. If A_0 is the total cross-sectional area and A_d is the effective area of the opening, steric hindrance was corrected for by the Eq. 201

$$A_d = A_0\left(1 - \frac{a}{r}\right)^2 \qquad \text{(Eq. 201)}$$

The frictional factor was corrected by the use of the Faxen equation (415, 431)

$$A_d/A_0 = 1 - 2.104(a/r) + 2.09(a/r)^3 - 0.9(a/r)^5 \qquad \text{(Eq. 202)}$$

where a is the radius of the permeating molecule.

The combined effect was given by

$$\frac{A_d}{A_0} = \left(1 - \frac{a}{r}\right)^2\left[1 - 2.104\left(\frac{a}{r}\right) + 2.09\left(\frac{a}{r}\right)^3 - 0.95\left(\frac{a}{r}\right)^5\right] \qquad \text{(Eq. 203)}$$

This may be recast to give

$$\frac{A_d}{d} = \frac{A_0}{d}\left[\left(1 - \frac{a}{r}\right)^2\left\{1 - 2.104\left(\frac{a}{r}\right) + 2.09\left(\frac{a}{r}\right)^3 - 0.95\left(\frac{a}{r}\right)^5\right\}\right] \qquad \text{(Eq. 204)}$$

TABLE XXX

MOLECULAR RADIUS (a) OF VARIOUS SUBSTANCES

Substance	Value used by Renkin (431), Å.	Value used by Durbin (78), Å.
H_3HO	1.97	
D_2O		1.9
Urea	2.70	2.70
Glucose	3.57	4.40
Antipyrine	3.96	
Sucrose	4.40	5.30
Maltose	4.44	
Raffinose	5.64	6.1
Hemaglobin	30	
Inulin		12
Bovin serum albumin		37

For the substances used A_d/d was determined by Renkin for the three membranes and plotted against a. Assigning suitable values for r, A_d/d was calculated from Eq. 204 for different substances (*i.e.*, particular value of a) and again plotted as a function of a. This was repeated to get that value of r which fitted the experimental curve best. This was done by Renkin and the values obtained are given in Table XXIX as r_d (restricted diffusion).

In addition to the two factors discussed above, it was noted by several investigators that molecular sieving depended on the rate of filtering or pressure. This generally produced a concentration gradient which led to diffusion of solute in the same direction as filtration. Pappenheimer, Renkin, and Borrero (407) considered this effect and derived Eq. 205 for the sieve coefficient (C_2/C_1)

$$\frac{C_2}{C_1} = \frac{1 + \frac{D_x}{Q}\left(\frac{A}{\mathrm{d}}\right)_w}{\frac{A_w}{A_x} + \frac{D_x}{Q}\left(\frac{A}{d}\right)_w} \qquad \text{(Eq. 205)}$$

where C_2 = solute concentration in filtrate, C_1 = solute concentration in filtrand, D_x = diffusion coefficient of solute in solvent, Q = filtration rates (volume per unit time), and A_w and A_x are effective pore area for solvent and for solute molecules, respectively.

Equation 205 in combination with the Ferry Eq. 206

$$\left(\frac{A_x}{A_0}\right)_f = \left[2\left(1 - \frac{a}{r}\right)^2 - \left(1 - \frac{a}{r}\right)^4\right] \times \left[1 - 2.104\left(\frac{a}{r}\right) + 2.09\left(\frac{a}{r}\right)^3 - 0.95\left(\frac{a}{r}\right)^5\right] \qquad \text{(Eq. 206)}$$

which gave the total restriction arising from steric hindrance at entrance during ultrafiltration due to Ferry (90) and frictional effect, has been used to predict the variation of C_2/C_1 with filtration rate and molecular size. The values of pore size obtained by this method are given in Table XXIX as r_f. With Visking dialysis tubing the value agreed with the other values but in case of the other two membranes, there was considerable difference which was considered systematic and was attributed to the differences in individual pore size. So Eq. 205 was applied individually to each class of pores and summed up. This type of computation gave r values which agreed with the other values.

Paganelli and Solomon (403) considered both the diffusional and filtrational effects and combined them to obtain a simple equation relating membrane pore radius to the radius of the diffusing molecule and the flow characteristics of the membrane. The derivation is based on the assumption that

$$\frac{\text{diffusional flow of tritiated water}}{\Delta C_{\text{THO}} D_{\text{THO}}} = \frac{\text{diffusional flow of water}}{\Delta C_{\text{H}_2\text{O}} D_{\text{H}_2\text{O}}}$$

Accordingly the flow of water $\dot{m}_{\text{H}_2\text{O}}$ (ml./sec.) is given by

$$\dot{m}_{\text{H}_2\text{O}} \approx D_{\text{H}_2\text{O}}(A_0/d) \qquad \text{(Eq. 207)}$$

Combining this with the Poiseuille's equation (403)

$$r^2 = (8\eta \dot{M}_{\text{H}_2\text{O}} D_{\text{H}_2\text{O}})/\dot{m}_{\text{H}_2\text{O}} \qquad \text{(Eq. 208)}$$

where $\dot{M}_{\text{H}_2\text{O}}$ is flow in ml./dyne sec.

In terms of the Pappenheimer–Renkin correction for restricted diffusion, *viz.*, Eq. 203, and restricted filtration, *viz.*, Eq. 206, $A_d = A_f = A_0$ in Eq. 208 only in the limiting case when $a/r \rightarrow 0$.

When $a/r \gg 0$, Paganelli and Solomon wrote Eq. 208 as

$$r^2 \cong \left(\frac{8\eta \dot{M}_{\text{H}_2\text{O}} D_{\text{H}_2\text{O}}}{\dot{m}_{\text{H}_2\text{O}}}\right)\left(\frac{A_d}{A_f}\right) \qquad \text{(Eq. 209)}$$

but

$$A_d/A_f = 1\Big/\left[2 - \left(1 - \frac{a}{r}\right)^2\right]$$

Substituting $\dot{K}$ for $8\eta\dot{M}_{\text{H}_2\text{O}}D_{\text{H}_2\text{O}}/\dot{m}_{\text{H}_2\text{O}}$, Eq. 209 became

$$r^2 \cong \frac{\dot{K}}{\left[2 - \left(1 - \frac{a}{r}\right)^2\right]} \qquad \text{(Eq. 210)}$$

The solution for this quadratic equation in r is given by

$$r \cong -a + \sqrt{2a^2 + \dot{K}} \qquad \text{(Eq. 211)}$$

Equation 211 is very useful in the case of studies with natural membranes where r is of the order of $2a$. But for the three membranes given in Table XXIX, r is completely determined by $\sqrt{\dot{K}}$, as $2a^2$ is negligible compared to $\dot{K}$, *i.e.*, $r = r_P$. Accordingly, r values (and $\dot{K}$ values of Table XXIX), calculated using Eq. 211, agree more closely with r_P values.

It is obvious from the above discussion that the Pappenheimer–Renkin treatment of treating the flow of solute through membranes as two flows, a flow by diffusion and a flow by filtration, did not give any general equation or set of equations consistent enough to cover the whole phenomena. Further, the coupling that exists between the solute and solvent flows are not expressed properly. Kedem and Katchalsky (217, 218, 220, 221) and Vink (569, 570) have approached this problem from the standpoint of the principles of irreversible thermodynamics and have derived a set of consistent equations describing the solvent and solute flows through the membrane.

The total volume flow per unit area is given by

$$J_v = \dot{n}_w\bar{v}_w + \dot{n}_s\bar{v}_s \qquad \text{(Eq. 212)}$$

$\dot{n}_w$ and $\dot{n}_s$ are the solvent and solute flows, respectively, in moles/sec./unit area and the $\bar{v}$'s are the partial molar volumes.

The differential velocity of solute to solvent flow, J_D, is given by

$$J_D = (\dot{n}_s/C_s) - (\dot{n}_w/C_w) \qquad \text{(Eq. 213)}$$

where C_s and S_w are the respective concentration of solute and solvent.

The flows may be expressed in terms of the forces ΔP and ΔC_s causing them. Accordingly

$$J_v = L_p\Delta P + L_{pD}RT\Delta C_s \qquad \text{(Eq. 214)}$$

$$J_D = J_{Dp}\Delta P + L_D RT\Delta C_s \qquad \text{(Eq. 215)}$$

$\Delta\pi = RT\Delta C_s$ and by Onsagar relation $L_{pD} = L_{Dp}$. L_p and L_D are the mechanical coefficients of filtration and diffusion, respectively. These must always be positive while L_{pD}, the cross coefficients indicating the interaction of flows may be + or −, and the magnitude is determined by the condition $L_pL_D - L_{pD}^2 > 0$.

Some special cases of interest are: (a) If no solute is present ($\Delta C_s = 0$) as in the measurement of L_p, Eq. 214 becomes

$$J_v = L_p\Delta P \qquad \text{(Eq. 216)}$$

and J_D is not defined.

(b) In the case of a solute to which the membrane is impermeable

$$J_v = \dot{n}_w\bar{v}_w \text{ and } J_D = -(\dot{n}_w/C_w) \qquad \text{(Eq. 217)}$$

For a dilute solution $(1/C_w) = \bar{v}_w$ and so

$$J_v = -J_D \qquad \text{(Eq. 218)}$$

Further if $\Delta P = 0$

$$J_v = L_{pD}RT\Delta C_s \qquad \text{(Eq. 219)}$$

$$J_D = L_D RT\Delta C_s \qquad \text{(Eq. 220)}$$

and as

$$J_v = -J_D,\ L_D = -L_{pD} \qquad \text{(Eq. 221)}$$

Inserting these values (Eq. 221) into Eq. 214 and 215 and adding them gives

$$(L_p + L_{Dp})\Delta P = 0 \qquad \text{(Eq. 222)}$$

As this is true for any value of ΔP, $L_p + L_{Dp} = 0$ or

$$L_p = -L_{Dp} \qquad \text{(Eq. 223)}$$

The conditions therefore for ideal membrane permeability are

$$J_v = -J_D \text{ and } L_p = L_D = -L_{pD} \qquad \text{(Eq. 224)}$$

Equation 214 therefore becomes

$$J_v = L_p(\Delta P - RT\Delta C_s) \qquad \text{(Eq. 225)}$$

and hydrostatic or osmotic pressures are equally effective in producing net flow.

(c) In very coarse membranes, the volume flow and the osmotic flow are independent, each being determined by ΔP or ΔC_s, respectively. In less permeable membranes the flows are interdependent. Concentration gradient may produce a volume flow even when $\Delta P = 0$ (osmotic flow). Similarly a pressure difference besides producing volume flow causes ultrafiltration by allowing solvent and solute to flow at different velocities. L_{pD} coefficient accounts for the interdependence of these flows.

Staverman (511, 512) has introduced the reflection coefficient and is expressed by

$$\sigma = -\frac{L_{pD}}{L_p} \qquad \text{(Eq. 226)}$$

Depending on the system, σ may take values between 0 (nonselective membrane) and 1 (semipermeable membrane). Meschia and Setnikar (339) measured σ for collodion membranes using different substances (Table XXXI) and Vink also measured σ for cellophane under a variety of conditions (570).

