CONTINUUM THEORY OF TRANSPORT THROUGH CAPILLARY MEMBRANES

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ABSTRACT

CONTINUUM THEORY OF TRANSPORT THROUGH CAPILLARY MEMBRANES

By

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Transport of fluids through membranes is treated in the theoretical framework of continuum, nonequilibrium thermodynamics. Analysis of theories in which the membrane is regarded as a discontinuity shows that such approach cannot provide insight into phenomena within the membrane and can be misleading when misapplied. Both one-dimensional transport through capillary membranes with charged capillary walls and two dimensional transport through capillary membranes with semi-permeable walls are treated in detail.

Comparison of the discontinuous approach of the Kedem-Katchalsky type and the continuum approach shows that (1) Kedem-Katchalsky theory is strictly applicable only to homogeneous membranes for thermodynamically ideal binary nonelectrolyte solutions; (2) For porous membranes, Kedem-Katchalsky theory can be used only when the barycentric

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velocity is linearly related to the external forces; (3) For porous membranes in isothermal binary solutions, reciprocity of the local phenomenological coefficients is the natural outcome of the linear dependence of the fluxes; and (4) For homogeneous membranes and for porous membranes satisfying (2), the Kedem-Katchalsky reciprocal relation $L_{pD} = L_{Dp}$ is valid only when the solution is thermodynamically ideal and the partial molar volumes of solute and solvent are equal. Moreover, the phenomenological coefficients in Kedem-Katchalsky theory in general depend on the driving forces.

The continuum approach is then employed to analyze the transport of electrolyte solution through a charged capillary with radius larger than the thickness of the diffuse double layer formed inside the capillary. Gradients of pressure, electrical potential and concentration are included in the analysis, along with the concentration polarization of the electrical double layer. The Navier-Stokes and Poisson-Boltzmann equations are solved for the velocity of the center of mass of the flowing liquid mixture. The final expression contains a concentration gradient term which represents capillary osmosis and which has usually been ignored. The general analytical expression for capillary osmosis in circular capillaries reduces, for large ratios of radius to Debye length, to that obtained by Derjaguin for flat surfaces from thermodynamic consideration.

The result for capillary osmosis is included in developing the theory of anomalous osmosis for capillary membranes. For KCl solutions, which have nearly equal diffusivities and mobilities, our equation predicts the same direction, similar shapes and similar magnitudes of the volume flow through both positively and negatively charged membranes. This agrees with Grim and Sollner's data on anomalous osmosis for KCl. Previous theories have not achieved this agreement.

The continuum approach is also used to determine two-dimensional concentration distributions and mass transfer rates in tubular membranes with finite wall permeabilities. Convective laminar flow and both axial and radial diffusion are included. The partial differential equation is solved in terms of Confluent Hypergeometric Functions. A numerical scheme called the "Overdetermined Collocation" method is used to overcome the difficulties of non-orthogonality. Eigenvalues up to the 10th and linear combination coefficients accurate to 9 significant figures are reported for various Peclet and wall Sherwood numbers. Radial concentration and local bulk concentration distributions and overall Sherwood number are also obtained for various values of Pe and N_{sh_w}.

CONTINUUM THEORY OF TRANSPORT
THROUGH CAPILLARY MEMBRANES

By

Ping I Lee

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To my parents, my wife,

and my daughter

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LIST OF SYMBOLS FOR CHAPTER II TO CHAPTER V

Roman Miniscules

a_α--activity of component α (2.33)*

$a_{\alpha\beta}$--phenomenological coefficient in the Hittorf frame (A.7)

b--parameter defined by (5.44)

c_α--molar concentration of component α (2.4)

c_α^0--molar concentration of α when the electrical potential is zero (4.16)

c_A', c_B'--molar concentration just inside both ends (A and B) of the capillary (5.35)

c_A, c_B--molar concentration just outside both ends of the capillary (5.36)

$\bar{c}_\alpha$--logrithmic mean concentration of α (3.23)

c--ionic concentration defined by (4.44)

d--parameter defined by (5.44)

f--parameter defined by (5.44)

f_α--activity coefficient of component α (2.33)

$g_{\alpha 1}$--ratio of the limiting partial molar volumes (4.13)

g--parameter defined by (5.44)

i--electric current (5.4)

$\bar{i}$--current averaged over the capillary cross section (5.19)

j_α--diffusion flux of component α relative to the center of mass velocity (2.6)

j_s--entropy flux (2.36)

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*These numbers refer to the equations where the symbol first appear.

j_α^H--diffusion flux in the Hittorf frame (A.2)

j_E--internal energy flux not due to the bulk flow (2.27)

ℓ--length of the capillary or thickness of the membrane (2.23)

$\ell_{\alpha\beta}$--averaged phenomenological coefficient (3.59)

p--total pressure (2.15)

q--heat flux (2.29)

r--radial coordinate (4.3)

$r_{\beta\alpha}$--averaged phenomenological coefficient (3.57)

t--time (2.1)

t_α--transference number of ionic component α (A.12)

u--center of mass velocity (2.5)

u_α--velocity of component α (2.3)

u_x, u_r, u_θ--axial, radial and azimuthal component of u (4.2)

u_p--pressure flow velocity (4.8)

u_{eo}--electroosmotic velocity (4.8)

u_{co}--capillary osmotic velocity (4.8)

$\bar{u}_x$--averaged velocity in x direction (5.18)

v_α--partial molar volume of α (2.48)

v_α^∞--partial molar volume of α at infintie dilution (2.48)

w_α--mass fraction of α (2.2)

x--Cartesian spacial coordinate (2.11)

x_α--mole fraction of component α (2.33)

x_α^0--mole fraction of α when the electrical potential is zero

y--Cartesian spacial coordinate (2.11)

z--Cartesian spacial coordinate (2.11)

z_α--ionic charge per mole of α (2.14)

Roman Majiscules

A--parameter defined by (5.44)

A_{ij}--element of the coefficient matrix of the averaged fluxes (5.22)

B--parameter defined by (5.44)

B_α--pressure term coefficient (5.3)

B_1--concentration term coefficient (5.40)

$\bar{D}$--parameter defined by (5.44)

D_α--diffusion coefficient defined by (A.19)

D--Fikian mutual diffusion coefficient (A.11)

D_α^c--diffusion coefficient defined by (A.24)

D_α'--diffusion coefficient defined by (A.22)

E--parameter defined by (5.44)

$\bar{E}$--specific internal energy not including external potentials (2.25)

$\bar{E}_T$--total specific energy (2.24)

F--Faraday constant (2.14)

$\bar{F}$--parameter defined by (5.44)

F_α^*--total frictional and thermal force in molar units (2.18)

G--parameter defined by (5.44)

$\bar{H}_\alpha$--partial specific enthalpy of α (2.29)

I--ionic strength in terms of molar concentration (4.16)

I_0--modified Bessel function of the first kind of order zero (4.30)

I_1--modified Bessel function of the first kind of order one (4.30)

J_{E_T}--total energy flux (2.24)

J_V--volume flow (3.21)

J_D--exchange flow (3.22)

J_α--total mass flux (3.5)

$\bar{J}_V$--averaged volume flow (5.21)

$\bar{J}'_V$--real volume flow observed (5.48)

K--parameter defined by (5.44)

$L_{\alpha\beta}$ or $L'_{\alpha\beta}$--local phenomenlogical coefficient (2.3)

L_p, L_D, L_{Dp} & L_{Dp}--averaged phenomenological coefficients in Kedem-Katchalsky theory (3.25)

M_α--molecular weight of α (2.9)

$\bar{M}$--mean molecular weight (A.5)

N_α--total molar flux (2.8)

N_s--solute flux (5.5)

$\bar{N}_s$--averaged solute flux (5.20)

P--externally applied pressure (4.5)

P'--pressure due to the presence of charge or concentration gradient (4.5)

R--gas constant (2.32)

Re--Reynolds number (2.23)

$R_{\alpha\beta}$--resistance phenomenological coefficient (2.44)

$\bar{S}$--specific entropy (2.31)

$\bar{S}_\alpha$--specific entropy of component α (2.39)

T--absolute temperature (2.31)

$\bar{V}$--specific volume (2.31)

$\overline{X}$--specific net external force (2.12)

$\overline{X}_\alpha$--specific external force on α (2.13)

X_α--molar external force on α (2.18)

Y_α--generalized driving force (2.30)

Greek Miniscules

α--proportional constant between velocity and driving force (3.42)

β--concentration ratio (5.43)

γ--distribution coefficient (5.36)

ε--dielectric permitivity (4.24)

$\overline{\varepsilon}$--porosity (5.48)

η--shear viscosity coefficient (2.15)

φ--bulk viscosity coefficient (2.15)

η_α--shear viscosity coefficient of component α (2.18)

κ--reciprocal of the Debye length (4.28)

λ_α--ionic conductance (A.12)

Λ--equivalent conductance (A.13)

φ_α--bulk viscosity coefficient of component α (2.18)

μ_α--molar chemical potential of α (2.18)

$\overline{\mu}_\alpha$--specific chemical potential of α (2.32)

$\mu_\alpha^\ominus$--molar chemical potential of α relative to a standard state (2.32)

$\overline{\mu}'_\alpha$--specific chemical potential of α including the external forces (2.39)

ν--number of components (2.1)

ν_α or ν^α--number of ion α per molecule (4.44)

ξ--parameter defined in (4.14)

$\xi\pm$--parameter defined in (4.45)

π--osmotic pressure (3.24)

ρ_α--partial mass density of (2.3)

ρ--total density (2.1)

σ--charge density on the wall (4.29)

$\bar{\sigma}$--reflection coefficient (3.27)

$\underset{\sim}{\sigma}$--stress tensor (2.15)

ϕ--electrical potential (2.14)

ϕ'--total entropy production (2.37)

ϕ_1--entropy production due to viscous dissipation (2.38)

ϕ_2--diffusive dissipation (2.38)

$\bar{\phi}_2$--averaged diffusive dissipation (3.19)

ψ--electrical potential due to the presence of charge on the wall or the concentration graident (4.6)

ω_α--mobility of ion α (5.1)

ω--solute permeability (3.28)

Greek Majiscules

Φ--externally applied electric potential (4.6)

Ψ--reduced electric potential ψ (4.12)

Ω--parameter defined by (5.43)

$\Omega_{\alpha\beta}$--local phenomenological coefficient in center of mass reference frame (2.40)

LIST OF SYMBOLS FOR CHAPTER VI

Roman Miniscules

a--capillary radius (6.3)

c_α--local concentration (6.1)

c_0--dialysate concentration (6.7)

c--reduced concentration (6.10)

$\bar{c}$--local bulk concentration (6.53)

D_α--diffusivity (6.1)

g--residue squared (6.50)

h_D--total mass transfer coefficient (6.57)

k--parameter defined by (6.59)

r--radial coordinate (6.3)

s_i--residue (6.49)

u--center of mass velocity (6.1)

u_x--axial component of u (6.3)

x--axial coordinate (6.4)

z--reduced axial coordinate (6.12)

Roman Majiscules

A_n--linear combination coefficient in classical Graetz series (6.30)

B_n--linear combination coefficient in extended Graetz problem with axial diffusion (6.33)

N_α--total molar flux (6.1)

N_{sh}--overall Sherwood number (6.56)

N_{sh_w}--wall Sherwood number (6.13)

$N_{\zeta w}$--radial diffusion flux at the wall (6.57)

P_m--permeability of the wall (6.9)

Pe--Peclect number (6.12)

R_n--nth radial eigenfunction in classical Graetz series (6.23)

Z_n--axial contribution to the concentration in classical Graetz problem (6.23)

W_n--solution of the Kummer's equation (6.37)

Y_n--radial eigenfunction in extended Graetz problem with axial diffusion (6.33)

Greek Miniscules

β_n--eigenvalue corresponds to Y_n (6.33)

ζ--reduced radial coordinate (6.11)

θ--azimuthal coordinate (6.3)

λ--eigenvalue in the classical Graetz problem (6.25)

ξ--transforamtion variable (6.36)

CHAPTER I

INTRODUCTION

Transport processes through membranes are the subject of rather extensive research in various fields ranging from industrial desalination to biological nerve excitation. Membrane research has occupied physical chemists, biophysicists, biologists, physiologists, biochemists and engineers since the 19th century. Teorell (1967) used the name "Membranology" to describe the achievements, problems and perspectives of these more or less isolated group of researchers. Diverisifed as the individual achievements may appear, it is yet possible to discern a common, ultimate objective in the strivings of all membranologists; *viz*., transport phenomena.