In an experiment to evaluate σ, a pressure difference ΔP is applied across a permeable membrane separating two large compartments containing the same well-stirred solutions ($\Delta C_s = 0$). At time $t = 0$, the pressure effect may be written as

$$J_v = \dot{n}_s\bar{v}_s + \dot{n}_w\bar{v}_w = L_p\Delta P \qquad \text{(Eq. 227)}$$

$$J_D = (\dot{n}_s/C_s) - (\dot{n}_w/C_w) = L_{Dp}\Delta P \qquad \text{(Eq. 228)}$$

Using the relation $\bar{v}_w = 1/C_w$, Eq. 227 and 228 are added and the result is divided by Eq. 227. Then

$$\frac{\dot{n}_s}{J_v}\left[\bar{v}_s + \left(\frac{1}{C_s}\right)\right] = 1 + \frac{L_{Dp}}{L_p} \qquad \text{(Eq. 229)}$$

For a dilute solution, $\bar{v}_s$ is small compared to $1/C_s$, and substituting $-\sigma$ for L_{Dp}/L_p in Eq. 229 and rearranging gives

$$\sigma = 1 - \frac{\dot{n}_s}{C_sJ_v} = 1 - \frac{A_d}{A_f} \qquad \text{(Eq. 230)}$$

TABLE XXXI

MEMBRANE FLOW CHARACTERISTICS

	Dialysis tubing (25)[a]			Cellophane (95)[a]			Wet gel (370)[a]			Collodion (339)
Substance	N.V.F.,[b] μl./M min.	σ	$\left(\frac{a}{r}\right)$	N.V.F., μl./M min.	σ	$\left(\frac{a}{r}\right)$	N.V.F., μl./M min.	σ	$\left(\frac{a}{r}\right)$	σ
D_2O	0.06	0.002	0.083	—			0.084	0.001	0.023	
Urea	0.60	0.024	0.117	0.6	0.006	0.066	1.5	0.004	0.033	
Glucose	5.10	0.20	0.19	4.2	0.044	0.107	5.8	0.016	0.054	0.01
Sucrose	9.20	0.37	0.23	7.0	0.074	0.13	10.4	0.028	0.065	0.013
Raffinose	11.00	0.44	0.26	8.5	0.089	0.15	13	0.035	0.074	0.019
Inulin	19.00	0.76	0.52	41.0	0.43	0.29	84	0.23	0.146	
Bovin serum albumin	25.50	1.02	1.6	98	1.03	0.9	270	0.73	0.45	
Dextran										1.0

[a] Value in parentheses is hydraulic flow in μl./24.4 atm. min. [b] Net volume flow.

Durbin (78) replaced $\dot{n}_s/C_sJ_v$, *i.e.*, ratio of moles of solute passing through the membrane in unit time to moles arriving at the membrane by that time, by A_d/A_f, where A_d is the effective pore area available to solute molecules and A_f the pore area available to solvent molecules.

Using three membranes of the type used by Renkin (431), Durbin measured both the filtration coefficient L_p and A/d. Using these values the pore radii were evaluated. These values are also given in Table XXIX for comparison.

Using the substances whose molecular radii are shown in Table XXX, net volume flow across the three membranes was measured and expressed as μl./M min. Hydraulic flow under a pressure equal to osmotic pressure when $\Delta C_s = 1$ (*i.e.*, $RT\Delta C_s = 24.4$ atm.) was calculated from the values of L_p (Table XXIX) for the three membranes and was also expressed as μl./24.4 atm. min. The ratio of these quantities is σ by definition. All these parameters along with the ratio a/r are given in Table XXXI for the three membranes.

These results show that σ increased as a/r increased. Comparison of the σ-values determined by Meschia and Setnikar for their collodion membranes (339) with the values of σ for wet gel indicate that the pore size of collodion membranes should be around 100–150 Å. If this is true, dextran then should have $\sigma < 1$ and thus should go through the membrane.

Durbin (78) computed A_d/A_f ratios using Eq. 206 for each substance in the case of one membrane (dialysis tubing) and calculated σ from Eq. 230 as a function of a/r and found satisfactory agreement with the experimental values given in Table XXXI.

Another coefficient ω_s, the solute permeability coefficient, has been defined by Kedem and Katchalsky (220, 221) and is expressed as

$$\omega_s = \left(\frac{L_pL_D - L^2_{pD}}{L_p}\right)C_s = (L_D - L_p\sigma^2)C_s \quad \text{(Eq. 231)}$$

The permeability coefficient, P_s, for the solute under conditions of zero volume flow is related to ω_s by

$$P_s = (\omega_s RT)_{J_v=0} \quad \text{(Eq. 232)}$$

In terms of σ, Eq. 214 is expressed as

$$J_v = L_p(\Delta P - \sigma\Delta\pi) \quad \text{(Eq. 233)}$$

and the solute flow is written as

$$J_s = (J_v + J_D)C_s = C_s(1 - \sigma)J_v + \omega_s\Delta\pi \quad \text{(Eq. 234)}$$

Choosing the frictional pore model of Spiegler (507) for a membrane, Kedem and Katchalsky (221) expressed the various coefficients in terms of distribution and friction coefficients for electrolytes and nonelectrolytes. For example, the solute permeability for nonelectrolytes is expressed as

$$\omega_s = \frac{K}{d(f_{sw} + f_{sm})} \quad \text{(Eq. 235)}$$

where the distribution coefficient $K = -\int_0^d K_c d\pi/\Delta\pi$ and $K_c = \bar{C}_s/C_s$.

Similarly, the Pappenheimer–Renkin expression for A_d/A_f expressed in terms of a and r is shown to be given by

$$\frac{A_d}{A_f} = \frac{Kf_{sw}}{\varphi_w(f_{sw} + f_{sm})} \quad \text{(Eq. 236)}$$

where φ_w is the volume fraction of water in the membrane.

The reflection coefficient σ is given by

$$\sigma = 1 - \frac{\omega_s\bar{v}_s}{L_p} - \frac{Kf_{sw}}{\varphi_w(f_{sw} + f_{sm})} \quad \text{(Eq. 107)}$$

$$= 1 - \frac{\omega_s\,\bar{v}_s}{L_p} - \frac{A_d}{A_f} \quad \text{(Eq. 237)}$$

In the case where solute and solvent pass through different pathways, $f_{sw} = 0$ and

$$\sigma = 1 - \frac{\omega_s\bar{v}_s}{L_p} \quad \text{(Eq. 108)}$$

If $\sigma \ll 1 - (\omega_s\bar{v}_s/L_p)$, capillary mechanism operates. Dainty and Ginzburg (61) have given an explicit expression for the inequality considering a lipid-pore model for the cell membrane.

Kedem and Katchalsky (221) have also considered the transport coefficients in solutions of heavy water and have given an expression relating pore radius of the membrane to the ratio of the volume flow to the diffusional flow of water. This ratio is shown to be given by

$$g = \frac{L_p}{\bar{v}_w \omega_s} \qquad \text{(Eq. 238)}$$

where L_p and ω_s in terms of frictional coefficients are given by

$$L_p = \frac{\varphi_w \bar{v}_w / d}{(1 - \bar{p}) f_{om} + \bar{p} f_{Dm}} \qquad \text{(Eq. 239)}$$

$$\omega_s = \frac{\varphi_w / d}{f_{Dm} + (1 + \bar{p}) f_{Do}} \qquad \text{(Eq. 240)}$$

where $\bar{p} = (C_D/C_o)$, *i.e.*, the average ratio of concentration of heavy to ordinary water. For $\bar{p} \ll 1$ (low heavy water content)

$$L_p = \frac{\varphi_w \bar{v}_w}{d f_{om}} \qquad \text{(Eq. 241)}$$

and

$$\omega_s = \frac{\varphi_w}{d(f_{Dm} + f_{Do})} \qquad \text{(Eq. 242)}$$

and therefore

$$g = (f_{Dm} + f_{Do})/f_{om} \qquad \text{(Eq. 243)}$$

Assuming $f_{Dm} \cong f_{om} \cong f_{wm}$

$$g = 1 + \frac{f_{Do}}{f_{wm}} \qquad \text{(Eq. 244)}$$

If the pores of the membrane are large enough to make

$$f_{Do} = f^{\circ}_{Do}/\vartheta \qquad \text{(Eq. 245)}$$

and since

$$f^{\circ}_{Do} = RT/D_D \qquad \text{(Eq. 246)}$$

where D_D is the self-diffusion of heavy water in ordinary water

$$f_{Do} = RT/(D_D \vartheta) \qquad \text{(Eq. 247)}$$

f_{wm} was evaluated from Poiseuille's equation

$$J_t = \frac{\eta \pi r^4 \Delta P}{8\eta d} \qquad \text{(Eq. 248)}$$

Applying the correction for tortuosity for viscous flow

$$J_t = \frac{\eta \pi r^2 \vartheta r^2 \Delta P}{8\eta d} \qquad \text{(Eq. 249)}$$

Volume flow per unit membrane area is ($\eta \pi r^2 = \varphi_w$)

$$J_v = \frac{\vartheta \varphi_w r^2}{8\eta d} \Delta P = L_p \Delta P \qquad \text{(Eq. 250)}$$

Therefore Eq. 241 and 250 give

$$f_{wm} = \frac{8\eta \bar{v}_w}{r^2 \vartheta} \qquad \text{(Eq. 251)}$$

Then

$$g = 1 + \frac{r^2 RT}{8\eta D_D \bar{v}_w} \qquad \text{(Eq. 252)}$$

g and D_D are measured (102) and hence r may be determined. Ginzburg and Katchalsky (102) determined the phenomenological permeation coefficients L_p, ω_s, and σ for two different membranes (dialysis tubing and Sylvania wet gel) using tagged water, urea, glucose, and sucrose. The membrane characteristics and the pore radii calculated using Eq. 252 are given in Table XXIX. The value for the tubing although compares reasonably with those of Renkin and Durbin, the value for the wet gel is less than half the other values.

From the measured permeation coefficients, the friction coefficients f_{sw}, f_{sm}, and f_{wm} were calculated from the following equations (102)

$$f_{sw} = \frac{\left(1 - \sigma - \dfrac{\omega_s \bar{v}_s}{L_p}\right) \varphi_w}{\omega_s d} \qquad \text{(Eq. 253)}$$

$$f_{sm} = \left[\frac{\sigma + \dfrac{\omega_s \bar{v}_s}{L_p}}{1 - \left(\sigma + \dfrac{\omega_s \bar{v}_s}{L_p}\right)}\right] f_{sw} \qquad \text{(Eq. 254)}$$

$$f_{wm} = \frac{\varphi_w \bar{v}_w}{d} \left\{ \frac{1}{L_p} - \frac{(1 - \sigma)\left(\sigma + \dfrac{\omega_s \bar{v}_s}{L_p}\right) C_s}{\omega_s} \right\} \qquad \text{(Eq. 255)}$$

Some of these values are given in Table XXXII.

The important points of this interesting study are: (1) σ, for a given membrane, decreased with increase in concentration of the solute. (2) Solute water interaction in the membrane (f_{sw}) increased with increase in concentration and the interaction was greater than it was in free solution ($f^{\circ}_{sw} = RT/D$) where also the interaction increased with increase in concentration. The ratio (f°_{sw}/f_{sw}) was a constant for any one substance and was independent of concentration. This ratio is ϑ, the tortuosity which varied from substance to substance. As the size of the substance increased the tortuosity decreased (THO = 0.308 and sucrose = 0.15). Lagos and Kitchener (267) in their studies of permeation of different substances through ion-ex-

TABLE XXXII

REFLECTION AND FRICTION COEFFICIENTS (DYNE SEC./MOLE CM.) IN MEMBRANES AS A FUNCTION OF SOLUTE CONCENTRATION

Concn. C_s, mole/ml.	$f^\circ_{sw} \times 10^{-16}$	σ	$f_{sw} \times 10^{-16}$	$\vartheta = \frac{f^\circ_{sw}}{f_{sw}}$	$f_{sm} \times 10^{-16}$	$\frac{f_{sw}}{f_{sm}}$	$f_{wm} \times 10^{-18}$
Dialysis Tubing							
THO	0.101		0.33	0.308			
Urea							
5.0×10^{-4}	0.172	0.006	0.66	0.261	0.065	10.2	8.3
Glucose							
1.25×10^{-5}	0.368	0.123	1.79	0.206	0.31	5.8	8.35
2.50	0.370	0.112	1.82	0.203	0.29	6.3	8.45
5.00	0.373	0.083	1.89	0.197	0.23	8.2	8.52
10.00	0.380	0.072	1.97	0.193	0.21	9.3	8.65
Sucrose							
1.25×10^{-5}	0.482	0.163	3.12	0.154	0.73	4.3	8.43
2.5	0.487	0.142	3.25	0.150	0.65	5.0	8.55
5.0	0.500	0.122	3.43	0.145	0.59	5.8	8.72
10.0	0.521	0.114	3.57	0.146	0.57	6.2	8.95
Wet Gel							
THO			0.114	0.89			
Urea							
5.0×10^{-4}		0.0016	0.282	0.61	0.0046	61.0	1.68
Glucose							
5.0×10^{-5}		0.024	0.78	0.48	0.030	26.0	1.71
10.0		0.024	0.78	0.49	0.031	26.0	1.72
Sucrose							
2.5×10^{-5}		0.036	1.12	0.43	0.066	16.8	1.72
5.0		0.036	1.13	0.44	0.067	16.8	1.74
10.0		0.036	1.14	0.45	0.068	16.8	0.79

changer ribbons emphasized this while considering the Meares correction for tortuosity. (3) Water membrane interaction (f_{wm}) was almost constant for each membrane and independent of the solute concentration and substance. As this coefficient is related to tortuosity (Eq. 251), tortuosity for the permeation of water was calculated to be 0.336 for dialysis tubing and 0.875 for wet gel. These values agree with the values determined by the ratio f°_{sw}/f_{sw}. (4) Solute membrane interaction (f_{sm}) is smaller than solute water interaction (f_{sw}) and, similarly, f_{wm} is smaller than f_{sm}. The main resistance to transport of solute and solvent is from their own interactions and not from the matrix of the membrane.

A similar type of analysis for charged membranes has been presented by Spiegler (507) and by Mackay and Meares (298).

VI. PHENOMENA DUE TO GRADIENT OF TEMPERATURE

All the phenomena hitherto described have been allowed to take place only in isothermal systems. Little attention has been paid to the study of phenomena arising across a membrane separating the same salt solution kept at two different temperatures. Maintenance of a temperature gradient across a membrane gives rise to (a) flow of solvent called thermoosmosis and (b) flow of electrolyte resulting in an e.m.f. called thermal diffusion potential.

A. THERMOOSMOSIS

Some work that exists in this neglected field has been stated briefly by Carr and Sollner (41). They have shown that no transport occurred across membranes with water or with aqueous solutions of nonelectrolytes existing on either side of the nonisothermal membrane system. With electrolyte solutions, transport occurred across ionic membranes and not across nonionic membranes. They showed further that thermoosmosis was an electrochemical phenomenon closely related to electroosmosis and anomalous osmosis.

Haase (129) has given a thermodynamic treatment of the flow processes in membranes separating water or solutions maintained at two different temperatures. He has also measured thermoosmosis across cellophane and copper ferrocyanide membranes and estimated the heats of transport for the two membranes. He did not, however, use electrolyte solutions (130).

When heat is supplied to a system at constant volume, the pressure of the system builds up. Rastogi, Blokhra, and Aggarwala (423, 424) applied thermodynamics of irreversible processes to the consideration of the interaction between mass flow, J_m, and heat flow, J_q, occurring in thermoosmosis and wrote the relationships as

$$J_m = L_{11}(-V/T)\Delta P + L_{12}(-\Delta T/T^2)$$

$$J_q = L_{21}(-V/T)\Delta P + L_{22}(-\Delta T/T^2)$$

where V is the specific volume, L_{11} is related to ordinary permeability, and L_{22} to thermal conductivity; nothing is known about L_{12}.

When $\Delta P = 0$

$$J_m = L_{12}(-\Delta T/T^2) = -L_{12}'\Delta T$$

L_{12}' is called thermoosmotic permeability which Rastogi, Blokhra, and Aggarwala (423, 424) measured across Dupont 600 cellophane membrane using water on either side. They found J_m to increase linearly with ΔT up to $\Delta T = 19°$ and above that, J_m increased rapidly. They also investigated the temperature dependence of L_{12} (424) keeping ΔT always 14° and found it to decrease with increase in temperature, reach a minimum, and then increase with further increase in temperature.

Thermoosmosis across cellophane membrane is not in agreement with the results of Carr and Sollner (41) who found no flow at all across collodion membrane separating water maintained at two different temperatures. Similarly, Lakshminarayanaiah (270) found thermoosmosis to be zero across cross-linked PMA membranes. The behavior of cellophane can then be ascribed to the greater porosity of the alkali-washed sample used in the experiments.

B. THERMAL MEMBRANE POTENTIAL

The temperature coefficient of an electrode is invariably measured in an isothermal cell of the type

Ag–AgCl|HCl of activity $a_\pm$|H_2, Pt (Type 256)

the standard e.m.f. $E°$ being measured over a range of temperature. The potential of the normal hydrogen

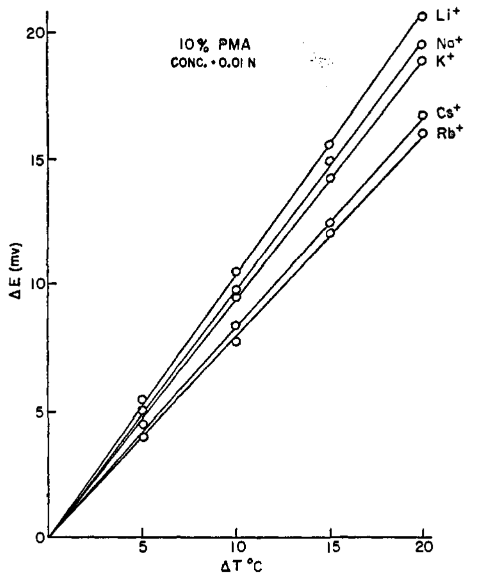


Figure 15.—Variation of thermo e.m.f. (ΔE) as a function of ΔT in a 10% PMA membrane in different ionic forms.

electrode is arbitrarily assumed to be zero at all temperatures and ($dE°/dT$) is then called the temperature coefficient of the Ag–AgCl electrode.

Several workers have attempted to determine the temperature coefficient of the hydrogen electrode by studying nonisothermal systems of the type

$$\text{electrode}\underset{T_1}{|}\text{solution}\underset{T_2}{|}\text{electrode} \qquad \text{(Type 257)}$$

by measuring the e.m.f. dE for a range of values of T_2 at constant T_1. The e.m.f. is due to three factors. They are: (1) temperature difference between the two electrodes, (2) diffusion of electrolyte because of temperature gradient across the boundary separating the two compartments, and (3) thermoelectric effects in the metallic leads (Peltier effect).

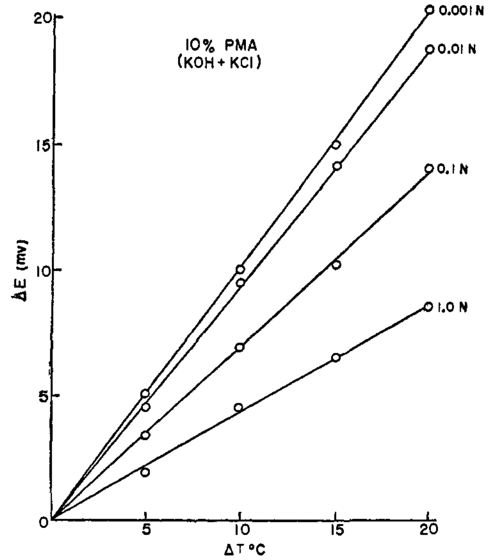


Figure 16.—Variation of thermo e.m.f. (ΔE) as a function of ΔT in a 10% PMA membrane in K^+ form at different external concentrations.

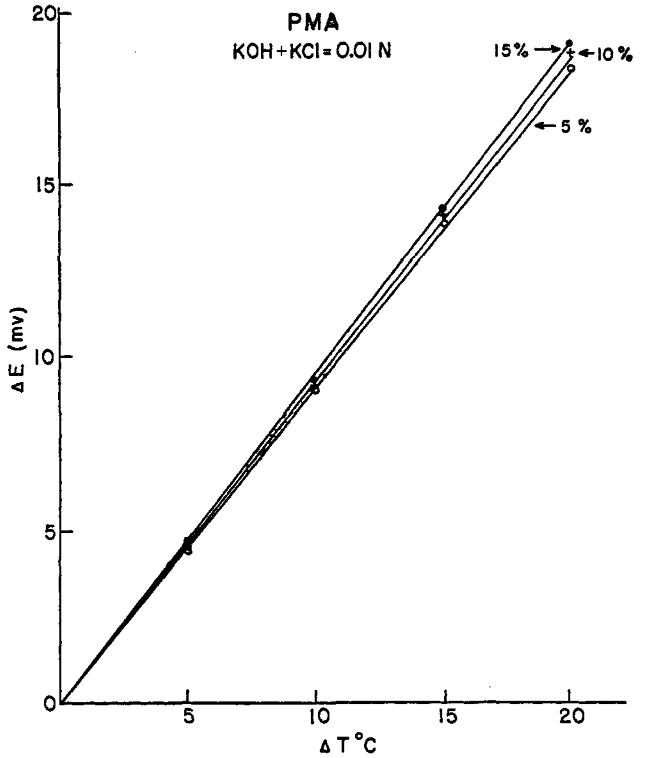


Figure 17.—Variation of thermo e.m.f. (ΔE) as a function of ΔT in differently cross-linked (5, 10, and 15%) PMA membranes in K^+ form.