The most intriguing transport phenomenon is the coupling between various processes. For example, living cells maintain a continuous exchange of matter with their surroundings, and at the same time they preserve concentration differences between intracellular and extracellular spaces. The membrane, which can be defined as a thin phase of material different from that on either side of it, generally exercises a complicated regulating function.

It allows material to pass through according to metabolic requirements, and it is able to distinguish sharply between similar compounds. It is often necessary for the cell membrane to extend chemical energy in order to transport substances against their chemical potential gradient. Thus, biological membranes act as both "barriers" and "pumps."

Coupled phenomena are also prevalent in transport through artificial, porous, charged membranes. A pressure gradient generates not only bulk flow of electrolyte solution through the membrane but also an electrical potential gradient across the membrane (streaming potential). A concentration gradient across the membrane produces flow behavior different from that described by Van't Hoff's Theory. The flow does not vary linearly with concentration but instead has maxima and minima. Moreover it is sometimes toward the more dilute solution (anomalous osmosis). These conversions of mechanical energy into electrical energy and of chemical energy into mechanical energy suggest consideration of artificial membrane as an energy converter.

It was not until recently that the rational description of these coupled phenomena was made possible by the theory of nonequilibrium thermodynamics. Kedem and Katchalsky (1958) formulated a membrane transport theory with the inclusion of coupling by a discontinuous nonequilibrium thermodynamic approach. This theory has been very popular among biologists. Spiegler (1958) pioneered a friction coefficient model, which afforded greater insight into the interactions inside the membrane. However, these "black box" type theories tend to rely heavily on lumped experimental parameters which conceal our ignorance of the exact physical nature of the processes inside the membrane. Kobatake and Fujita (1964) employed a continuous nonequilibrium thermodynamic approach but were only partially successful in predicting the results of Grim and Sollner (1957) on anomalous osmosis. They failed to predict the observation that KCl solutions flow in only one direction and to about the same extent in both positively and negatively charged membranes. Since then, various other continuum theories (cf. Toyoshima, et al., 1967; Fujita and Kobatake, 1968; Gross and Osterle, 1968; Fair and Osterle, 1971) have been developed. However, they are all unsatisfactory in one way or another. This will be discussed in more detail in Chapters VI and V.

The purpose of this Thesis is to present a systematic continuous, nonequilibrium thermodynamic theory of transport processes through capillary membranes. In addition to the utility of the final equations for describing actual processes, the systematic treatement affords greater insight into the internal mechanisms involved.

Previous inconsistencies, such as the application of electrokinetic equations for uniform solution concentrations to systems in which concentration variations dominate, are avoided.

The general hydrodynamic and nonequilibrium thermodynamic equations for transport processes in multicomponent system are presented in Chapter II. Chapter III deals with membrane transport phenomena in general. Particular emphasis is placed on the relationship between the type of membrane (porous, semipermeable, etc.) and the method and result of flows. The mechanism of ordinary osmosis is discussed in detail. We also clarify the difference between various reference frames in membrane transport. Finally, we compare the Kedem-Katchalsky theory with the more rigorous continuous nonequilibrium thermodynamic theory and show that the Kedem-Katchalsky theory is strictly valid only for homogeneous membranes at infinite dilution.

Chapters IV and V are concerned with flow through charged circular capillaries in the presence of a concentration gradient. Capillary osmosis, which occurs when there is a diffuse double layer along a wall to which a concentration gradient is tangential, is itself analyzed in Chapter IV and is included in the analysis of anomalous osmosis in Chapter V. In Chapter IV we consider the concentration polarization of the electric double layer and derive, from the Navier-Stokes equation and the Poisson-Boltzmann equation, a general analytical expression for the capillary osmotic velocity distribution in a charged cylinder. In the limit of zero concentration gradient, our barycentric velocity equation reduces to the equation for ordinary electrokinetic flow in capillary tubes. In the limit of large ratios of radius to Debye length, our equation reduces to that obtained by Derjaguin, et al. (1969) for flat surfaces by classical thermodynamics. In Chapter V we develop a theory which successfully describes anomalous osmosis as observed in charged porous membranes. We use the capillary membrane model described in Chapter IV, and take into account capillary osmosis. The capillary osmosis term is of the same order of magnitude as the electroosmosis term under the experimental conditions of anomalous osmosis. The results agree with Grim and Sollner's data on anomalous osmosis of KCl solutions through both positively charged and negatively charged membranes.

Finally, in Chapter VI we solve a general problem of laminar flow convective diffusion, including axial diffusion, through tubular membranes of finite wall permeabilities. The partial differential equation is solved in terms of Confluent Hypergeometric Functions. A numerical scheme called the "Overdetermined Collocation" method is used to overcome the difficulties of nonorthogonality.

Eigenvalues (up to the 10th) and linear combination coefficients to 9 significant figures for various Peclet number (Pe) and wall Sherwood number (N_{sh_w}) values are reported. Radial concentration and local bulk concentration distributions and overall Sherwood number are obtained for various values of Pe and N_{sh_w}.

CHAPTER II

EQUATIONS OF TRANSPORT

A. Introduction

In this chapter we lay the foundation for the discussion of transport phenomena in multicomponent systems. We consider only continuous, isothermal, isotropic fluids in which no chemical reactions occur and which are subject to a variety of driving forces (gradients of concentration, pressure, electric potential), but not to a magnetic field. We begin by presenting the necessary conservation equations in their most general form and then the general set of phenomenological equations of nonequilibrium thermodynamics. Specialized equations used in the study of membrane transport processes are deduced along with appropriate boundary conditions. For a more detailed discussion of the transport equations see, for example, Kirkwood and Crawford (1952), Bird, Stewart and Lightfoot (1960), de Groot and Mazur (1962), Fitts (1962), Horne (1966), Hasse (1969) and, particularly for transport in living systems, Lightfoot (1974).

B. Equations of Hydrodynamics

The behavior of a flowing liquid in which heat and mass transfer occur is described by the conservation equations, along with general thermodynamic equations of state. The conservation equations are partial differential equations which describe the change in macroscopic properties of the fluid (for example, the local density, center of mass velocity and temperature) in terms of the mass flux, momentum flux and energy flux. The basic equations of continuity, motion and energy balance correspond respectively to the fundamental principles of conservation of mass, momentum and energy. These equations have been derived for very general conditions both in classical and quantum theory.

<u>Equation of Continuity</u>

In the absence of chemical reactions, for a fluid mixture containing ν chemical species, the ν independent equations of continuity of mass are

$$(d\rho/dt) + \rho \, \underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0 \tag{2.1}$$

and
$$\rho(dw_\alpha/dt) + \underset{\sim}{\nabla} \cdot \underset{\sim}{j}_\alpha = 0 \;, \quad \alpha=1,\ldots,\nu, \tag{2.2}$$

(2.1) is for the fluid as a whole and (2.2) is for component α. Equivalent expressions for (2.2) are

$$(\partial\rho_\alpha/\partial t) + \underset{\sim}{\nabla} \cdot \rho_\alpha \, \underset{\sim}{u}_\alpha = 0 \tag{2.3}$$

or
$$(\partial c_\alpha/\partial t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{N}_\alpha = 0 \;, \tag{2.4}$$

where ρ is total mass density, w_α is mass fraction, ρ_α is partial mass density with $\rho_\alpha = w_\alpha \rho$, $\underset{\sim}{u}$ is the center of mass, or barycentric, velocity, $\underset{\sim}{u}_\alpha$ is the velocity of component α with respect to a laboratory reference frame, c_α is the molar concentration and $\underset{\sim}{j}_\alpha$ and $\underset{\sim}{N}_\alpha$ are respectively the mass diffusion flux and total molar flux of component α. The barycentric velocity $\underset{\sim}{u}$ is defined by

$$\underset{\sim}{u} = \sum_{\alpha=1}^{\nu} w_\alpha \underset{\sim}{u}_\alpha \; . \tag{2.5}$$

The diffusion flux $\underset{\sim}{j}_\alpha$ is defined by

$$\underset{\sim}{j}_\alpha = \rho_\alpha (\underset{\sim}{u}_\alpha - \underset{\sim}{u}) \; , \qquad \alpha=1,\ldots,\nu \; . \tag{2.6}$$

The diffusion fluxes are not all independent,

$$\sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha = 0 \; . \tag{2.7}$$

The total molar flux is defined by

$$\underset{\sim}{N}_\alpha = c_\alpha \underset{\sim}{u}_\alpha = (\rho_\alpha / M_\alpha) \underset{\sim}{u}_\alpha \; , \tag{2.8}$$

which is related to the mass diffusional flux $\underset{\sim}{j}_\alpha$ by

$$\underset{\sim}{N}_\alpha = c_\alpha \underset{\sim}{u} + (\underset{\sim}{j}_\alpha / M_\alpha) \; , \tag{2.9}$$

where M_α is the molecular weight of component α. Substantial time derivatives d/dt are related to local time derivatives $\partial/\partial t$ by

$$(d/dt) = (\partial/\partial t) + \underset{\sim}{u} \cdot \underset{\sim}{\nabla} \; , \tag{2.10}$$

which represents the time rate of change following a fluid element which is moving with a velocity u. The operator "$\underset{\sim}{\nabla}$" is defined by

$$\underset{\sim}{\nabla} = \underset{\sim}{i}\,(\partial/\partial x) + \underset{\sim}{j}\,(\partial/\partial y) + k\,(\partial/\partial z) \; , \tag{2.11}$$

where $\underset{\sim}{i}$, $\underset{\sim}{j}$ and $\underset{\sim}{k}$ are the unit vectors of the three dimensional Cartesian coordinate system. For more detailed analysis in other coordinate systems, see, for example, Bird, Stewart and Lightfoot (1960).

Equation of Motion

The general equation describing the isothermal flow of a Newtonian fluid is the Navier-Stokes equation. It is based on Newton's Second Law of Motion, supplemented by Newton's hypothesis of fluid friction that the shearing stress is directly proportional to the rate of strain. It may be written as (Horne, 1966)

$$\rho(d\underset{\sim}{u}/dt) - \nabla \cdot \underset{\approx}{\sigma} = \rho\underset{\sim}{\overline{X}} \; , \tag{2.12}$$

where $\rho\underset{\sim}{\overline{X}}$ is the net external force and where $\underset{\approx}{\sigma}$ is the stress tensor. The net external force is related to the external forces acting on component α by

$$\rho\underset{\sim}{\overline{X}} = \sum_{\alpha=1}^{\nu} \rho_\alpha \, \underset{\sim}{\overline{X}}_\alpha \tag{2.13}$$

where the bar indicates that it is a specific quantity. When there are only gravitational and electric fields

$$\rho_\alpha \bar{\underset{\sim}{X}}_\alpha = - M_\alpha \underset{\sim}{\nabla}\Gamma - z_\alpha F\underset{\sim}{\nabla}\phi \ , \qquad (2.14)$$

where z_α is the ionic charge per mole of α , F is Faraday's constant, Γ is the gravitational potential and ϕ is the electrostatic potential. The stress tensor $\underset{\sim}{\sigma}$ is given approximately by the Newtonian linear phenomenological relation

$$\underset{\sim}{\sigma} = - [p + (\tfrac{2}{3}\eta - \varphi) \ (\underset{\sim}{\nabla}\cdot\underset{\sim}{u})] \ \underset{\approx}{I} + 2\eta \ \mathrm{sym} \ \underset{\sim}{\nabla} \ \underset{\sim}{u} \ , \qquad (2.15)$$

where $\underset{\approx}{I}$ is the unit tensor, p is the pressure, sym $\underset{\sim}{\nabla}\underset{\sim}{u}$ is the symmetric part of the tensor $\underset{\sim}{\nabla}\underset{\sim}{u}$, and η and ψ are the coefficients of shear viscosity and bulk viscosity, respectively. Combination of (2.12) and (2.15) yields the Navier-Stokes equation:

$$\rho(d\underset{\sim}{u}/dt) + \nabla[\tfrac{2}{3}\eta - \varphi) \ \underset{\sim}{\nabla}\cdot\underset{\sim}{u}] - 2\underset{\sim}{\nabla}\cdot\eta \ \mathrm{sym} \ \underset{\sim}{\nabla}\underset{\sim}{u}$$

$$= \rho\bar{\underset{\sim}{X}} - \underset{\sim}{\nabla}p \ . \qquad (2.16)$$

Another form of the Navier-Stokes equation can be obtained by introducing (2.10) into (2.16) and rearranging,

$$\rho(\partial\underset{\sim}{u}/\partial t) + \rho\underset{\sim}{u}\cdot\underset{\sim}{\nabla}\underset{\sim}{u} = \rho\bar{\underset{\sim}{X}} - \underset{\sim}{\nabla}p + \eta\underset{\sim}{\nabla}^2\underset{\sim}{u}$$

$$+ (\tfrac{1}{3}\eta + \varphi)\underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\underset{\sim}{u}) \ , \qquad (2.17)$$

where we take η and φ to be constants.

Bearman and Kirkwood (1958) have derived macroscopic equations of motion for each component of a multicomponent system by the use of statistical mechanics; similar results have also been obtained from the consideration of rational (or continuum) mechanics (Bartelt, 1968; Bartelt and Horne, 1970; Ingle, 1971). Their equations are

$$\partial \rho_\alpha \underset{\sim}{u}_\alpha / \partial t + \underset{\sim}{\nabla} \cdot (\rho_\alpha \underset{\sim}{u}\underset{\sim}{u}) = \eta_\alpha \nabla^2 \underset{\sim}{u} + (\tfrac{1}{3}\eta_\alpha + \varphi_\alpha) \underset{\sim}{\nabla} (\underset{\sim}{\nabla} \cdot \underset{\sim}{u}) - c_\alpha \underset{\sim}{\nabla} \mu_\alpha$$

$$+ c_\alpha \underset{\sim}{F}^*_\alpha + c_\alpha \underset{\sim}{X}_\alpha \ , \quad \alpha = 1, \ldots, \nu \ , \qquad (2.18)$$

where μ_α is the isothermal chemical potential of component α in molar units (not including the external potential), $\underset{\sim}{F}^*_\alpha$ is the total frictional and thermal force in molar units which arises from intermolecular forces, $c_\alpha \underset{\sim}{X}_\alpha$ is the external force acting on component α, with $c_\alpha \underset{\sim}{X}_\alpha = \rho_\alpha \underset{\sim}{\overline{X}}_\alpha$ and η_α and φ_α are the partial coefficients of shear viscosity and bulk viscosity, respectively. These quantities have the properties that

$$\eta = \sum_{\alpha=1}^{\nu} \eta_\alpha \ , \qquad \varphi = \sum_{\alpha=1}^{\nu} \varphi_\alpha \ ,$$

$$\sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{F}^*_\alpha = 0$$

$$\sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{\nabla} \mu_\alpha = \underset{\sim}{\nabla} p \ . \qquad (2.19)$$

When (2.18) is summed over all components with the help of (2.19), the macroscopic Navier-Stokes equation (2.17) is obtained.

Since the general solution of the complete time dependent Navier-Stokes equation is not possible, various approximation schemes must be invoked. If the system considered is at steady state, which implies $(\partial \underset{\sim}{u}/\partial t) = 0$, then

$$\underset{\sim}{\nabla} p - \bar{X} = \eta \nabla^2 \underset{\sim}{u} + (\tfrac{1}{3}\eta + \varphi)\underset{\sim}{\nabla}(\underset{\sim}{\nabla}\cdot\underset{\sim}{u}) - \rho\underset{\sim}{u}\ \underset{\sim}{\nabla}\underset{\sim}{u}\ . \qquad (2.20)$$

In addition, most fluids except very dense ones and very dilute ones are essentially incompressible. For an incompressible fluid, the density ρ is constant in time and position. Thus according to (2.1),

$$\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$$

The Navier-Stokes equation for an incompressible fluid in a steady state is, then, for constant η ,

$$\underset{\sim}{\nabla} p - p\underset{\sim}{\bar{X}} = \eta \nabla^2 \underset{\sim}{u} - \rho\underset{\sim}{u} \cdot \nabla\underset{\sim}{u}\ . \qquad (2.21)$$

Furthermore, for slow flow characterized by small Reynolds number (of, say, the order of 1), the inertial term $\rho\underset{\sim}{u}\cdot\nabla\underset{\sim}{u}$ is very small in order of magnitude compared with the viscous term $\eta\nabla^2\underset{\sim}{u}$. Omission of inertial terms results in the so-called creeping motion or Stokes equation,

$$\underset{\sim}{\nabla} p - \rho \underset{\sim}{\overline{X}} = \eta \nabla^2 \underset{\sim}{u} \tag{2.22}$$

The Reynolds number is defined as

$$Re = \ell u \rho / \eta \ . \tag{2.23}$$

This dimensionless parameter describes in a general way the ratio of inertial to viscous forces, where ℓ and u are characteristic linear dimension and velocity, respectively. Thus, the smaller the Reynolds number, the better the neglect of the inertial term. (2.22) is quite satisfactory in most membrane systems, where the flows are slow and the Reynolds numbers are smaller than one. For more detailed discussion of low Reynolds number flow, see Happel and Brenner (1965).

Equation of Energy Transport

The general equation of Conservation of energy is

$$(\partial \rho \overline{E}_T / \partial t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_{E_T} = 0 \ , \tag{2.24}$$

where $\underset{\sim}{J}_{E_T}$ is the total energy flux and where $\overline{E}_T$ is the total specific energy,

$$\overline{E}_T = \overline{E} + 1/2\ u^2 \ , \tag{2.25}$$

where $\overline{E}$ is the specific internal energy not including external potentials and $u^2/2$ is the local kinetic energy of the center of mass. Note also that

$$u^2 = \underset{\sim}{u} \cdot \underset{\sim}{u} \ . \tag{2.26}$$

It is possible, however, to obtain the kinetic energy by summing over the kinetic energies of the components (Bartelt and Horne, 1970; and Ingle, 1971). We assume that the difference between the two definitions is negligible for the present purpose (Horne, 1966).

The energy transport equation can be expressed as

$$\rho(d\bar{E}/dt) = -\underset{\sim}{\nabla}\cdot\underset{\sim}{j}_E + \underset{\approx}{\sigma} : \underset{\sim}{\nabla}\underset{\sim}{u} + \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \cdot \underset{\sim}{X}_\alpha \ , \tag{2.27}$$

where $\underset{\sim}{j}_E$ is the internal energy flux not due to the bulk flow. The first term on the right represents the change of internal energy due to internal energy flux (this includes, in an isothermal system, energy flux due to a concentration gradient and energy transport by molecular diffusion); the second term includes both the internal energy change due to the PV-work, and that due to viscous dissipation; and the third term describes the change due to the work done by diffusing molecules to overcome the external forces. The internal energy flux is related to the total energy flux by

$$\underset{\sim}{\nabla}\cdot\underset{\sim}{j}_E = \nabla\cdot[\underset{\sim}{J}_{E_T} - \rho\bar{E}\underset{\sim}{u} + \underset{\sim}{u}\cdot\underset{\approx}{\sigma}] + \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{u}_\alpha \cdot \underset{\sim}{\bar{X}}_\alpha \ . \tag{2.28}$$

The internal energy flux can further be related to the second law heat flux $\underset{\sim}{q}$ by

$$\underset{\sim}{j}_E = \underset{\sim}{q} + \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \overline{H}_\alpha , \tag{2.29}$$

where $\overline{H}_\alpha$ is the partial specific enthalpy of component α.

C. Equations of Nonequilibrium Thermodynamics

The previous sections are all based on conservation equations. In order to relate the mass, momentum and energy fluxes to concentration, pressure, electrostatic potential, velocity and temperature gradients as required by most physical problems, one has to introduce a set of constitutive equations from nonequilibrium thermodynamics and reduce them with the aid of a fourth fundamental principle, the entropy inequality. We could start from the rational, fundamental approach of Truesdell (1969), Müller (1968), Bartelt (1968), Bartelt and Horne (1970), Gyarmati (1970) and Ingle (1971). However, for simplicity, we adopt the conventional approach represented by de Groot and Mazur (1962), Fitts (1962), and Hasse (1969). It has to be emphasized that the more fundamental approach gives the same results for the simple systems investigated here (Bartelt and Horne, 1970).

We now introduce two fundamental assumptions of conventional nonequilibrium thermodynamics for the system under consideration. The first assumption is:

Postulate I: The principle of local state

For a system in which irreversible processes are taking place, all thermodynamic functions of state exist for each element of the system. These thermodynamic quantities for the nonequilibrium system are the same functions of the local state variables as the corresponding equilibrium thermodynamic quantities.

The second assumption is

Postulate II: The assumption of locally linear fluxes

The fluxes $\underset{\sim}{j}_\alpha$ are linear, homogeneous functions of the forces $\underset{\sim}{Y}_\alpha$. That is

$$\underset{\sim}{j}_\alpha = \sum_{\beta=1}^{\nu} L_{\alpha\beta} \underset{\sim}{Y}_\beta \ . \tag{2.30}$$

The forces $\underset{\sim}{Y}_\beta$ are "driving forces" for the fluxes; for example, $\underset{\sim}{\nabla}\ell nT$ is the driving force for heat flux $\underset{\sim}{q}$. The phenomenological coefficient $L_{\alpha\beta}$ are independent of the forces. The diagonal coefficients $L_{\alpha\alpha}$ relate conjugate fluxes and forces, while the off-diagonal elements $L_{\alpha\beta}(\alpha\neq\beta)$ characterize cross phenomena. As in the case of postulate I, postulate II is presumably most nearly valid when the system is close to equilibrium. Thus, both postulates apply to systems with small spacial and time nonuniformities of the local thermodynamic variables.

By postulate I, we may use the Gibbsian equation for $d\bar{E}$

$$d\bar{E} = Td\bar{S} - pd\bar{V} + \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha \, dw_\alpha \ , \tag{2.31}$$

where $\bar{S}$ and $\bar{V}$ are respectively the specific entropy and the specific volume, and $\bar{\mu}_\alpha$ is the chemical potential of component α in mass units,

$$M_\alpha \bar{\mu}_\alpha = \mu_\alpha = \mu_\alpha^\ominus(T,p) + RT \ \ell n \ a_\alpha \ , \tag{2.32}$$

where μ_α is the chemical potential of component α in molar units, M_α is molecular weight of α , T is absolute temperature, p is pressure, R is the gas constant, a is the activity of component ,

$$a_\alpha = x_\alpha \ f_\alpha \tag{2.33}$$

with x_α the mole fraction of component α and where $\mu_\alpha^\ominus$ and the activity coefficnet f_α are defined relative to an appropriate standard state in which there are no effective external fields. Note that f_α is a function of temperature, pressure and composition. Since we treat only aqueous solutions here, the appropriate standard state is the pure solvent (denoted by the running index 1),

$$\mu_\alpha^\infty = \lim_{x_1 \to 1} [\mu_\alpha - RT \ \ell n x_\alpha] \tag{2.34}$$

whence

$$\lim_{x_1 \to 1} f_\alpha = 1 \ .$$

Rearranging (2.31) and differentiating with respect to time, the rate of entropy production,

$$\rho(d\bar{S}/dt) = \rho/T(d\bar{E}/dt) - (p/\rho T)(d\rho/dt)$$

$$- (\rho/T) \sum_{\alpha=1}^{\nu} \bar{\mu}_\alpha (dw_\alpha/dt) . \tag{2.35}$$

Substitution of (2.1), (2.2) and (2.27) into (2.35) yields for entropy production equation,

$$\rho(d\bar{S}/dt) = \phi'/T - \nabla \cdot \underset{\sim}{j}_s , \tag{2.36}$$

with the internal entropy production ϕ'/T written as the sum of two terms (again for an isothermal system)

$$\phi'/T = \phi_1+\phi_2/T , \tag{2.37}$$

$$\phi_1 = (\underset{\approx}{\sigma}+p\underset{\approx}{I}):\underset{\sim}{\nabla}\underset{\sim}{u}$$