Even after neglecting (3), it has not been possible so far to separate the contributions of the first two factors. Nevertheless, the absolute temperature coefficient of a single electrode is an extremely interesting property because a knowledge of its value could lead to the evaluation of single ion entropies

$$\Delta S° = F\frac{dE°}{dT}$$

Cells of the Type 257 called thermocells have been considered by Eastman (80) and by Wagner (574). They have used quasi-thermodynamic methods developed by Thomson (547) to deduce the equation for a thermocell, *viz.*

$$F\frac{dE}{dT} = \Delta S - \sum \frac{t_i Q_i^*}{z_i T} \qquad \text{(Eq. 258)}$$

where ΔS is the entropy change for the electrode reaction and Q_i^* is the heat of transfer. An equation of the same form (Eq. 46) has been derived by Hills, Jacobs, and Lakshminarayanaiah (179, 180, 270) for thermal diffusion potentials within a membrane.

Lakshminarayanaiah (270) has used nonisothermal membrane cells of the type

$$\text{Ag–AgCl}\left|\begin{matrix}\text{solution (}'\text{)}\\ \text{MCl + MOH}\\ T_1\end{matrix}\right|\begin{matrix}\text{PMA}\\ \text{membrane}\\ \end{matrix}\left|\begin{matrix}\text{solution (}''\text{)}\\ \text{MCl + MOH}\\ T_2\end{matrix}\right|\text{AgCl–Ag}$$

(Type 259)

TABLE XXXIII

CALCULATION OF $Y(a)$ FROM EQ. 262

KCl $a_{\pm}$	$\frac{dE}{dT}$, mv. deg.$^{-1}$	$\left(\frac{R}{F}\right)\ln a_{\pm}$, mv. deg.$^{-1}$	$\left(\frac{RT}{F}\right)\left(\frac{d\ln a_{\pm}}{dT}\right)$, mv. deg.$^{-1}$	$Y(a)$, mv. deg.$^{-1}$
0.00049	1.0125	−0.6567	−0.0014	0.3544
0.00464	0.9375	−0.4631	−0.0043	0.4701
0.04209	0.7000	−0.2730	−0.0127	0.4143
0.32550	0.4300	−0.0967	−0.0337	0.2996

and measured the electrical potentials arising across a 10% cross-linked PMA membrane, in each of the alkali metal forms (0.01 N) for $T_1 = 25°$ and $T_2 = 30, 35, 40$, and 45° (Figure 15). The effect of concentration of external solution (Figure 16) and of the degree of cross linking (Figure 17) on the thermal membrane cell potential has also been investigated.

The results (Figures 15–17) show that ΔE varied linearly with ΔT in the range investigated ($\Delta T = 20°$) and that ΔE is not very dependent on the degree of cross linking of the membrane.

The e.m.f. of the cell is (neglecting contact potentials and thermoelectric effects in the terminals) given by

$$dE = dE_{\text{rev}} + d\psi$$

dE_{rev} is evaluated considering the electrode reactions occurring in the membrane cells of Type 259 and $d\psi$ is given by Eq. 46. The full expression for (dE/dT) was expressed as (270)

$$\frac{dE}{dT} = \frac{\Delta S°}{F} - \left(\frac{R}{F}\right)\ln a_{\text{Cl}^-}'' - \left(\frac{RT}{F}\right)\left(\frac{d\ln a_{\text{Cl}^-}''}{dT}\right) - \sum_{\text{k}} \frac{\bar{t}_{\text{k}^+}Q_{\text{k}^+}^*}{FT} \quad \text{(Eq. 260)}$$

The second term on the right-hand side of Eq. 260 is known and the third which is small can be estimated from the Debye–Hückel theoretical expression for $\gamma_{\pm}$. Plots of ΔE and ΔT are all linear so that dE/dT is independent of T_2 in the temperature range used. Transposing all known terms to the left yields

$$FY(a) = \Delta S° - \sum \bar{t}_{\text{k}^+}Q_{\text{k}^+}^*/T \quad \text{(Eq. 261)}$$

$$\text{where } Y(a) = \frac{dE}{dT} + \left(\frac{R}{F}\right)\ln a_{\text{Cl}^-}'' + \left(\frac{RT}{F}\right)\left(\frac{d\ln a_{\text{Cl}^-}''}{dT}\right) \quad \text{(Eq. 262)}$$

From Eq. 261, it might seem that it would be possible to get enough number of equations to solve for all the unknowns. But it was shown by Lakshminarayanaiah (270) that it was not possible to determine either $\Delta S°$ or individual heat of transfer without making special assumptions. However $Y(a)$ may be evaluated as a function of concentration (Table XXXIII).

For dilute solution since $\bar{t}_{\text{k}^+} \to 1$, the value of $FY(a)$, *i.e.*, 34.2 joules deg.$^{-1}$, is approximately equal to $\Delta S° - Q_{\text{k}^+}^*/T$.

TABLE XXXIV

RELATIVE HEATS OF TRANSFER

M$^+$	$FT\frac{dE}{dT}$, joules (308°K.)	Q^*, cal. (270)	Eastman (80) Q^* (298°K.)	Wirtz (592) Q^*	Goodrich, *et al.* (109) Q^*
Li$^+$	30,680	0	30	0	−3020
Na$^+$	29,120	370	270	2300	−1800
K$^+$	27,880	670	300	2600	−1550
Rb$^+$	23,770	1650	330	2100	
Cs$^+$	24,960	1370			
Cl$^-$			0	0	

In a series of salts with varying cation M, at constant OH$^-$ and Cl$^-$ molalities, Eq. 261 and 262 yield

$$\left[\frac{dE}{dT}\right]_{\text{M}_1} - \left[\frac{dE}{dT}\right]_{\text{M}} = -\frac{\bar{t}_{\text{M}_1}Q_{\text{M}_1}^* - \bar{t}_{\text{M}_2}Q_{\text{M}_2}^*}{FT} \approx \frac{Q_{\text{M}_2}^* - Q_{\text{M}_1}^*}{FT} \quad \text{(Eq. 263)}$$

Thus relative heats of transport for a cation series may be found. These values relate to the solution and not to the membrane; as it follows from the definition of heat of transport which represented the heat absorbed in chamber (′) and liberated in chamber (″) when 1 mole of a species was transferred from (′) to (″) at constant T and P, apart from the change in heat content necessarily associated with the removal of the species concerned.

Despite the fact that single ion heats of transfer are not accessible experimentally, three different tabulations of these quantities exist, all based on different assumptions. These values together with the relative values found by Lakshminarayanaiah (270) are given in Table XXXIV.

The order is the same in each series but the absolute values vary with the assumption made. Clearly, a reliable table even of relative heats of transfer cannot be prepared at the present time.

Ikeda (196), unlike Lakshminarayanaiah (270), eliminated the dE_{rev} by constructing cells of the type

$$\text{Ag–AgCl}|\text{KCl }(C)|\text{KCl–agar }(C)|\underset{T}{\underset{(C)}{\text{aq. KCl}}}\Big\|\begin{matrix}\text{membrane}\\ \text{collodion}\end{matrix}\Big\|\underset{T+\Delta T}{\underset{(C)}{\text{aq. KCl}}}\Big|\underset{T}{\underset{(C)}{\text{KCl–agar}}}\Big|\underset{T}{\underset{(C)}{\text{KCl}}}\Big|\underset{T}{\text{AgCl–Ag}} \quad \text{(Type 264)}$$

using 0.1 N KCl, measured the thermal membrane potentials, and found them to vary linearly with ΔT. He obtained a slope of 0.052 mv. deg.$^{-1}$ which was later found (197) to be in error and the actual value was found to be 0.0246 mv. deg.$^{-1}$.

Ikeda and Tsuchiya (199) have also measured thermal electrical potentials of cells of type

$$\text{Hg, Hg}_2\text{Cl}_2|\text{aq. KCl }(m)|\text{ aq. MCl }(m)|\text{ aq. KCl }(m)\ |\text{Hg}_2\text{Cl}_2\text{, Hg} \quad \text{(Type 265)}$$

in which two semipermeable membranes were kept at the dotted lines and a temperature difference maintained between the two membranes. A method for determining Soret coefficient from these thermal membrane potentials has also been suggested (198). Besides these potentials, voltage–ampere characteristics under nonisothermal conditions for both porous and ion-exchange membranes have also been reported (63).

Kobatake (234) assuming ΔT to be small and $\bar{u}$ and $\bar{v}$ to be constant obtained, for the thermomembrane potential, the expression

$$\Delta\psi = -\frac{\bar{v}}{\bar{u}+\bar{v}} \cdot \frac{2RTS_T}{1+\dfrac{\bar{u}\Theta}{C(\bar{u}+\bar{v})}} \cdot \frac{\Delta T}{F} + \frac{Q_+^*\Delta T}{FT} \qquad \text{(Eq. 266)}$$

S_T is the Soret coefficient given by $(Q_+^* + Q_-^*)/2RT^2$. $\Theta\bar{u}/(\bar{u}+\bar{v}) = \beta$ was evaluated from Eq. 137 and, from this, Θ was estimated to be 2.228. Using this value and the value of the Soret coefficient in bulk solution, *i.e.*, $S_T = 0.12 \times 10^{-2}$, the concentration dependence of $\Delta\psi$ was calculated and compared with the observed values. He found good agreement.

On extrapolation of $\Delta\psi$ *vs.* C curve to $C = 0$, $\Delta\psi$ was obtained and was equated to Q_+^*, the heat of transport of positive ion. Q_+^* was found to be 370 kcal./mole. Combining this with the value of the Soret coefficient, $Q_{Cl^-}^*$ was calculated to be 60 kcal./mole. This evaluation of single ion heat of transfer, although not unambiguous, seems to indicate the direction in which further efforts must be concentrated to measure what has all along eluded measurement.

If the Kobatake approach (234) to evaluate $Q_{k^+}^*$ is assumed correct, the value obtained for $\Delta S^\circ - Q_{k^+}^*/T$, *i.e.*, 34.2 joules deg.$^{-1}$, by Lakshminarayanaiah (270) may be combined with the $Q_{k^+}^*$ value of Kobatake to obtain a value for ΔS°, the entropy change accompanying the electrode reaction

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$$

when Cl^- is at unit activity. The value for ΔS° comes out to be about 1240 cal./deg.

PART B

VII. PREPARATION OF MEMBRANES

As the success attending many chemical operations using membranes, like demineralization by electrolysis, salt filtration by application of pressure, etc., depends on the availability of suitable membranes, considerable attention has been paid, in recent years, to the development of membranes with particular and predetermined specific properties. A variety of compounds and processes have been used to prepare them. The basic materials and the chemical processes involved are summarized in a few books and review articles. Wagner and Moore (575) have contributed a section on "osmotic" membranes in "Technique of Organic Chemistry" edited by Weissberger. There are two chapters, one on cellulose membranes and the other on synthetic resin membranes, in the book "Diffusion and Membrane Technology" by Tuwiner (556). Short introductions on the preparation of ion-exchange membranes are written by Kitchener in his Methuen monograph (227), by Kunin in his book "Ion Exchange Resins" (263), and by Spiegler in "Ion Exchange Technology" edited by Nachod and Schubert (506). Similarly, a section and two chapters exist in the books "Ion Exchange" by Helfferich (154) and "Demineralization by Electrodialysis" edited by Wilson (586), respectively.