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}'_\alpha \tag{2.38}$$

where $$\underset{\sim}{j}_s = \underset{\sim}{q}/T + \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \bar{S}_\alpha$$

$$\underset{\sim}{\nabla}\bar{\mu}'_\alpha = \underset{\sim}{\nabla}\bar{\mu}_\alpha - \underset{\sim}{x}_\alpha . \tag{2.39}$$

Although it would seem that from postulate II we should relate all the conjugate driving forces and fluxes, one does not have to consider all the interactions indicated by (2.20). It can be shown on the basis of symmetry (Curie's theorem) that, for isotropic systems, coupling can occur only between driving forces and fluxes of the same order or between those which differ in tensorial characters by even integers. This implies that only $\nabla\bar{\mu}'_\alpha$ is related to j_α . By postulate II, the linear phenomenological equations are

$$- j_\alpha = \sum_{\beta=1}^{\nu} \Omega_{\alpha\beta}\nabla\bar{\mu}'_\beta , \qquad \alpha=1,\ldots,\nu , \tag{2.40}$$

where the Ω's are the phenomenological, or Onsager coefficients. These coefficients are not all independent since, by (2.22),

$$\sum_{\alpha=1}^{\nu} \Omega_{\alpha\beta} = 0 , \qquad \beta=1,\ldots,\nu . \tag{2.41}$$

Furhter, due to the requirement of positive entropy production, it has been shown (Bartelt and Horne, 1969) that

$$\sum_{\beta=1}^{\nu} \Omega_{\alpha\beta} = 0, \qquad \alpha=1,\ldots,\nu . \tag{2.42}$$

Thus, for the ν-1 independent fluxes $j_1,\ldots,j_\nu$, the linear phenomenological equations are

$$- j_\alpha = \sum_{\beta=1}^{\nu=1} \Omega_{\alpha\beta} \nabla(\bar{\mu}'_\beta - \bar{\mu}'_\nu) \qquad \alpha=1,\ldots,\nu-1 . \tag{2.43}$$

If the fluxes and forces of (2.43) satisfy Onsager's (1931) condition, then the matrix of Onsager coefficients is symmetric; i.e. $\Omega_{\alpha\beta} = \Omega_{\beta\alpha}$ for $\alpha,\beta=1,\ldots\nu-1$. However, since total experimental verification of the Onsager Reciprocal Relations (ORR) is still an open question (Miller, 1960, 1969), we only accept them as postulates. We discuss applicability of the ORR in membrane transport systems in the next chapter. For most purposes it is more convenient to use (2.40) and consider the phenomenological coefficients as conductance coefficients. However, sometimes it is useful to invert (2.43) so that the forces can be expressed as linear functions of the fluxes. The result is

$$- \nabla(\bar{\mu}'_\alpha - \bar{\mu}'_\nu) = \sum_{\beta=1}^{\nu=1} R_{\alpha\beta}\, \underset{\sim}{j}_\beta \tag{2.44}$$

with the resistance coefficient

$$R_{\alpha\beta} = |\Omega|_{\alpha\beta}/|\Omega| \;, \qquad \alpha,\beta=1,\ldots,\nu-1 \;, \tag{2.45}$$

where $|\Omega|$ is the determinant of only those phenomenological coefficients which appear in (2.43) and $|\Omega|_{\alpha\beta}$ is the appropriate cofactor. If the matrix of $\Omega_{\alpha\beta}$ is symmetric, then the matrix of $R_{\alpha\beta}$ is also symmetric.

The friction coefficient description of Bearman and Kirkwood (1958) and Bearman (1959) is equivalent to this resistance coefficient formulation.

The expression for the chemical potential gradient, which appears in (2.40), (2.43) and (2.44) has the form (Horne, 1966)

$$M_\alpha \underset{\sim}{\nabla} \bar{\mu}'_\alpha = \underset{\sim}{\nabla} \bar{\mu}'_\alpha = v^\infty_\alpha \underset{\sim}{\nabla} p + RT \underset{\sim}{\nabla} \ell n a_\alpha + M_\alpha \underset{\sim}{\nabla} \Gamma + z_\alpha F \underset{\sim}{\nabla} \phi \; . \qquad (2.46)$$

The Gibbs-Duhem equation including the external forces can be expressed as

$$\underset{\sim}{\nabla} p - \rho \underset{\sim}{\bar{X}} = \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{\nabla} \bar{\mu}'_\alpha \; . \qquad (2.47)$$

In (2.46), v^∞_α is the partial molar volume at infinite dilution and is related to the partial molar volume of component α by

$$v^\infty_\alpha = \lim_{x_1 \to 1} v_\alpha \; , \qquad (2.48)$$

this implies the equality of v^∞_α and v_α at thermodynamic ideality.

Due to the arbitrariness of choosing the fluxes and forces in (2.38), one can define the fluxes and forces differently in order to suit particular purposes. Scattergood and Lightfoot (1965, 1968) and Lightfoot (1974) have chosen, instead of all the diffusional fluxes summed to zero, all the forces summed to zero. They end up with a set of Stefan-Maxwell equations and a set of Stefan-Maxwell diffusivities show a smaller composition dependence than the usual phenomenological coefficients and they reduce to the more familiar Fickian diffusion coefficient for ideal binary solutions. For the purpose of this Thesis we use only the conventional linear phenomenological equations (2.43) and (2.44). In fact it can be shown that the Stefan-Maxwell equations are equivalent to (2.44).

For more general discussion about the physical implication of various phenomenological coefficients, see Fitts (1962), de Groot and Mazur (1962), Haase (1969), Horne (1966) and Lightfoot (1974).

CHAPTER III

CONTINUOUS AND DISCONTINUOUS APPROACHES OF MEMBRANE TRANSPORT PROCESS

A. Introduction

The system used in most passive membrane transport experiments consists essentially of two large reservoirs (regions I & II) containing an isotropic, ν component solution, connected by a small capillary, porous wall or another homogeneous phase as a membrane (region III). In general the reservoirs may differ in pressure, solute concentration and electrical potential (we consider only isothermal systems in this thesis). The membrane may be itself charged or uncharged. However, no chemical reactions occur in the three regions.

There are two types of treatment of passive membrane transport processes. If one considers the region III as so small that it can be almost disregarded, then in passing from region I to II the state variables (or the thermodynamic properties) suffer discontinuous jumps and the system is usually referred to as a <u>discontinuous system</u>. In this case the membrane is treated as a black box, and no detailed knowledge of the structure or function is required. All flows and driving forces refer to regions I and II, while the membrane merely appears as a barrier which sustains finite differences in pressure, concentration and electrical potential. The transport equations are in finite difference form, and the phenomenological coefficients appearing in them can be used to characterize the membrane.

In some cases it is possible to analyze the flow inside the membrane in terms of the differential transport equation obtained in Chapter II where the state variables (or thermodynamic properties) are continuous functions of space coordinates and of time. This is usually referred to as a continuous system. In order to be applicable experimentally, the differential transport equations for the continuous system have to be integrated across the membrane for some model membrane structure. The final working equations are expressed in terms of the differences in state variables (or thermodynamic properties) of regions I and II. These are the same as those for the discontinuous systems. However, by going from a continuous to a discontinuous formulation, one can obtain an explicit knowledge of the empirical phenomenological coefficients in terms of more fundamental properties of the solution and the membrane, such as diffusion coefficients, viscosity coefficient, charge density, pore radius, concentration, dielectric constant, etc. More importantly, one can also gain a better understanding of the mechanism of various membrane processes. This point will be emphasized in the next few chapters.

There are generally three classes of membranes. de Groot and Mazur (1962) distinguish only two classes, while Mears, et al. (1967) classify four types. However, three classes are enough for the present purpose: (a) Macroporous membranes--relatively large capillaries or pores compared to the mean free path of the molecules (say greater than 25°A radius). Species are transported through these pores primarily by convective flow. (b) Microporous membranes--the dimension of the pores is smaller than the mean free path of the molecules (very small pores). Species are transported through these pores by convection as well as by diffusion. (c) Homogeneous membranes--a separate homogeneous phase, sometimes considered as a solvent through which permeants are transported by diffusion. In cases (a) and (c), the fluid may be treated as a continuum and the flow in the membrane may be described by local macroscopic transport equations. From these the phenomenological equations describing transport between regions I and II as a discontinuous system can be derived by integration with the inclusion of appropriate boundary conditions at the membrane/solution interfaces. Relevant boundary conditions include equilibrium distribution coefficients and pressure and concentration discontinuities. These boundary conditions are generally due to membrane structural and chemical factors and cannot be accounted for by an inert continuous membrane model which is open to both the solute and solvent (e.g., one dimensional models or capillary models). Many authors (Kobatake and Fujita, 1964; Gross and Osterle, 1968; Fair and Osterle, 1971; Chen, 1971) have attempted to derive discontinuous membrane equations from continuous local transport equations. However, they fail to include these structural boundary conditions, which give rise to the ordinary osmotic phenomenon.

In case (b), the mean free path of the molecules is larger than the pore dimension, and the collisions between fluid molecules and bounding surfaces become more important. There are fewer molecules in the flow cross section, and the continuum description of the transport becomes less precise. It seems reasonable to suppose that, even then, the continuum description should retain some validity in a statistical sense. In fact, Levitt (1973), who has done molecular dynamics calculations on kinetics of diffusions and convection in small pores, has shown that the continuum hydrodynamic theory can be extrapolated, at least qualitatively, to pores 3.2 Å in radius! Therefore, the discontinuous membrane equation can still be obtained from local transport equations although they have to be used with caution for membranes of class (b).

In the following sections, we illustrate the mechanism of ordinary osmosis and the boundary conditions that describe this. We then discuss transport equations and reference frames for these three different types of membrane. We also derive the discontinuous membrane transport equations from the local equations and compare them with the widely used Kedem-Katchalsky formulation.

B. Mechanism of Ordinary Osmosis

The passage of water through semi-permeable porous membranes is of great interest in many fields. Two mechanisms of osmotic flow have been considered. These are (1) diffusion of solvent down a gradient of chemical potential and (2) bulk flow through pores under a hydrostatic pressure gradient.

Discussions of semi-permeability have usually been concerned with non-ionic solutes whose molecules are sufficiently large to be excluded from the pores by mechanical sieving. Two kinds of experiments are common: (i) experiments with an osmotically induced volume flow and (ii) self-diffusion experiments with isotopically labelled water. Some conceptual difficulties have resulted from the following experimental observations: (a) A hydrostatic pressure difference and an equal osmotic pressure difference produce the same flow through a semi-permeable membrane (Mauro, 1957, 1960). (b) The volume flow produced by a difference in total chemical potential may differ from (and can be much greater than) the self-diffusive transfer produced by an equal potential difference arising from an isotopic concentration difference (Durbin, Frank and Solomon, 1956).

Chinard (1952) gave a careful and detailed account of the case in favor of diffusion as the main mechanism of solvent transport. This is consistent with the homogeneous membrane discussed in the last section, which is capable of water transport due to the chemical potential gradient. However, Chinard's viewpoint cannot explain the result (b) above observed for porous membranes. On the other hand, the result (b) is consistent with the viewpoint (Pappenheimer, 1953; Koefoed-Johnson and Ussing, 1953) that osmotic transfer takes the form of a pressure induced bulk flow.

A thorough, but less fundamental comparison of the two theories as applied to plant membranes has been given by Ray (1960) and later on improved by Dianty (1963). However, they all consider rapid water diffusion at the pore exit. This notion of joint diffusion-viscous flow has been criticized by Philip (1969).

It is not obvious how the concentration difference across a semi-permeable porous membrane could induce bulk flow when there is no measurable pressure difference across it. However, there is ample experimental evidence that this is so, and the mechanism of the phenomenon has been proposed by Mauro (1957, 1960), who acknowledged his debt to Onsager and by Longsworth (1960), who acknowledged his debt to Kirkwood.

Thermodynamically, the total chemical potential across a semi-permeable membrane separating pure water and a solution at the same hydrostatic pressure also at steady state, and in the absence of external fields must vary continuously across the membrane (Fig. 3.1). At each point in the pore the total chemical potential contains contributions due to the water concentration (or activity) and the hydrostatic pressure. If the mechanism of semi-permeability is the total exclusion of solute from the pores of the membrane, the steep change (or discontinuity) of the water concentration in the interfacial layer at the pore opening between the pure water phase and the solution phase must be accompanied by a steep change in the hydrostatic pressure. The pressure change in the interfacial layer is sustained by the interface. The pressure change along the pore will cause a flow of water through it; i.e., the osmotic flow. Hence, an osmotic pressure difference (or concentration difference) across the semi-permeable membrane produces water flow by exactly the same kind of mechanism as a hydrostatic pressure difference.

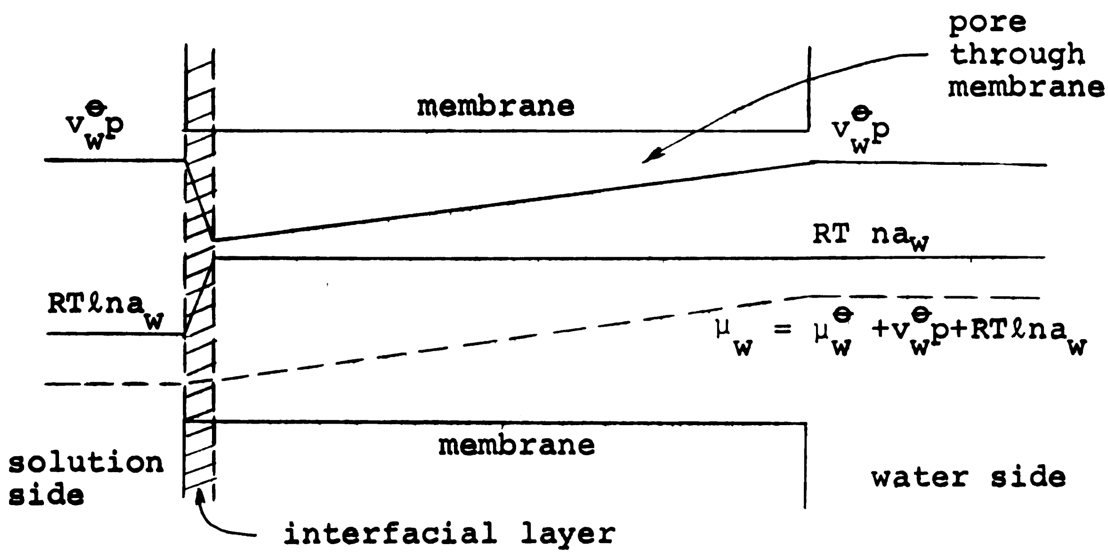


Fig. 3.1--Pressure and concentration profiles in a semi-permeable membrane at steady state

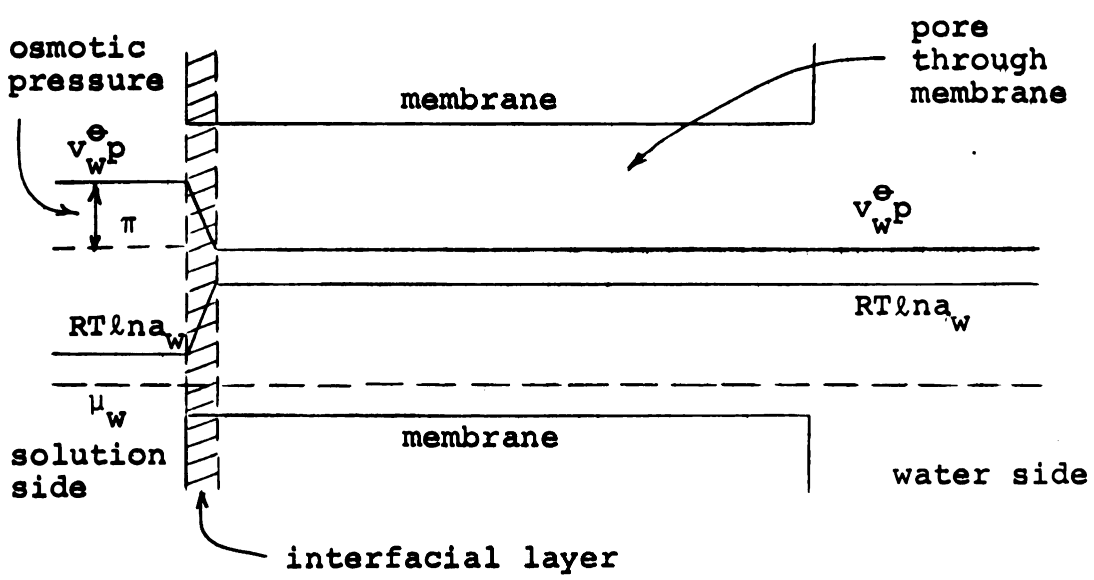


Fig. 3.2--Pressure and concentration profiles in a semi-permeable membrane at osmotic equilibrium

Molecularly, the total reflection of the solute molecules and the partial transmission of the solvent molecules at the membrane/solution interface causes an asymmetry in the momentum transfer by the thermal motions of the molecules. Since the average momentum transfer is prescribed by the hydrostatic pressure of the phase, the asymmetry (or deficiency) in momentum due to the finite size of the pore gives rise to a sharp change in the pressure sustained by the interface in the interfacial layer and a pressure gradient within the pore. Since the pore is filled with water this pressure gradient inside it causes a flow in exactly the same way as a directly applied hydrostatic pressure gradient.

In the self-diffusion of water through porous membranes no asymmetry in momentum transfer accompanies the gradient of labelled water, therefore no bulk flow occurs. This is the explanation of the result (b) mentioned in this section.

The pressure and concentration profiles in a semipermeable membrane at osmotic equilibrium are shown in Fig. 3.2. In comparison with the profiles for steady-state osmotic flow in Fig. 3.1. We see that the sharp changes in pressure and concentration in the interfacial layer between the pure water phase and the solution phase are always sustained by the interface, and it is only the gradient of pressure or concentration inside the pore that gets equilibrated. It must be emphasized that the interfacial layer, across which the sharp changes of pressure and concentration occur, is not a diffusion layer which could be removed by effective stirring; its thickness is determined by the membrane pore and surface structure and by the dimensions and mean free path of the molecules.

It is now widely accepted that osmotic flow of water through a membrane which contains pores is a pressure induced bulk flow. The mechanism given here can be generalized to membranes which separate solutions of different concentrations and to cases of incomplete solute exclusion. Renkin (1954) has considered the case of incomplete solute exclusion and has calculated the permeability of pores to molecules of various sizes. By using this treatment and assuming that flow in the pores could be described by Poiseville's law, Durbin, Frank and Solomon (1956) have shown that the study of the permeation of non-ionic solutes of graded sizes in molecular diameters permits an estimation of effective total area and radii of the pores in a membrane. For membranes with adsorption of solute and solvent in the pores, the adsorption force field affects the steady state pressure distribution during osmosis because the adsorption force also contributes to the total chemical potential (Banin and Low, 1971). In the case of charged porous membranes, ordinary osmosis is still effective, but additional phenomena due to the charge occur simultaneously. This is discussed in detail in the next chapter. For more detailed discussion of the mechanism of ordinary osmosis see Mauro (1957, 1960), Longsworth (1960), Mears (1966) and Philip (1969).

C. Mechanical Restraints and Reference Frames

In the nonequilibrium thermodynamic study of transport processes in free solution, the local center of mass is the usual reference frame for diffusional flows (de Groot and Mazur, 1962). Other available reference frames are the local center of volume or any of the individual components of the system, particularly the solvent. In membrane transport, the most convenient reference frame, both experimentally and theoretically is the one fixed on the membrane itself because the membrane does not move. Therefore it is advantageous to transform the reference frame from the local center of mass, upon which almost all the transport equations are based, to the membrane framework. In doing so, it is necessary to ascertain whether or not such changes of reference frame preserve Onsager Reciprocal Relations in the local phenomenological equations. Coleman and Truesdell (1960) have shown that the transformations of fluxes and forces have to follow certain transformational properties in order to preserve the reciprocal relations. Kirkwood, et al. (1960) gave a detailed discussion on the importance of reference frames in testing the Onsager Reciprocal Relations for isothermal diffusion in liquids. We demonstrate in the next section the effect of changing reference frames on the Onsager Reciprocal Relations in a membrane transport system. For the time being we consider the effect of mechanical restraints and reference frames on the total entropy production and the phenomenological equations.

It is a common practice, without justification, to consider the membrane system to be in a state of mechanical equilibrium (Katchalsky and Curran, 1965; Hanley, 1967, 1969) such that, according to Prigogine's theorem (Prigogine, 1955), in the entropy production ϕ_2 of Eq. (2.38) the barycentric velocity $\underset{\sim}{u}$ occurring in the definition of the diffusion flux $\underset{\sim}{j}_\alpha$ can be replaced arbitrarily by another velocity. In this case the membrane velocity is a natural choice because it is essentially zero. According to de Groot and Mazur (1962), the mechanical equilibrium state is the state in which both the acceleration $d\underset{\sim}{u}/dt$ and the velocity gradient $\underset{\sim}{\nabla}\underset{\sim}{u}$ vanish and therefore also the stress tensor may be neglected. Bartelt and

Horne (1970) derive necessary and sufficient conditions for mechanical equilibrium. At mechanical equilibrium, the Navier-Stokes equation (2.16) has the form

$$\rho \underset{\sim}{\overline{X}} - \underset{\sim}{\nabla} p = 0 \ . \tag{3.1}$$

The Gibbs-Duhem equation (2.47), for the mechanical equilibrium state, becomes

$$\sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{\nabla} \overline{\mu}'_\alpha = 0 \ . \tag{3.2}$$

Based on (3.2), Prigogine's theorem follows immediately from (2.38):

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \cdot \underset{\sim}{\nabla} \overline{\mu}'_\alpha \tag{2.38}$$

$$= - \sum_{\alpha=1}^{\nu} \rho_\alpha (\underset{\sim}{u}_\alpha - \underset{\sim}{u}) \cdot \underset{\sim}{\nabla} \overline{\mu}'_\alpha$$

$$= - \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{u}_\alpha \cdot \underset{\sim}{\nabla} \overline{\mu}'_\alpha + \underset{\sim}{u} \cdot \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{\nabla} \overline{\mu}'_\alpha$$

$$= - \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{u}_\alpha \cdot \underset{\sim}{\nabla} \overline{\mu}'_\alpha + \underset{\sim}{u}^a \cdot \sum_{\alpha=1}^{\nu} \rho_\alpha \underset{\sim}{\nabla} \overline{\mu}'$$

$$= - \sum_{\alpha=1}^{\nu} \rho_\alpha (\underset{\sim}{u}_\alpha - \underset{\sim}{u}^a) \cdot \underset{\sim}{\nabla} \overline{\mu}'_\alpha \tag{3.3}$$

where $\underset{\sim}{u}^a$ is an arbitrary reference velocity. When the membrane is taken as the reference frame, $\underset{\sim}{u}^2 = \underset{\sim}{u}_m = 0$ with $\underset{\sim}{u}_m$ the membrane component velocity. Eq. (3.3) reduces to

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{J}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}'_\alpha \ , \tag{3.4}$$

where $\quad \underset{\sim}{J}_\alpha = \rho_\alpha \underset{\sim}{u}_\alpha \ .$ (3.5)

Eq. (3.4) and its integrated form are used in a large number of membrane transport literatures (see, for example Katchalsky and Curran, 1965) without questioning the validity of the mechanical equilibrium assumption. Generally, in macroporous membranes (class a) and sometimes in microporous membranes (class b) where viscous flow dominates, mechanical equilibrium does not hold. In order to demonstrate this, we distinguish between the cases when the membrane can be taken as a component and when it cannot be.

Mikulecky and Caplan (1966) and Mikulecky (1969) have considered the membrane as a component for macroporous membranes, but the entropy production they obtained for the membrane system is the same as the one which excludes the membrane as a component. This is because they make the trivial assumption that the partial mass density of the membrane, ρ_m , is zero.