In the recent review articles, Krishnaswamy (256) and Bergsma and Kruissink (18, 19) have included the patent literature on the preparation of ion-exchange membranes, usually a few hundred microns thick; whereas, Carnell and Cassidy (39) provide correlated information about the preparation from various materials, of thick and thin, ion-exchange and nonion-exchange membranes. The developments since the time of these reviews are presented in this section. Recently, another review on the synthesis of ion-exchange membranes has appeared (296).

A. CLASSIFICATION OF MEMBRANES

Unlike the classification based usually on either the nature of the product, *i.e.*, coherent gel or otherwise, or the nature of the chemical reaction, *i.e.*, addition or condensation reaction producing the product, a different mode of classification based on the ultimate use of the membrane is followed for the purpose of this article.

The efforts of various workers have been directed towards (1) preparing or manufacturing membranes, mostly ion exchangers, with good chemical and mechanical stability and favorable electrical performance, suitable for fundamental transport studies and for applications in some industrial operations like treatment of brackish waters, saline water conversion, etc.; (2) building suitable model systems to mimic the properties of natural membranes; and (3) preparing composite membranes containing cationic and anionic groups in suitable arrangement to demonstrate and to study the physico-chemical phenomena associated with rectification of alternating current and other special membranes for specific purposes. The attempts categorized in (2) and (3) overlap somewhat, but they are retained for clarity of presentation.

A large amount of work is primarily concerned with the preparation of operationally useful membranes categorized in (1), and so a variety of methods have been used to prepare them. A rational classification of these many procedures is difficult to present. They are therefore treated under the following heads: (a) homogeneous membranes; and (b) heterogeneous membranes, which are subdivided into (1) nonreinforced membranes, (2) woven fabric-backed membranes, (3) membranes formed by chemical treatment of other films or membranes, (4) membranes formed by mechanical treatment of membrane forming monomers or polymers, and (5) membranes formed by photochemical treatment.

B. MATERIALS AND METHODS

1. *Operationally Important Membranes*

The procedures invoked to prepare these useful membranes are unique and some very novel. A number of chemical substances have been used. Kressman (247) has recently reviewed the type of materials which may be used in the preparation of ion-exchange membranes. Mostly, cellulose derivatives have been used in the preparation of nonion-exchange membranes.

a. Homogeneous Membranes

There has been little work published in recent years about the preparation of homogeneous membranes which are essential for fundamental studies involving transport processes in membranes. In this respect polymethacrylic acid (PMA), phenolsulfonic acid (PSA), and polystyrene sulfonic acid (PSSA) have proved very useful. The details of preparation of membranes from the first two materials are given by a number of workers (182, 204, 208, 270, 278, 313, 401); whereas the successful preparation of membranes from the latter substance, although accomplished by Graydon and Stewart (113) by copolymerization of the propyl ester of *p*-styrenesulfonic acid, styrene, and divinylbenzene (DVB), requires some details which are not given in the literature and without which the attempts to prepare the membranes prove unsuccessful. The preparation of cross-linked polystyrene membranes is quite straightforward, but uniform sulfonation is hard to achieve without producing cracks. Lagos and Kitchener (267) were able to prepare thin ribbons only by successive equilibrations of the sulfonated product in solutions of sulfuric acid of decreasing concentration. The procedure has been improved upon by Zundel, Noller, and Schwab (608). They polymerized styrene and DVB with benzoyl peroxide (Bz_2O_2) as the catalyst between glass plates separated by aluminum spacers for 5 days at 75° and for another 2 days at 90°. The thickness of the membrane was 5 μ. The membrane was dried thoroughly and treated, under anhydrous conditions, with chlorosulfonic acid. After removal of excess acid, it was equilibrated with water at 18°. Hydrolysis required about 6–8 weeks. Elevated temperatures and quicker hydrolysis with stronger solutions of NaOH damaged the membrane.

Sulfonated phenol or anisole with HCHO may be cast on glass plate or mercury and cured at 90° to give cation-exchange membranes. These existing simple procedures have been patented by slight modifications (127, 378). Likewise, amines, *e.g.*, *m*-phenylenediamine or aliphatic amino compounds such as polyethylenediamine or dicyandiamide, have been used with HCHO to form anion-exchange membranes (378).

Loeb and Sourirajan (286–288) described a procedure for the preparation of cellulose acetate "osmotic" membranes suitable for demineralizing saline waters. Cellulose acetate was dissolved in acetone and made up with water to which magnesium perchlorate had been added. The materials were taken in the proportion 22.2:66.7:10:1.1, respectively. Solution was cast on cold glass plates at 0–10°. Uniformity of thickness was obtained by passing an inclined knife across the top of the plate. Solvent was allowed to evaporate in the cold box for about 3–4 min. after which the plate with the film was immersed in ice–water for at least an hour. Membrane was removed from the glass plate and heated in hot water at 75–82°. These membranes withstood pressures up to 1500 p.s.i.

Semipermeable membranes for use in osmotic pressure determinations have been prepared by Condal and Bek (52). A 3% solution of cellulose nitrate in a mixture of solvents (acetone, methyl ethyl ketone, and cyclohexanone in the ratio 60:39:1) was deposited on mercury surface. Solvents were allowed to evaporate in a CO_2 atmosphere, and the membrane was left overnight in the same environment.

Harper (144) has prepared ethyl cellulose membranes by spreading a solution of it in chloroform and drying. The porosity of the membrane may be increased by incorporating polyglycol E-4000 into the membrane and later extracting the polyglycol with cold water.

Reid and Spencer (427) have prepared a variety of membranes for use as filters in their studies on ultrafiltration of salt solutions. Their technique of preparation was to cast the solution of the polymer material on a level glass plate. The solution was spread using a doctor blade, and the solvent was evaporated. Membranes formed were conditioned suitably. In this way, membranes were prepared from polyvinyl alcohol (solvent: water), from co-polymer of methyl vinyl ether and maleic anhydride (solvent: water), from polyvinyl methyl ketone (solvent: acetone or acetic anhydride), from polyvinyl acetate, from cellulose isobutyrate, from cellulose acetate butyrate (solvent: acetone) and from Nylon 6 (solvent: formic acid). Cellophane was also used after treating it with a 15% solution of formaldehyde containing traces of NH_4Cl and baking it at 110–120° for 30 min. Using a similar technique, Kumins and London (262) prepared membranes from polyvinyl acetate, from polyvinyl chloride, and from a copolymer of vinyl acetate and vinyl chloride.

b. Heterogeneous Membranes

Nonreinforced Membranes.—These are prepared by employing suitable casting techniques for the solutions of membrane forming substances. Membranes may be cast on metal, glass, or mercury surfaces.

Cellulose acetate butyrate or its product with phenyl phosphonyl chloride or other organochlorophosphates, dissolved in a mixture of solvents (benzene, ethyl alcohol, ethylene dichloride, and dioxane 3:3:3:1 ratio) has been cast on chrome-plated panels (319). In another method (548, 554) ethyl acrylate was prepolymerized at 80° under nitrogen atmosphere until it became viscous. DVB, ethylvinylbenzene, dimethyl phthalate, and Bz_2O_2 (catalyst) were added and polymerized under nitrogen at 50° for 40 hr., at 70° for 24 hr., and at 100° for another 24 hr., to form plastic sheets. These were hydrolyzed by refluxing with 30% NaOH solution for 48 hr. and washed. Similarly, copolymerization of vinylsulfonyl chloride with styrene and DVB in presence of a plasticizer and subsequent saponification gave an ion-exchange membrane (383).

Polystyrene has been used with polyethylene or polyvinyl chloride (PVC). They were melted and mixed thoroughly with or without solvents, cooled, and extruded into films which may be sulfonated or chloromethylated and aminated in the usual way to form cation- or anion-exchange membranes (92). PSSA itself has been used in another procedure (348). It is dispersed in butyrolactone and mixed with another solution of film forming uncross-linked polymer, *e.g.*, copolymer of vinyl chloride and acrylonitrile in the same solvent, and sprayed as a thin layer. The solvent was removed by heating (90–180°). Use of polyvinylbenzyltrialkylammonium iodide instead of PSSA gave an anion-exchange membrane. Sulfonated styrene and DVB polymer were ground with $ZnCl_2$ solution and mixed with a solution of $ZnCl_2$ containing polyacrylonitrile. This was cast to form a cation-exchange membrane (64). Dimethyl sulfoxide or ethylene carbonate may be used as solvents. Films of poly-*p*-styrenesulfonic acid and poly-*p*-trimethylammoniomethylstyrene hydroxide (45) have also been prepared with or without supports. Propylene-4-vinylbenzene sulfonate was mixed with styrene, DVB, and Bz_2O_2 and cast between glass plates and polymerized at 110° for 2 hr. in a drying oven. The membrane was saponified by boiling with Na_2CO_3 (596). Dynel (copolymer of acrylonitrile and vinyl chloride) and PSSA taken in a mixture of cyclohexane and methanol (116) or cyclohexanone and methanol (117) was coated onto a glass plate at 50° and dried for 17 hr. The membrane was removed by soaking the plate in water. Electropositive membranes may be obtained by using polyvinylbenzyltrialkylammonium salts in place of PSSA (118). Anion-exchange membranes derived from 2-vinyl-5-ethylpyridine have also been prepared (384). In one method, strips of synthetic rubber (0.75 g.) were dissolved in a mixture of 2-vinyl-5-ethylpyridine, styrene, and DVB taken by volume in the proportion 5:3:2, respectively. The mass was polymerized in presence of the catalyst (Bz_2O_2) between two glass plates at 60° for 16 hr. The resulting membrane, after swelling with methanol, was quaternized with methyl iodide.

A membrane was prepared by drying at 70° a solution of polyethylenimine (1 kg.) and polyvinyl alcohol (1 g.) in hot water (15 kg.) poured on a glass plate. It was converted into an anion-exchange membrane (393) by drying and acetalizing in a bath containing H_2SO_4, Na_2SO_4, and HCHO at 70–80°.

A polyelectrolyte gel formed by allowing N-Cu-$(NO_3)_2$ solution to react with 1% solution of sodium alginate was soaked with methyl methacrylate after dehydrating it with acetone. It was polymerized in presence of Bz_2O_2 to form a membrane (546).

Polychloroprene (120 parts) was dissolved in styrene (1000 parts) and polymerized with DVB (160 parts) and Bz_2O_2 (10 parts). The product was soaked in a solution of $AlCl_3$–$(C_2H_5)_2O$ complex in dichloroethane to form a thin membrane (397), which may be converted into a cation or anion exchanger by sulfonation or amination in the usual way.

Krishnaswamy and Suryanarayana (260) have used rubber latex with a fine dispersion of cation exchanger (cashew nut shell liquid, formaldehyde, and sulfuric acid) or anion exchanger (melamine, hexamine, and formaldehyde) in water (Darvan No. 1 dispersing agent). A thorough mixture was cast on a glass plate and cured at 105° for 3.5 hr. After cooling, the membrane was peeled under water.

An aqueous emulsion of polystyrene (or copolymer of styrene–butadiene, styrene–acrylic ester, etc.) mixed with an emulsion of butadiene–acrylonitrile (or vinylidene chloride–acrylonitrile, etc.) was poured onto a glass plate to form a membrane which was later immersed in chloromethyl ether containing $AlCl_3$ for 16 hr. at room temperature. It was washed and dried and immersed in a 30% aqueous solution of trimethylamine for 16 hr. It was rinsed with water, treated with HCl, washed with water, and dried to form an anion-exchange membrane (248). Runge, Wolf, and Bachmann (442) copolymerized styrene and DVB at 70° between polished glass plates in presence of azodibutyronitrile as catalyst and allowed the polymer to react with monochlorodimethyl ether in presence of $SnCl_4$. Chlorine was slowly replaced by dilute trimethylamine in petroleum ether to form an anion-exchange membrane. Bachmann, Wehlend, and Wolf (11) in another procedure copolymerized styrene and butadiene between glass plates at 70° for 48 hr. with 0.1% azodiisobutyronitrile as catalyst and chloromethylated and aminated the membrane as above. They (580) have also prepared membranes cross linked with DVB containing strong acid groups or strong acid and weak acid groups or only weak acid groups from different combinations of sulfonated styrene and methacrylic and acrylic acids. Nishimura, Uchiyama, and Sugihara (386), on the other hand, have prepared ion-selective membranes containing various ratios of acidic and basic groups by copolymerizing 2-vinyl-5-ethylpyridine, methacrylic acid, styrene, and DVB.

An aqueous solution of thermoplastic resin (polyvinyl alcohol, polyacrylonitrile, or polystyrene) containing glycerol (plasticizer) and a wetting agent was sprayed on a drum-formed casting support of stainless steel and dried. Next the material for formation of an ion-selective membrane was sprayed on top of that. This may be an organic solution of a mixture of 40–90% acrylonitrile–vinyl chloride copolymer and 60–10% linear polyelectrolyte. Organic solvent was evaporated and both films were stripped together and separated (349).

A paste of polytetrafluoroethylene powder in absolute alcohol may be coated to form porous membranes (51).

Ultrafilter membranes of different pore size (417) may be obtained by spreading a solution of powdered PVC dissolved in methylcyclohexanol at its boiling point. Larger pores may be obtained by adding alcohol or CCl_4 to the spreading solution. A solution of PVC (1 g.), methylcyclohexanol (10 g.), calcium stearate (0.01 g.), acetone (10 g.), and palatinol AH (0.05 ml.) is claimed to produce membranes of definite pore size (25 mμ).

Membranes suitable for dialysis have been made from block copolymers based on polyoxyethylene glycol and polyethylene terephthalate (295). A typical polyesterification reaction to form the block copolymer was carried out in a glass tube by melting the following mixture at 197°: 13.7 g. of dimethyl terephthalate, 29.41 g. of polyoxyethylene glycol, 7.45 g. of ethylene glycol, 0.022 g. of calcium acetate monohydrate, and 0.005 g. of antimony trioxide. Nitrogen gas was bubbled through the melt which was maintained at 197° for 3 hr. and at 222° for another 0.5 hr. Methanol and glycol distilled over. The polymerization was carried out at 270° and 0.2 mm. pressure for 3 hr.

Thin, clear, and tough membranes were prepared by casting a 15–20% solution of the polymer in dichloromethane solvent on a glass plate. A doctor knife was used to spread the solution uniformly. After air drying, the membrane was removed from the glass plate by immersion in water.

Woven Fabric-Backed Membranes.—The steps involved in the preparation of these membranes are: (a) solubilization of monomers in suitable solvents or preparation of partially polymerized gels, (b) impregnation of a cloth with the solution of the monomer or partially polymerized gel, (c) curing to complete polymerization with or without pressure, and (d) introduction of ionogenic groups, if necessary, by conventional procedures like sulfonation or chloromethylation followed by amination.

A number of recipes given in the previous section have been used in a slightly modified form with fabrics or gauzes made from polyvinyl chloride (255, 354, 357), polyvinylidene chloride (201), polyacrylonitrile (349, 354, 356, 358, 548, 595), polyvinyl alcohol (82), polyester (140), dynel (294), and glass (214, 380, 394, 395, 605), in order to form and to strengthen the membranes.

PVC or polyvinylidene chloride cloth impregnated with resins from anthranilic or salicylic acid and resorcinol and cured in a moist atmosphere showed selectivity to Fe, Co, Ni, Cu, and Zn (355).

Commercially available ion exchangers (Amberlite IR-120) were pulverized and dried and mixed with petroleum ether (fraction b.p. 80–155°) containing a copolymer of styrene–butadiene to form a viscous mixture. A Saran screen was dipped into it and dried three times to form a cation exchanger of improved mechanical strength and flexibility (200). In another process (206), epoxy derivatives of polyhydric alcohol and Bisphenol A have been used. A polyvinylidene chloride net (50 mesh, 360 deniers) was soaked in an alcoholic solution of the derivatives. After allowing it to stand for 24 hr. at room temperature, it was next soaked in a 28% aqueous solution of ammonium hydroxide for 24 hr. It was washed and kept in 0.5 N NaCl solution. The membrane had a base capacity of 2.3 mequiv./ml.

Anion-exchange membranes suitable for physicochemical research were prepared (226) using polyacrylonitrile fabric supports. The coating solution was made up by mixing a triglycidyl ether (condense epichlorhydrin with products of the reaction of ethylene oxide with 1,2-propylene oxide and $CH_3CH_2(CH_2OH)_3$ or pentaerythritol $(CH_2OH)_4C$) with an amine (dipropylenetriamine or bis-3-aminopropylmethylamine) at 40° until it became viscous.

Membranes Formed by Chemical Treatment.—Polyethylene sheets have been used in a number of processes. A polyethylene sheet was converted into a cation exchanger by simply soaking it in chlorosulfonic acid and subsequently washing it with NaOH solution and water (134, 135, 216, 568). Its resistivity may be reduced by treating it with hypochlorite solution (231). In another method, it was dipped into styrene without (606) or with 2% DVB (6, 147, 148) and containing Bz_2O_2 and polymerized. It may be sulfonated or chloromethylated to get a cation- or anion-exchange membrane.

Some elaborate treatments (136) have also been described. For example, a polyethylene sheet was soaked in styrene, DVB (2:1), and 0.05% hydroquinone and heated to 80°. It was washed with dichloroethane, soaked in 3:1 mixture of $TiCl_4$ and dichloroethane for 15 min., and polymerized. The product was washed with dichloroethane containing 20% methanol and dried. It was again treated with tetrachloroethane and soaked in tetrachloroethane and chloromethyl ether mixture (1:1) containing $SnCl_4$ for 24 hr. at 30°. The product was washed with methanol and aminated with methanolic solution of trimethylamine to give an anion-exchange membrane. Analogous procedures have been used to convert 0.15-mm. thick membrane of polyethylene mixed with a copolymer of styrene and butadiene into an anion exchanger (139). Blending and cyclization of the film in mixed vapors of BF_3 and CCl_4 (183) (or ethylene dichloride solution of $AlCl_3$–$(C_2H_5)_2O$ containing small amounts of either water in the form of $AlCl_3{\cdot}6H_2O$ (382) or butyl alcohol (379)) have also been used. Chloromethylation of the cyclized film with a mixture of $ClCH_2OCH_3$ and BF_3 in the vapor phase or with $ClCH_2OCH_3$ alone and subsequent amination of the film with a solution of trimethylamine in methanol gave an anion-exchange membrane. Just styrene–butadiene copolymerized membrane, cyclized and swollen (137), has been converted into a cation-exchange membrane by sulfonation. Chlorinated polyethylene, chlorinated rubber, or PVC have been treated with tetraethylenepentamine or other polyamine to form an anion-exchange membrane (413).

PVC films, unplasticized (376) or plasticized (with dialphanol phthalate (193) or trixylenyl phosphate (191)) and swollen, have been sulfonated. In another method (484) PVC (unplasticized) was cross linked with ethylenediamine hydrate in presence of 8-aminoquinoline and quaternized with dimethyl sulfate, or picryl amino groups were introduced by boiling with ethylenediamine and finally heating with a saturated solution of picryl chloride in alcohol (485). de Korosy and Shorr (241, 242) have chlorophosphonated, in presence of oxygen, polymer films such as polyethylene, PVC, and rubber. The resulting products were either hydrolyzed or aminolyzed to form cation- or anion-selective membranes. They found that opaque aminated PVC film became translucent upon subjecting it to heat treatment at 120° for 20 min. This film may be quaternized with 25% solution of methyl bromide in alcohol (244). Cation-exchange membranes have been prepared from fluorination of polymeric materials (7). Polytetrafluoroethylene film was immersed in styrene at an elevated temperature. Thus polystyrene was incorporated. The membrane was later chloromethylated and hydrolyzed in the usual way, or it may be chloromethylated and treated with amines to form anion-selective membranes (72). Similarly ion-exchange membrane has been prepared from polyvinylidene fluoride film by sulfonating the preswollen film with oleum (432).

A glass fiber sheet (0.07 mm. thick) immersed for 1 hr. in a styrene (29%)–butylene copolymerized latex, dried in air (6 hr.) at 80°, may be sulfonated to form a cation-exchange membrane (9). After sulfonation with 95.5% H_2SO_4, it was equilibrated in stages with 80, 60, and 30% H_2SO_4 (30 min. each) and finally with water.

Cellulosic material has been used in some processes. Parchment paper has been treated with an acidic solution containing a salt with N-hydroxylmethylamide group and a phenol and HCHO (502). Impregnation with aqueous solutions of HCHO and guanidium salts and drying at 110° has also been used (353). A parchment film was impregnated with a benzene solution of polymer from styrene, ethylvinylbenzene, DVB, and an alkali chloride. It was heated at 60° and immersed in benzenesulfonic acid to form a cation exchanger (480). It may be converted into an anion exchanger by amination (481). In another method, a sirupy liquid was formed by stirring and heating together phenol, Na-*p*-phenol sulfonate, HCHO, anisole, and NaOH. It may be diluted by adding a mixture of ethanol and methanol. A cellophane membrane was soaked in it and dried at 140° (523). Repeated impregnation and curing gave better membranes (246). Anion-selective membranes have been prepared from polytetraallylammonium chloride (503). Tetraallylammonium chloride (1 l.) was mixed with a solution of ammonium persulfate (0.05 g. in 2 g. of water) in the cold; triallylamine and HCl were added. A sheet of kraft paper was immersed in the solution for 1.5 hr. and cured in an oven at 50° for 16 hr.

Richards and White (433) have prepared cation-exchange membranes from paper and acrylic acid. Parchment (filter or kraft) paper was immersed in monomers (acrylic acid, acrylonitrile, or methyl acrylate) containing ceric ammonium nitrate at 25°. The polymerization was allowed to proceed for the required time. Sorbed ceric ions were removed by washing with 5 N H_2SO_4, water, and methanol, and the grafted paper was dried. Hydrolysis with 2.5 N NaOH gave the Na form of the membrane. Polyacrylic acid paper may be cross linked by refluxing (5 min.) with a solution of toluene 2,4-diisocyanate in Na-dried benzene.

Peterson and Livingston (415) have cross-linked cellophane membrane with dialdehyde starch. An aqueous solution (10%) of dialdehyde starch with 0.1% pyridine hydrochloride catalyst and a trace of wetting agent (sodium dodecyl sulfate) was coated on dry cellophane surface and was dried at 130° for 15 min.