Besides, although they intended to derive the entropy production for stationary situations in which mechanical equilibrium does not necessarily hold, they implicitly adopt the requirement of mechanical equilibrium (see their equations (5) and (6)). Therefore the validity of their final results is questionable. Hanley (1967, 1969) later discussed the cases in which the membrane may or may not be taken as a component. He also reconciled the continuous and discontinuous approach for the case that the membrane is treated as a component. However, he and most other authors have failed to recognize that in either case the membrane component is fixed in space by an external constraint which is generally not accounted for in the transport equations.

More than a decade ago, in dealing with diffusion in porous media, Vink (1961) and Evans, Watson and Mason (1962) simultaneously, but independently, introduced the idea of an external constraint on the lattice component of the porous media. The external constraint acts only on the lattice and arises simply from whatever clamping system the experimenter uses to keep his porous diaphragm from being moved along just like any other diffusing species. This is described mathematically as if a separate body force acted on each constituent of the lattice to keep it stationary. Aranow (1963), Scattergood and

Lightfoot (1968) and Lightfoot (1974) later applied this to membrane transport systems.

Based on this we shall derive, from the equation of motion for each component, criteria for the applicability of mechanical equilibrium.

(i) Membrane as A Separate Phase

Membrane and solution are considered as separate phases. This is suitable for macroporous membranes (class a) and with some reservation for microporous membranes (class b). The membrane merely behaves as a stationary boundary and the entropy production occurs only in the fluid phase. This system allows viscous bulk flow.

For stationary incompressible fluid and slow flow, the component equation of motion (in this case the Stokes equation) can be obtained from (2.18). For simplicity we assume the membrane is uncharged and the gravitational force can be neglected. Of course it is still isothermal.

Membrane phase:

The equation of motion is

$$\eta_m \nabla^2 \underset{\sim}{u}_m - c_m \underset{\sim}{\nabla} \mu_m + c_m \underset{\sim}{F}^*_m + c_m \underset{\sim}{X}_m = 0 \ , \qquad (3.6)$$

where the subscript m stands for the membrane.

The body force exerted by the clamping support on the membrane is transmitted to the membrane matrix and can be considered as uniformly distributed. We may then write this body force locally (Lightfoot, 1974)

$$\underset{\sim}{X}_m = c_m^{-1} \underset{\sim}{\nabla} p \, . \tag{3.7}$$

Also Gibbs-Duhem equation gives

$$c_m \underset{\sim}{\nabla} \mu_m = \underset{\sim}{\nabla} p \, . \tag{3.8}$$

Since this phase only has one component, the total frictional and thermal force $\underset{\sim}{F}_m^* = 0$. Therefore (3.6) reduces to

$$\eta_m \nabla^2 \underset{\sim}{u}_m = 0 \, . \tag{3.9}$$

By the requirement of no acceleration across the membrane and the physical boundary condition of no movement, the solution of (3.9) is simply

$$\underset{\sim}{u}_m = 0 \, . \tag{3.10}$$

For this membrane phase alone, (3.7) fulfills the requirement of mechanical equilibrium (3.1).

<u>Solution phase</u>:

The equation of motion for each species is

$$\eta_\alpha \nabla^2 \underset{\sim}{u} - c_\alpha \underset{\sim}{\nabla} \mu_\alpha + c_\alpha \underset{\sim}{F}_\alpha^* + c_\alpha \underset{\sim}{X}_\alpha = 0 \, , \; \alpha = 1, \ldots, \nu \, . \tag{3.11}$$

Summing over all components and using the previously obtained relations

$$\eta = \sum_{\alpha=1}^{\nu} \eta_\alpha$$

$$\sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{F}_\alpha^* = 0$$

$$\sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{\nabla} \mu_\alpha = \underset{\sim}{\nabla} p \ , \tag{2.19}$$

we obtain

$$\eta \nabla^2 \underset{\sim}{u} - \underset{\sim}{\nabla} p + \sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{X}_\alpha = 0 \ . \tag{3.12}$$

Therefore, unless the external forces exactly balance the pressure gradient, mechanical equilibrium generally does not exist due to the presence of appreciable viscous flow and velocity gradients. In the case of no external forces, mechanical equilibrium is impossible in the solution phase with the presence of pressure gradient. This has a very important bearing on the entropy production.

For the system as a whole, the entropy production occurs only in the solution phase. Due to the general nonexistence of mechanical equilibrium in the solution phase, Prigogine's theorem cannot be applied. The entropy production for this membrane system is given by (2.38)

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{j}_\alpha \cdot \underset{\sim}{\nabla}\overline{\mu}'_\alpha \tag{2.38}$$

where the diffusion flux $\underset{\sim}{j}_\alpha$ is still referred to the barycentric velocity. Since at steady state only $\underset{\sim}{J}_\alpha = \rho_\alpha \underset{\sim}{u}_\alpha$ is constant, the integration of (2.38) over the membrane volume is not so easy as the integration of (3.4). This is discussed in more detail in the reconcilation of the continuous and discontinuous approaches in the next section.

<u>(ii) Membrane as A Component</u>

Membrane and solution are considered as a homogeneous phase. This is suitable for homogeneous membranes (class c) and for some very fine microporous membranes (class b). The membrane component is interspersed among the components of the permeating fluid in the molecular level. The system approximates a thermodynamic mixture or solution, and the entropy production occurs in this single phase. This is essentially a diffusion system and contains no mechanism for viscous flow other than a simple diffusion mechanism.

The equation of motion for the membrane component is the same as (3.6)

$$\eta_m \nabla^2 \underset{\sim}{u} - c_m \underset{\sim}{\nabla} \mu_m + c_m \underset{\sim}{F}^*_m + c_m \underset{\sim}{X}_m = 0 \ . \tag{3.6}$$

Again, we assume an uncharged membrane and neglect the gravitational force for simplicity. Since the membrane component partakes in the transport processes by frictional and other interactions, the body force on the membrane component is still

$$\underset{\sim}{X}_m = (1/c_m)\underset{\sim}{\nabla} p \ . \tag{3.7}$$

The equation of motion for the solution is the same as (3.11)

$$\eta_\alpha \nabla^2 \underset{\sim}{u} - c_\alpha \underset{\sim}{\nabla} \mu_\alpha + c_\alpha \underset{\sim}{F}^*_\alpha + c_\alpha \underset{\sim}{X}_\alpha = 0 \ , \quad \alpha=1,\ldots,\nu \ . \tag{3.11}$$

where $\underset{\sim}{X}_\alpha$, in this case, contains only the electrical force.

Summing over all components including the membrane component and using (2.19), we obtain

$$\eta \nabla^2 \underset{\sim}{u} = 0 \ , \tag{3.14}$$

where we use the relation $\sum_{\alpha=1}^{\nu} c_\alpha \underset{\sim}{X}_\alpha = 0$ for electroneutrality of the whole system.

By the requirement of no acceleration across the membrane, the solution of (3.14) is

$$\underset{\sim}{u} = \text{constant} \ , \tag{3.15}$$

in agreement with the outcome of the diffusion mechanism. Eq. (3.14) implies the validity of (3.1) for this homogeneous membrane-solution phase, hence the mechanical equilibrium requirement is fulfilled.

The entropy production for this system reduces to one similar to (3.4) due to the mechanical equilibrium condition

$$\phi_2 = - \sum_{\alpha=1}^{\nu,m} \underset{\sim}{J}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}'_\alpha \ , \qquad (3.16)$$

where the membrane component is also included. However, the membrane component is fixed in space by the external mechanical restraint, and $\underset{\sim}{u}_m = 0$. This implies $\underset{\sim}{J}_m = \rho_m \underset{\sim}{u}_m = 0$, and eq. (3.16) reduces to

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{J}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}'_\alpha \ . \qquad (3.4)$$

It has to be emphasized here that although the membrane component also contributes to the entropy production through frictional and other interactions with the solution components, it does not appear in the final entropy production equation due to the mechanical equilibrium condition. At steady state, $\underset{\sim}{J}_{\alpha} = \rho_{\alpha}\underset{\sim}{u}_{\alpha}$ is constant by the continuity equation. The integration of (3.4) across the membrane gives the form of the entropy production which is widely used in discontinuous membrane transport theory. However, the previous analysis indicates that it is strictly applicable in homogeneous membranes. For very fine microporous membranes, it can only be used as a good approximation.

D. Reconciliation of Continuous and Discontinuous Treatments--Comments on Kedem-Katchalsky Theory

More than a decade ago Kedem and Katchalsky (1958, 1961) derived the "practical" integrated flow equations for describing solute and water transport across uncharged membranes from nonequilibrium thermodynamic considerations. These equations have since become very popular alongside the Nernst-Planck equation and the Goldman equation as standard working models for physiologists and biophysicists. Nevertheless, there remain several aspects of the Kedem-Katchalsky equations which are a source of confusion and should be clarified. In particular, it is necessary to point out: (a) These equations are one dimensional and are strictly applicable only to homogeneous membranes with thermodynamically ideal binary solutions; (b) For porous membranes, the Kedem-Katchalsky equations can be used only when the barycentric velocity is linearly related to the external forces; and (c) The reciprocal relation in Kedem-Katchalsky's theory is strictly valid only when the system is thermodynamically ideal and the partial molar volumes of solute and solvent are equal. For a porous membrane in a binary solution, the reciprocity of the local coefficients is the natural outcome of the dependence of fluxes and cannot be tested by independent experiments.

First, we outline Kedem-Katchalsky theory briefly. They started from the entropy production

$$\phi_2 = - \sum_{\alpha=1}^{\nu} \underset{\sim}{N}_\alpha \cdot \underset{\sim}{\nabla}\mu'_\alpha \tag{3.17}$$

which is essentially the same as (3.4), since

$$\underset{\sim}{N}_\alpha \cdot \underset{\sim}{\nabla}\mu'_\alpha = c_\alpha u_\alpha \cdot \underset{\sim}{\nabla}\mu'_\alpha = \rho_\alpha \underset{\sim}{u}_\alpha \cdot 1/M_\alpha \underset{\sim}{\nabla}\mu'_\alpha$$

$$= \underset{\sim}{J}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}' \ .$$

At steady state, (2.4) gives

$$\underset{\sim}{\nabla} \cdot \underset{\sim}{N}_\alpha = 0 \ ,$$

or, for the one dimensional case considered here,

$$N_\alpha = \text{constant} \tag{3.18}$$

at any point in the system. Integrating (3.17) across the membrane from surface A to surface B and evaluating the entropy production per unit area of the membrane as a whole, we obtain

$$\bar{\phi}_2 = \int_A^B \phi_2 dx = - \sum_{\alpha=1}^{\nu} N_\alpha (\mu'^B_\alpha - \mu'^A_\alpha)$$

or $$\bar{\phi}_2 = \sum_{\alpha=1}^{\nu} N_\alpha \Delta\mu'_\alpha \ , \tag{3.19}$$

where the x component of $\underset{\sim}{N}_\alpha$ is denoted by $\underset{\sim}{N}_\alpha$ and x is the direction of flow across the membrane.