Membranes from inorganic precipitates and gels have also been prepared. Unlike ion exchangers which show selectivity to cations or anions depending on the nature of the ionogenic groups fixed to the organic matrix, the electric charge on the membrane formed from inorganic precipitates is not determined entirely by the precipitate itself. The precipitate and the nature of the surrounding electrolyte solution determine the character of the membrane. Fischer and Babcock (91) formed membranes from $BaSO_4$ and $BaCrO_4$ by holding the respective precipitates bound in paraffin. They have investigated the $BaSO_4$–paraffin membrane as a potential indicator electrode in potentiometric titrations. Similarly, Pungor and Toth (420) formed nickel dimethylglyoxime–paraffin membrane electrode and used it to estimate the concentrations of nickel ions potentiometrically. Hirsch-Ayalon (184) deposited $BaSO_4$ in cellophane by using it to separate solutions of H_2SO_4 and $Ba(OH)_2$. These $BaSO_4$–cellophane membranes exhibited very interesting electrochemical properties (185, 186). Tendeloo and Krips (530) have studied a paraffin membrane containing calcium salt of low solubility and a nonionic detergent as an electrode for estimation of Ca^{2+} in solutions.

Malik and Ali (307) have prepared thorium tungstate membranes by depositing thorium tungstate in the pores of a parchment thimble. Thorium nitrate (0.1 *M*) was kept inside the thimble which was suspended in 0.1 *M* sodium tungstate solution. After a day or two, the solutions were interchanged. In a similar manner, Malik and Siddiqi have prepared cobalt and manganese ferrocyanide membranes (308) and also chromic ferro- and ferricyanide membranes (309).

Membranes Formed by Mechanical Treatment.— The simple principle used to prepare these membranes is to bind a polyelectrolyte or a conventional ion exchanger at ordinary or at elevated temperature to a thermoplastic polymer by application of mechanical pressure or to bind two polymers together by mechanical pressure and later to introduce the ionogenic groups by following the conventional procedures.

Amberlite IR-120 (powdered) was molded with a copolymer of vinyl acetate and vinyl chloride and triphenyl phosphate (plasticizer). A roll surface temperature of 130–150° was used (525). In another procedure (88), the same Amberlite was kneaded at 150–180° with powdered polyethylene and butyl oleate and molded. Membrane was immersed in alcohol for 5–7 days to remove the oleate. Without the oleate, molding could not be done. Amberlite IRA-400 (finely powdered) was dispersed in a solution of polyethylene in hot benzene. Evaporation of the solvent and pressing with a roller at 130° for 15 min. gave another membrane (131, 526). Strong or weakly basic ion-exchange membranes were obtained by binding similar ion-exchange resins to either polytetrafluoroethylene or polytrifluoroethylene (27). Corrosion resistance was conferred if PVC or polyethylene was incorporated into the membrane during rolling (160°) and compressing (1000 atm. at 148°). A 0.7-mm. thick membrane was made by simply pressing at 130° (200 p.s.i.) cross-linked polystyrene resin (quaternary ammonium groups) with polyethylene (562). Similarly, a paste of polytetrafluoroethylene in alcohol (418) coated onto a metal sheet (corrosion resistant) was made into a membrane by repeated passage of heavy rollers. The alcohol was removed by evaporation. Polyethylene granules or films were heated with styrene containing 1% Bz_2O_2 in a closed vessel under nitrogen for 8 hr. The product was compressed into a sheet (100) at 120° and 6000 p.s.i. pressure (607). Similar treatment may be given to a mixture of polystyrene (30 parts) and polyethylene (70 parts) (93) or polystyrene–butadiene and polyethylene (265). These membranes may be sulfonated or chloromethylated and aminated in the usual way.

Inorganic precipitates like zirconium phosphate or antimonate have been placed dry on glass fiber sheet and pressed at 150 atm. to form membranes. Similarly, other inorganic membranes have been prepared, for example, by hot pressing ammonium molybdophosphate with polyethylene powder (2).

Kuwata, Yoshikawa, and Uchida (266) have prepared anion-exchange membranes by kneading a copolymer (100 parts) of styrene and butadiene with tetramethylthiuram disulfide (3 parts), stearic acid (3 parts), Zn white (5 parts), and sulfur (2 parts). The mixture was molded into a 0.2-mm. thick membrane and vulcanized by heating at 150° and pressure 100 kg./cm.^{2}. The membrane was swollen with tetrachloroethane and chloromethylated and aminated. Similarly, SBR rubber was calendered into a film (381), cyclized in $SnCl_4$ or $TiCl_4$, and converted into an anion exchanger. Some elastometric materials have also been used. Polyethylacrylate rubber was placed on a rubber mill at 65° and banded slowly adding Dow 529-K, stearic acid, ZnO, mercaptobenzothiazole, tetramethylthiuram disulfide, carbon black, triethylenetetramine, and sulfur. The material was stripped from the mill and vulcanized in a flash mold at 167°. Hot caustic was used for 6 days to hydrolyze the cured rubber (188). Ethyl acrylate has also been used in another process (189) with styrene, maleic anhydride, and DVB (with ethylstyrene and Bz_2O_2). The clear solution was heated in a mold for 18 hr. at 72–75°. Membrane was hydrolyzed by soaking it in hot NaOH solution. Anion exchangers can also be made in a similar process with 4-vinylpyridine replacing ethyl acrylate.

Pale creep rubber has been used with anion or cation exchangers to form membranes (260, 524). Powdered ion exchanger with pale creep rubber was milled on a rubber mill to form membranes. The rolls were kept cold while milling by circulation of cold water. These membranes may be reinforced with Saran or other fabric if desired. The reinforced ones may be made by molding together ion exchanger, rubber, and fabric support (260).

Certain polymers of nuclear-substituted styrenes (*e.g.*, vinyltoluene, ethylvinylbenzene, etc.) were milled at 100–110° with dicumyl peroxide and later at 150° for 15 min. to form hard and tough colorless sheets (331).

Wichterle (583) prepared semipermeable membranes by partially crosslinking water-soluble polymers. An aqueous solution of polyvinyl alcohol (20%), adipic acid (2%), and HCl (5%) was heated in a mold at 50–80°. Resulting structure was washed in water and then in 3–5% boric acid. Polyacrylic acid may be used for cross linking.

Films of PVC, polyvinylidene chloride, and polyethylene were dipped into a mixture of styrene, DVB, solvent, and Bz_2O_2. The swollen films were covered with cellophane and heated to 70°, or they may be kept between sheets of reinforcing materials such as cloth or nets of PVC and heated in a hot press (350). These may be converted into ion-selective membranes by conventional treatment.

Semipermeable membranes of graded porosity have been prepared from cellulosic fibers (399). Flocs of wood cellulose were dispersed in dry toluene and treated in an inert atmosphere with $TiCl_4$ at room temperature for 0.5 hr. CH_3MgBr was added and the temperature was raised to 60°. Gaseous ethylene was passed for 6 hr. and then cooled and, after dilution with methanol, coated cellulose fibers were separated and molded under light pressure at 150°. A porous sheet was obtained. The porosity can be controlled by the molding pressure.

A block polymer was made by polymerizing the following: polystyrene (20 parts), a linear copolymer of 70% styrene and 30% butadiene (60 parts), styrene (551 parts), butadiene (160 parts), DVB (120 parts), and ethylvinylbenzene (89 parts). A plasticizer, dimethyl phthalate, may be added if necessary. The polymerization was carried out under nitrogen at 80° for 2 days and at 100° for 3 days. Membrane sheets were cut out of this block polymer. These sheets may be swollen in benzene and sulfonated (555).

Membranes Formed by Photochemical Treatment.— Powerful ionizing radiations have been used in this method to bring about the polymerization of monomers incorporated into various materials. In this work, polyethylene films have been used by a number of workers. The film was soaked in styrene and treated with γ-rays from Co^{60} (5, 141, 230, 340, 483, 553, 563) to form the graft copolymer which was later sulfonated or aminated to form ion-selective membranes. Grafting of methyl acrylate, ethyl acrylate, or acrylonitrile to polyethylene film has also been done (604). Alkaline hydrolysis gave carboxylic acid type membranes.

Monomers (acrylic acid, methyl methacrylate, or dimethylaminoethyl acrylate) carried on glass fibers or polyethylene have been polymerized using high-voltage electrons, X-rays, or γ-rays (43). Even ultraviolet radiation (37, 44) and incandescent lamp light (241, 243) have been used in presence or absence of sensitizers like benzophenone. Copolymer of styrene and butadiene (1:1) was hot-rolled to obtain a thin membrane which was later irradiated with γ-rays from Co^{60} and soaked in 94% H_2SO_4 to sulfonate it (138). Exposure to γ-rays or X-rays increased the degree of sulfonation (338). Simultaneous grafting of styrene and acrylonitrile (238) on ethylene–propylene copolymer has also been done. Simultaneous grafting is claimed to improve strength and elasticity as compared with styrene only. At low radiation dose, grafting in 80% methanol of monomers is found to increase the rate of grafting. Ion-exchange resins (PSSA) have been immersed in polyvinyl alcohol and $K_2Cr_2O_7$. The mixture has been spread to form a film which has been stabilized by irradiation with ultraviolet light (514).

2. Membranes to Serve as Models for Natural Membranes

Extensive literature describing the preparation and the physico- or electrochemical behavior of thick collodion membranes exists. They have been considered as models simulating the behavior of cell membranes (492). Recent application of electron microscopy to the study of the structure of cell membranes (436) appear to support the view already held on theoretical grounds, that the living membrane is a bimolecular leaflet of lipid, 75–100 Å. thick, the aqueous surfaces of which are bounded by protein (65). It is wondered whether membranes of this order of thickness built from polymeric materials, lipids, or phospholipids would constitute a living membrane in its electrochemical behavior. Preparation of thin membranes is a prerequisite to such a study. Although such membranes have been prepared (24, 39) from various materials, the study of their electrochemical properties is hindered owing to difficulties in handling such fragile structures. Some progress in this direction has been reported (277). The recent methods developed to prepare thin membranes to resemble at least the physical dimensions of natural membranes are presented below.

Gershfeld (101) has cast thin films (300 Å. or less) on an aqueous surface using a parlodion solution in isoamyl acetate. Lakshminarayanaiah and Shanes

(276) have improved his technique of casting to prepare thin membranes, 50–1000 Å. thick. Their procedure consisted in gently transferring a known volume of parlodion solution to the aqueous surface to cover a fixed area and allowing the solvent to evaporate under controlled conditions. Capacitance and resistance measurements have established the integrity of the membranes, and the former provided corroboration for the thickness inferred from the amount of parlodion deposited. Consequent upon this, Lakshminarayanaiah (274) has used capacitance measurements to estimate the thickness of parlodion membranes (95–3000 Å. thick) prepared by the Carnell–Cassidy technique (39), which consisted in dipping a clean and dry glass plate into parlodion solution and drying it under controlled conditions of evaporation and floating the membrane off the glass plate onto an aqueous surface. These two techniques have been used (275) to incorporate stearic acid or phopholipids into the membrane phase. By the first technique about 6% lipids (w.r.t. wt. of nitrocellulose) and by the second technique about 20% lipids could be incorporated.

Membranes, specific to transport of particular ions, have been reported. A polyvinylchloroethyl ether polymer membrane reinforced with glass fibers and soaked in β,β'-dichlorodiethyl ether retained iron preferentially and thus enabled its separation from aluminum by dialysis or electrodialysis (25). Similarly, alginate membrane, prepared from PVC containing alginic acid and cross linked with formaldehyde using cyclohexanone as a mixing agent, showed lower permeability to Fe^{3+} (475). The preparation of a polymer membrane with complex-forming properties has also been described (215).

Lipid-permeable collodion membranes have been prepared by Banaszak and McDonald (13). This was done by casting a solution of collodion containing paraffin oil (5 g./100 ml.) on a rotating test tube (20 r.p.m.). The membrane was dried for 1 hr. at room temperature and then soaked overnight in distilled water. The membrane was pulled off the test tube. These membranes were readily permeable to cholesterol in partially aqueous dialysis systems. Unlike ordinary collodion or cellophane membranes, lipids equilibrated readily through these membranes.

Tobias, Agin, and Pawlowski (550) used a millipore filter disk (cellulose nitrate–cellulose acetate material, pore size 100 ± 20 Å., 0.15 mm. thick) to prepare a phospholipid or phospholipid–cholesterol membrane. Cholesterol and "animal" cephalin (phophatidyl serine, 60–85%; phosphatidyl ethanolamine, 15%; traces of inositol; and spingomyelin) were dissolved in terpene-free benzene and a millipore disk was dipped into it. After evaporation of the solvent, the disk was again dipped and dried. This process was repeated until about 1 to 1.8 mg. of lipid was deposited per cm.^{2} area. The resistance of this lipid barrier can be controlled by the ambient $CaCl_2$, NaCl, or KCl concentrations. $CaCl_2$ solutions always gave higher membrane resistances which were lowered by additions of NaCl or KCl. Recently Nash and Tobias (368) have shown that the high resistance of the membrane in presence of $CaCl_2$ solution is due to the interaction of Ca^{2+} cation with the negatively charged polar head of phosphatidyl serine. This they did by preparing membranes separately from pure compounds of phosphatidylserine, phosphatidylethanolamine, and phosphatidylcholine and studying the variation of electrical resistance of membranes using different salt solutions (Ca^{2+}, Na^+, K^+).

Phosphorylated fatty alcohols and amines with water make stable gels which may be made into membranes on water or may be impregnated on a sheet of porous polyethylene (352). These sheets, one positively and the other negatively charged, may be sandwiched to form interesting models for cellular membranes. Similarly, Saunders (445) has formed phosphatide membranes at the boundary between a phosphatide sol and a salt solution whose concentration was sufficient enough to precipitate the sol. Lecithin films containing other components such as lysolecithin, cholesterol, and plasma albumin have been examined for their salt permeabilities.

Curran and McIntosh (60) have used a cellophane membrane with sintered glass disk as a model for a biological system to demonstrate water movement from high salt concentration side to low concentration side. A similar improved system using Visking dialysis tubing and Dupont wet gel membranes has been constructed by Ogilvie, McIntosh, and Curran (396).

Nonaqueous liquid membranes (438, 439, 471) have been used as models to study the selective flux of salts and ions and the influence of amphoteric surface-active agents (phospholipids) on diffusion and carrier transport of salt and ions through short-chain alkyl alcohols (*e.g.*, butanol, pentanol, etc.) and other nonaqueous membranes. The liquid membrane was formed by placing the nonaqueous liquid (about 300 ml. and 2 cm. thick) on top of aqueous solutions placed in the two compartments of a partitioned polystyrene box.

Sollner and Shean (498) have reported formation of liquid ion-exchange membranes of high selectivity. These are solutions in water-insoluble organic solvents of substances containing ionogenic groups and sparingly soluble in aqueous electrolyte solutions. A 20% solution of lauryltrialkylmethylamine in xylene may be floated on two aqueous solutions separated by a glass wall to form a liquid anion-selective membrane.

Mueller, Rudin, Ti Tien, and Wescott (359–361) have developed a technique to prepare bimolecular lipid membranes, 60–90 Å. thick. Complex mixture of lipids or proteolipids extracted from ox brain using chloroform–methanol (2:1 by volume) containing 0.1 ml. of α-tocopherol was spread on loops or frames kept under water. Diffusion or evaporation of solvent from the films led to the formation of a bimolecular leaflet of complex and unknown composition. This process of membrane formation is similar to the generation of "black" soap films in air.

To facilitate study of the electrical properties of these lipid bilayers, the films were formed on a pin hole (1-mm. diameter) in the side of a polyethylene cup resting on a petri dish. Both the cup and the dish compartments were filled with aqueous electrolyte solutions (0–1 *M*). With a trimmed sable brush, membrane forming solution was painted on the pin hole. In a similar manner (133), lecithin film has been formed on a hole in a Teflon sheet.

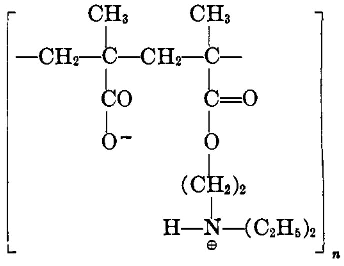
This technique of membrane formation has been used by Huang, Wheeldon, and Thompson (195) to prepare thin phospholipid membranes of simple composition. They have used pure phospholipid preparations of known composition, free from products of autoxidation, and have studied the effects of lipid composition, solvent composition, and temperature on the formation and stability of bimolecular leaflets. The sequence of events following membrane formation, as viewed in a wide field microscope have been described. Membrane thickness (61 Å.) was established by quantitative optical measurements.

3. *Composite and Other Special Membranes*

Simple anion- and cation-exchange membranes can be joined in various configurations. Depending on the way they are joined, these composite structures exhibit a number of interesting phenomena which have been, in some cases, predicted on theoretical grounds (291). The possible configurations are: (1) cationic and anionic regions are intermingled so completely that they are physically indistinguishable to form an amphoteric membrane, (2) mosaic membrane in which both anionic and cationic areas are clearly defined and distinguishable, and (3) bipolar array membranes formed by a laminar conjunction of individual anionic and cationic membranes either physically touching or separated by a porous spacer. If the boundary between the two laminar regions is very sharp, it has been called a step-junction bipolar membrane (96).

All these types have been prepared and exhibit diverse electrical properties.

Jacobson (207) has fabricated a membrane that is capable of being changed both in charge density and in charge sign. A polyampholyte (weakly acidic and weakly basic groups) was formed from monomers, methacrylic acid, and N-diethylamino-2-ethyl methacrylate. The material has the structure



and consequently has an isoelectric point which enables changing polarity and charge density with pH, the behavior typical of a zwitterionic membrane. This material with dynel was dissolved in N,N-dimethylformamide at 90°. The solution was cast to form membranes 50 μ thick.

Amphoteric ion-selective membranes with strong basic and weak acidic groups have also been prepared by copolymerization (385). A homogeneous solution containing N-methyl-2-vinyl-5-ethylpyridinium salt, methacrylic acid, styrene, and DVB has been copolymerized in presence of a plasticizer to form a membrane.

de Korosy (240) has prepared mosaic membranes from polyethylene sheets. Certain area was sulfonated to make it cationic and the rest of the sheet, after protecting the sulfonated area by covering it with rubber, was treated with ethylenediamine and quaternized with methyl bromide to make it anion selective and thus a border line between two selective membranes was formed.

Lovreček, Despić, and Bockris (291) have constructed a bipolar array membrane from Nepton CR-61 AD (H^+ form) and Nepton AR-111 AD (OH^- form) using thin perforated Teflon sheet (0.02 mm. thick) spacer in between and have used it in electrolyte systems to demonstrate the rectification of alternating currents passed through the systems.

Pastelike substance was applied to a cation exchanger which, after suitable treatment and irradiation, was made into an anion–cation bipolar membrane (363). For example, a polyethylene film (0.05 mm. thick) was dipped into styrene monomer and was graft-polymerized by irradiating it with Co^{60}. It was sulfonated and converted to Na form and washed and dried.

4-Vinylpyridine was mixed with 0.5% Bz_2O_2 and heated to 70° for 1 hr. to form a viscous polymer. It was cooled and mixed with Epikote 562 and 828 (condensates of epichlorhydrin and glycerol). This paste was coated on one side of Na form cation exchanger and then irradiated with Co^{60}. The transport numbers of H^+ or OH^-, Na^+, and Cl^- were 0.92, 0.01, and 0.07, respectively, when a current of 20 ma./cm.^{2} was passed through the system

$$0.5\,N\ \mathrm{NaOH}\ \|\ \underset{\text{anionic}\qquad\text{cationic}}{\text{membrane}}\ \|\ 0.5\,N\ \mathrm{HCl}$$

Friedlander (96), using a similar procedure, prepared thermoplastic ion exchangers of both types. Each cationic and anionic membrane was dried at 100°. Dry samples were placed on top of each other between sheets of Al foil and molded in a laboratory molding press at 150°. A pressure of 35 kg./cm.^{2} was applied for 2–3 min. By shortening the pressure time to 6–20 sec., a semipermanent membrane capable of being pulled apart later was made. A highly fused membrane showed no asymmetry whereas a lightly fused one did show asymmetry. Similar procedure was used by Schwartz and Case (473) and by Mauro (324) to fuse cationic AMF C-103 and anionic AMF A-104. These ion exchangers were of the thermoplastic, polyethylene type and therefore could be fused this way by mechanical pressure. Others which could not be fused this way may be cemented together using a solvent (dimethylformamide) and mechanical pressure (324).

Frilette (97) has used bipolar membrane to study electrical potentials arising across it when it separated salt solutions. The potentials observed were erratic. Maslov and Ovodova (320) have used diaphragms formed from finely powdered cation- and anion-exchange resins. Rubbery binders have been used to hold the particles together (553).

Some special type membranes, which have been prepared possessing specific properties, are the following. (1) Hemin (hematin + HCl) incorporated into collodion membrane may be used to determine Cl^- activities over a range of pH (404). Acid salts of esterified denatured ovalbumin pressed into a film may be used after conditioning to determine anion activities of electrolyte solutions (405). (2) Pyrocatechol or *p*-phenolsulfonic acid with HCHO polymerized to form membrane electrodes may be used to determine K^+ or Na^+ activities (16). (3) Cellophane membrane coated with nitrocellulose acts as a cation-selective membrane (478). (4) Metal ion deposited on an ion-exchange membrane may be made to take up another metal ion by reduction (reducing agent, sodium hypophosphite) of the metal salt solution. This metallized membrane acted as a porous barrier (528). (5) Multilayer membranes have been made by coating glass with stearates of alkaline earth cations (114, 469) using the technique of Langmuir and Schaefer (279). These may be used as electrodes in estimating the activities of salts in mixed electrolytes.

ACKNOWLEDGMENT.—The preparation of this paper was supported by Grant NB-03322 from the National Institute of Neurological Diseases and Blindness, and by Grant GB-865 from the National Science Foundation.

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