This rearranges, for a binary nonelectrolyte solution, to

$$\bar{\phi}_2 = \sum_{\alpha=1}^{2} N_\alpha \Delta\mu'_\alpha = J_V \Delta p + J_D \Delta\pi \tag{3.20}$$

where 1 stands for the solvent and 2 for the solute, and where the total volume flow J_v and the exchange flow J_d are defined by

$$J_V = v_1 N_1 + v_2 N_2 \tag{3.21}$$

$$J_D = (N_2/\overline{c}_2) - (N_1/\overline{c}_1) \ . \tag{3.22}$$

The quantities v_1 and v_2 are partial molar volumes in the external phase and

$$\overline{c}_\alpha = (c_\alpha^A - c_\alpha^B)/\ell n \ (c_\alpha^A/c_\alpha^B) \ , \quad \alpha=0,1 \ . \tag{3.23}$$

In (3.20), Δp is the change in pressure and $\Delta\pi$ is the change in osmotic pressure across the membrane, where

$$\Delta\pi = RT \ (c_2^A - c_2^B) = RT\Delta c_2 \ . \tag{3.24}$$

The phenomenological equations are

$$J_V = L_p \Delta p + L_{pD} \ \Delta\pi$$

$$J_D = L_{Dp} \Delta p + L_D \ \Delta\pi \tag{3.25}$$

with

$$L_{pD} = L_{Dp} \ ,$$

where the L's are phenomenological coefficients. Two other transport coefficients defined from these four phenomenological coefficients have appears in membrane transport literature frequently. These are the reflection coefficient $\bar{\sigma}$ introduced by Staverman (1952) and defined by

$$\bar{\sigma} = - L_{pD}/L_p \tag{3.27}$$

and the solute permeability coefficient ω defined by

$$\omega = (L_D - \bar{\sigma}^2 L_p)\ \bar{c}_2 \ . \tag{3.28}$$

The set of coefficients L_p, $\bar{\sigma}$ and ω is more convenient for description of membrane systems than the set L_p, L_{pD} and L_D, because the former set of coefficients can more easily be related to the transport characteristics of greatest interest:

(1) L_p measures the mechanical filtration capacity or the hydraulic permeability of the membrane.

(ii) The reflection coefficient $\bar{\sigma}$ can be considered as a measure of the membrane permselectivity. When $\bar{\sigma}=1$ all the solute is "reflected" from the membrane; this is a semipermeable membrane. $\bar{\sigma}<1$ means that part of the solute penetrates, and we therefore have a leaky membrane. It is also possible that $\bar{\sigma}<0$, which would mean that the transfer of the solute is more rapid than that of the solvent. Such cases are known and are called negative anomalous osmosis.

(iii) ω can be considered as a measure of the membrane diffusional permeability for the solute.

Next, we demonstrate the remarks made at the beginning of this section. In order to compare with Kedem-Katchalsky's "practical" flow equations, we start from the local entropy production and the local phenomenological equations for which the reciprocity of the Onsager coefficients has been established. Integration of the local phenomenological equations then has the advantage of tracing the reciprocity to compare with Kedem-Katchalsky's lumped phenomenological coefficients.

We consider isotropic, non-reacting aqueous solutions of single nonelectrolytes at different concentrations, separated by a rigid simple membrane which acts as a permeability barrier for the solute molecules. We also assume that each compartment is well stirred and the unstirred layer effect is minimized and can be neglected. There are pressure and concentration gradients maintained across the rigid membrane. Furthermore, the whole system is isothermal and subject to no external forces. The basic transport equations are those described in previous chapters.

For <u>homogeneous membranes</u>, it is easy, according to the last section, to write down the local entropy production

$$\phi_2 = - \sum_{\alpha=1}^{2} \underset{\sim}{J}_2 \cdot \underset{\sim}{\nabla}\overline{\mu}' = - \sum_{\alpha=1}^{2} \underset{\sim}{N}_\alpha \cdot \underset{\sim}{\nabla}\mu_\alpha'$$

and the phenomenological equations

$$- \underset{\sim}{N}_1 = L'_{11} \underset{\sim}{\nabla}\mu'_1 + L'_{12} \underset{\sim}{\nabla}\mu'_2$$

$$- \underset{\sim}{N}_2 = L'_{21} \underset{\sim}{\nabla}\mu'_1 + L'_{22} \underset{\sim}{\nabla}\mu'_2 \ . \qquad (3.29)$$

Since the fluxes are independent of each other and the gradients are independent of each other, the Onsager Reciprocal Relation (Onsager, 1931) can be assumed for the phenomenological coefficients

$$L'_{12} = L'_{21} \ . \qquad (3.30)$$

In the case of <u>porous membranes</u>, the analysis in the last section shows that the local entropy production takes the form

$$\phi_2 = - \sum_{\alpha=1}^{2} \underset{\sim}{j}_\alpha \cdot \underset{\sim}{\nabla}\bar{\mu}'_\alpha$$

and the phenomenological equation can be written according to the usual procedures of nonequilibrium thermodynamics,

$$- \underset{\sim}{j}_1 = \Omega_{11} \underset{\sim}{\nabla}\bar{\mu}_1 + \Omega_{12} \underset{\sim}{\nabla}\bar{\mu}'_2$$

$$- \underset{\sim}{j}_2 = \Omega_{21} \underset{\sim}{\nabla}\bar{\mu}'_1 + \Omega_{22} \underset{\sim}{\nabla}\bar{\mu}'_2 \ . \qquad (3.31)$$

If the fluxes were independent of each other and if the gradients were independent of each other, then the next step would be to assume the Onsager Reciprocal Relation

$$\Omega_{12} = \Omega_{21} \ . \qquad (3.32)$$

However, the fluxes are not independent since, by (2.7),

$$\underset{\sim}{j}_1 + \underset{\sim}{j}_2 = 0 \; . \tag{3.33}$$

Thus, by (3.31)

$$\Omega_{11} + \Omega_{21} = 0 = \Omega_{12} + \Omega_{22} \; . \tag{3.34}$$

Moreover, Bartelt and Horne (1969) showed that the positive definiteness of ϕ_2 (i.e., the Second Law of Thermodynamics) requires for fluxes obeying (3.33)

$$\Omega_{11} + \Omega_{12} = 0 = \Omega_{21} + \Omega_{22} \; . \tag{3.35}$$

Consequently,

$$\Omega_{11} = - \Omega_{12} = - \Omega_{21} = \Omega_{22} \; . \tag{3.36}$$

Hence, the validity of (3.32) in this case is due to the dependence of the fluxes and to the Second Law; it need not be taken as an extra assumption and it cannot be tested by independent experiments. By (3.31), (3.33) and (3.36), the only independent diffusion flux equation is

$$- \underset{\sim}{j}_1 = \Omega_{11} \, \underset{\sim}{\nabla}(\overline{\mu}_1' - \overline{\mu}_2') \; . \tag{3.37}$$

This formula could also have been obtained directly from the correct entropy production formula

$$\phi_2 = - \underset{\sim}{j}_1 \cdot \underset{\sim}{\nabla}(\overline{\mu}_1' - \overline{\mu}_2') \; , \tag{3.38}$$

which results from substitution of (3.33) into the entropy productions equations. However, (3.35) is required to show that the Ω_{11} resulting from (3.38) is identiçal to the one of (3.31). Note that (3.36) allows us to use either (3.31) or (3.37). Although (3.31) is the usual choice, it must be remembered that only one diffusion process occurs in a binary isothermal system.

In order to generalize the treatment to include both homogeneous and porous membranes, we rearrange (3.31) into the form of (3.29). From (2.6) and (2.8),

$$\underset{\sim}{N}_\alpha = (\underset{\sim}{j}_\alpha / M_\alpha) + c_\alpha \underset{\sim}{u} \qquad \alpha=1,2 \; . \tag{3.39}$$

It is important to note that N_α depends explicitly upon the reference velocity $\underset{\sim}{u}$ and therefore is not, a priori, a diffusion flux for which an Onsager equation can be written.

By (3.31) and (3.39),

$$- \underset{\sim}{N}_\alpha = \sum_{\beta=1}^{2} (\Omega_{\alpha\beta}/M_\alpha M_\beta) \; \underset{\sim}{\nabla} \mu'_\beta - c_\alpha \underset{\sim}{u} \; , \quad \alpha=1,2 \; . \tag{3.40}$$

The x component of (3.40) is

$$- N_\alpha = \sum_{\beta=1}^{2} (\Omega_{\alpha\beta}/M_\alpha M_\beta)(\partial \mu'_\beta / \partial x) - c_\alpha u_x \; , \quad \alpha=1,2 \; . \tag{3.41}$$

where the x component of $\underset{\sim}{u}$ is denoted by u_x , and the x component of $\underset{\sim}{N}_\alpha$ is denoted by N_α . The x component of the barycentric velocity u for this porous membrane system can be obtained by solving the Navier-Stokes equation provided that suitable geometry and boundary conditions are given. For systems of slow and steady laminar flow, with no external forces, the resulting u_x generally has the form

$$u_x = \alpha(\partial p/\partial x) \tag{3.42}$$

where α is usually a function of the viscosity of the solution in the membrane and of the geometry of a cross-section of the passages through the membrane. However, in some cases, the short range surface crystalline forces in the membrane lattice.can cause a considerable nonlinear behavior of u_x at low pressure gradient range (Klausner and Kraft, 1965, 1966). When this nonlinear behavior of u_x occurs, the reciprocal relation in Kedem-Katchalsky theory is definitely not valid. For the time being we continue the treatment for the case that u_x is a linear function of the pressure gradient. When a capillary model is assumed for the porous membrane and (2.22) is used,

$$\alpha = -\ (4\eta)^{-1}\ (a^2 - r^2) \tag{3.43}$$

where a is the capillary radius and r is the radial coordinate.

Since there are no external forces, the Gibbs-Duhem equation (2.47), in molar units for one dimensional case, reduces to

$$(\partial p/\partial x) = \sum_{\beta=1}^{2} c_\beta (\partial \mu'_\beta/\partial x) \ . \tag{3.44}$$

Combination of (3.41) (3.42) and (3.44) yields

$$- N_\alpha = \sum_{\beta=1}^{2} L_{\alpha\beta} (\partial \mu'_\beta/\partial x) \qquad \alpha=1,2 \ , \tag{3.45}$$

where $L_{\alpha\beta} = (\Omega_{\alpha\beta}/M_\alpha M_\beta) + \alpha c_\alpha c_\beta \qquad \alpha,\beta=1,2 \ .$ (3.46)

Schlögl (1956) obtained equations similar to (3.45) and (3.46), but he did not pursue them further. By (3.32), we obtain from (3.46)

$$L_{12} = L_{21} \ . \tag{3.47}$$

However, the $L_{\alpha\beta}$ are not Onsager coefficients since the fluxes of (3.45) are not defined relative to an internal reference velocity. Moreover, the $L_{\alpha\beta}$ are not independent. By (3.36),

$$\begin{aligned} L_{11} &= - (M_2/M_1)\ L_{12} + \alpha(c_1\overline{M}/vM_1) \\ L_{12} &= L_{21} \\ L_{22} &= - (M_1/M_2)\ L_{12} + \alpha(c_2\overline{M}/vM_2) \end{aligned} \tag{3.48}$$

where, with mole fraction $x_\alpha = c_\alpha v$,

$$\overline{M} = x_1 M_1 + x_2 M_2 \tag{3.49}$$

$$v = x_1 v_1 + x_2 v_2 , \tag{3.50}$$

where v is the total molar volume and v_α is the partial molar volume of component α. It has to be emphasized here that the linear behavior of u_x in (3.42) leads to (3.46) and, hence, the reciprocal relation (3.47). For systems with nonlinear behavior of u_x, as mentioned before, the reciprocal relation (3.47) does not hold.

The next step is the integration of (3.45) from one side of the membrane to the other and subsequent rearrangement into a form that can be compared with the Kedem-Katchalsky theory. Since (3.45) for the porous membrane and (3.29) for the homogeneous membranes have the same form and the same reciprocal properties, the general result we obtain from (3.45) is good for both cases.

By (3.18), N_α is constant in the x-direction, and therefore

$$- N_\alpha \int_A^B dx = \sum_{\beta=1}^{2} \int_A^B L_{\alpha\beta} \, (\partial \mu'_\beta / \partial x) dx \ , \quad \alpha=1,2 \ . \tag{3.51}$$

Without knowledge of the concentration dependence of the phenomenological coefficients $L_{\alpha\beta}$, there is no way to evaluate the integrals. The goal, however, is to obtain equations for the N_α in terms of the solute concentration difference Δc_2 and the pressure difference Δp , both across the membrane; <u>i.e.</u>,

$$\Delta c_2 = c_2^A - c_2^B ; \qquad \Delta p = p^A - p^B . \tag{3.52}$$

To this end, we employ a trick due originally to Kirkwood (1954). Using Cramer's rule, we solve (3.45) for the chemical potential gradients,

$$(\partial \mu_\beta'/\partial x) = - \sum_{\alpha=1}^{2} R_{\beta\alpha} N_\alpha , \qquad \beta=1,2 , \tag{3.53}$$

with

$$R_{\beta\alpha} = |L|_{\beta\alpha}/|L| \tag{3.54}$$

where $|L|$ is the determinant of the matrix of the $L_{\alpha\beta}$ and $|L|_{\beta\alpha}$ is the appropriate minor. Unlike the corresponding matrix of the $\Omega_{\alpha\beta}$, the matrix of the $L_{\alpha\beta}$ is non-singular. By (3.48),

$$|L| = L_{11}\, L_{22} - L_{12}\, L_{21} = \alpha(\overline{M}^2/vM_1M_2)(\alpha c_1 c_2 - 1) \tag{3.55}$$

Since the N are constants, integration of (3.53) yields

$$\Delta\mu_\beta' = \sum_{\alpha=1}^{2} r_{\beta\alpha} N_\alpha , \qquad \beta=1,2 , \tag{3.56}$$

with

$$r_{\beta\alpha} = \int_A^B R_{\beta\alpha} dx , \qquad \alpha,\beta=1,2 . \tag{3.57}$$

Inversion of (3.56) yields

$$N_\alpha = \sum_{\beta=1}^{2} \ell_{\alpha\beta}\Delta\mu'_\beta \qquad \alpha=1,2 \ , \qquad (3.58)$$

$$\ell_{\alpha\beta} = |r|_{\alpha\beta}/|r| \ , \qquad \alpha,\beta=1,2 \ . \qquad (3.59)$$

Since $L_{12} = L_{21}$, $R_{12} = R_{21}$. Likewise, $r_{12} = r_{21}$ and therefore $\ell_{12} = \ell_{21}$. However, to emphasize again, this is not an Onsager Reciprocal Relation. Rather, it follows from (3.36), (3.42), and (3.48). Just as we can express all the $L_{\alpha\beta}$ in terms of L_{12} (and α), so we expect to be able to express all the ℓ_{12} in terms of ℓ_{12} (and α). Derivation of an explicit formula for the $\ell_{\alpha\beta}$ in terms of $\Omega_{\alpha\beta}$ requires detailed knowledge of the concentration dependence of $\Omega_{\alpha\beta}$. Without such knowledge, the integrals of (3.57) cannot be performed.

In order to proceed further, we write the flux equations not in terms of differences of chemical potentials, but in terms of differences of pressure and concentration. For isothermal ideal solutions the chemical potential differentials can be expressed, from (2.46), as

$$d\mu'_\alpha = v_\alpha dp + RTd\ell n x_\alpha \ , \qquad \alpha=1,2 \ . \qquad (3.60)$$

Some authors (Kedem and Katchalsky, 1958; Mason <u>et al.</u>, 1972) have used a different expression.

$$d\mu'_\alpha = v_\alpha dp + RTd\ell nc_\alpha \ , \qquad \alpha=1,2 \ ,$$

but this equation is correct only when the total molar volume v is constant. However, for membrane transport, the concentration and therefore the total molar volume changes across the membrane. Hence it is necessary to use the more general (3.60).

To convert from mole fraction to molar concentration, we use $x_\alpha = c_\alpha v$ and therefore

$$dx_\alpha = c_\alpha dv + vdc_\alpha \ . \tag{3.61}$$

For isothermal system $v = v(p,x_2)$,

$$dv = - v\beta dp + (v_2 - v_1)dx_2 \ , \tag{3.62}$$

where β is the isothermal compressibility. Solving (3.61) and (3.62) for $d\ell nx_\alpha$, we find

$$d\ell nx_\alpha = [1 - c_\alpha(v_\alpha - v_\beta)]^{-1} [d\ell nc_\alpha - \beta dp] , \qquad \alpha,\beta=1,2,\alpha\neq\beta \ . \tag{3.62a}$$

For convenience, we express (3.62a) in terms of the solute concentration c_2 , with neglect of the compressibility term,

$$d\ell nx_2 = [1 - c_2(v_2 - v_1)]^{-1} d\ell nc_2 \tag{3.63}$$

$$d\ell n x_1 = -\ (x_2/x_1)\, d\ell n x_2$$

$$= -\ (c_2/c_1)\, d\ell n x_2$$

$$= -\ v_1\ \{(1 - c_2 v_2)[1 - c_2(v_2 - v_1)]\}^{-1}\ dc_2\ , \qquad (3.64)$$

where we have used the relation

$$c_1 v_1 + c_2 v_2 = 1\ . \qquad (3.65)$$

Substitution of (3.63) and (3.64) into (3.60) yields, for the solvent,

$$d\mu_1' = v_1 dp - v_1 RT(1 - c_2 v_2)^{-1}\ [1 - c_2(v_2 - v_1)]^{-1}\ dc_2\ , \qquad (3.66)$$

and for the solute,

$$d\mu_1' = v_2 dp + RT[1 - c_2(v_2 - v_1)]^{-1}\ d\ell n c_2\ . \qquad (3.67)$$

Integrating across the membrane with v constant, we find

$$\Delta\mu_1' = v_1 \Delta p + RT\Delta\ell n\{(1 - c_2 v_2)/[1 - c_2(v_2 - v_1)]\}\ , \qquad (3.68)$$

and

$$\Delta\mu_2' = v_2 \Delta p + RT\Delta\ell n\{c_2/[1 - c_2(v_2 - v_1)]\}\ . \qquad (3.69)$$

Following Kedem and Katchalsky, we define the total volume flow

$$J_V = v_1 N_1 + v_2 N_2\ , \qquad (3.70)$$

and the exchange flow

$$J_D = (N_2/\bar{c}_2) - (N_1/\bar{c}_1) \ , \tag{3.71}$$

with the logrithmic average concentration $\bar{c}_\alpha$ defined by

$$\bar{c}_\alpha = (c_\alpha^A - c_\alpha^B)/\ell n(c_\alpha^A/c_\alpha^B) = \Delta c_\alpha/\Delta \ell nc \quad , \quad \alpha=1,2 \ , \tag{3.72}$$

which reduces to

$$\bar{c}_\alpha = (c_\alpha^A + c_\alpha^B)/2 \tag{3.73}$$

when the concentration difference is small, i.e., $(c_\alpha^A/c_\alpha^B) \sim 1$.

Substituting (3.68), (3.69) and (3.58) into (3.70) and (3.71) we obtain

$$J_V = L_p \Delta p + L_{pD} \Delta \pi \tag{3.74}$$

$$J_D = L_{Dp} \Delta p + L_D \Delta \pi \tag{3.75}$$

with

$$\Delta \pi = RT\Delta c_2 \ , \tag{3.76}$$

$$L_p = \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} \ell_{\alpha\beta} v_\alpha v_\beta \ , \tag{3.77}$$

$$L_{pD} = \left(\sum_{\alpha=1}^{2} \ell_{\alpha 1} v_\alpha\right)(\Delta c_2)^{-1} \Delta \ell n\{c_2/[1 - c_2(v_2 - v_1)]\}$$

$$+ \left(\sum_{\alpha=1}^{2} \ell_{\alpha 2} v_\alpha\right)(\Delta c_2)^{-1} \Delta \ell n\{(1-c_2 v_2)/[1-c_2(v_2-v_1)]\} , \quad (3.78)$$

$$L_{Dp} = \left(\sum_{\alpha=1}^{2} \ell_{1\beta} v_\beta\right)(\Delta c_2)^{-1} \Delta \ell n c_2$$

$$+ \left(\sum_{\alpha=1}^{2} \ell_{2\beta} v_\beta\right)(v_1/v_2)(\Delta c_2)^{-1} \Delta \ell n(1 - c_2 v_2) , \quad (3.79)$$

$$L_D = \left(\sum_{\alpha=1}^{2} (-1)^{\alpha-1} \ell_{\alpha 2} \Delta \ell n c_\alpha/\Delta c_\alpha\right)(\Delta c_2)^{-1} \Delta \ell n\{c_2/[1-c_2(v_2-v_1)]\}$$

$$+ \left(\sum_{\alpha=1}^{2} (-1)^{\alpha-1} \ell_{\alpha 1} \Delta \ell n c_\alpha/\Delta c_\alpha\right)(\Delta c_2)^{-1} \Delta \ell n\{(1-c_2 v_2)/[1-c_2(v_2-v_1)]\} . \quad (3.80)$$

For small solute concentration difference (small Δc_2 or $c_2^A/c_2^B \sim 1$) , we have

$$\Delta \ell n c_2 = \ell n(c_2^A/c_2^B) = - \ell n[1-(c_2^A-c_2^B)/c_2^A] = - \ell n(1-\Delta c_2/c_2^A)$$

$$= (\Delta c_2/c_2^A) + \frac{1}{2} (\Delta c_2/c_2^A)^2 + \frac{1}{3} (\Delta c_2/c_2^A)^3 + \ldots ,$$

$$\Delta \ell n c_2/\Delta c_2 = (c_2^A)^{-1}[1 + \frac{1}{2} (\Delta c_2/c_2^A) + \frac{1}{3} (\Delta c_2/c_2^A)^2 + \ldots] , \quad (3.81)$$

$$\Delta \ell [1-c_2(v_2-v_1)]/\Delta c_2 = - (v_2 - v_1)[1+\bar{c}_2(v_2-v_1) + \ldots] \quad (3.82)$$

with $\bar{c}_2$ described by (3.73),

$$\Delta \ln(1 - c_2 v_2)/\Delta c_2 = - v_2(1 + \bar{c}_2 v_2 + \ldots) \; , \qquad (3.83)$$

and from (3.65)

$$\Delta \ln c_1/\Delta c_1 = -(v_1/v_2)\Delta \ln(1 - c_2 v_2)/\Delta c_2 \; . \qquad (3.84)$$

Substitution of (3.81)--(3.84) into (3.78)--(3.80) yields

$$L_{pD} = (\sum_{\alpha=1}^{2} \ell_{\alpha 1} v_\alpha)\{(c_2^A)^{-1}[1 + \tfrac{1}{2}(\Delta c_2/c_2^A) + \tfrac{1}{3}(c_2/c_2^A)^2 + \ldots]$$

$$+ (v_2 - v_1)[1 + \bar{c}_2(v_2 - v_1) + \ldots]\}$$

$$+ (\sum_{\alpha=1}^{2} \ell_{\alpha 2} v_\alpha)\{(v_2 - v_1)[1 + \bar{c}_2(v_2 - v_1) + \ldots] - v_2(1 + \bar{c}_2 v_2 + \ldots) \; , \qquad (3.85)$$

$$L_{Dp} = (\sum_{=1} \ell_{\alpha 2} v_\alpha)\{(c^A)^{-1}[1 + \tfrac{1}{2}(\Delta c_2/c_2^A) + \tfrac{1}{3}(\Delta c_2/c_2^A)^2 + \ldots]$$

$$- (\sum_{\beta=1}^{2} \ell_{2\beta} v_\beta) v_1(1 + \bar{c}_2 v_2 + \ldots) \; , \qquad (3.86)$$

$$L_D = v_1(1 + \bar{c}_2 v_2 + ..)\ell_{12} - (c_2^A)^{-1}[1 + \tfrac{1}{2}(\Delta c_2/c_2^A) + \tfrac{1}{3}(\Delta c_2/c_2^A) + ..]\ell_{22}$$

$$\times\{(c_2^A)^{-1}[1 + \tfrac{1}{2}(\Delta c_2/c_2^A) + \tfrac{1}{3}(\Delta c_2/c_2^A)^2 + ..]$$

$$+ (v_2 - v_1)(1 + \bar{c}_2(v_2 - v_1) + ..)\} + \{v_1(1 + \bar{c}_2 v_2 + ..)\ell_{11}$$

$$- (c_2^A)^{-1}[1 + \tfrac{1}{2}(\Delta c_2/c_2^A) + \tfrac{1}{3}(\Delta c_2/c_2^A)^2 + ..]\ell_{21}\}$$

$$\times \{(v_2 - v_1)[1 + \bar{c}_2(v_2 - v_1) + ..] - v_2(1 + \bar{c}_2 v_2 + ..)] \; , \qquad (3.87)$$

and by $\ell_{\alpha\beta} = \ell_{\beta\alpha}$

$$L_{pD} - L_{Dp} = \left(\sum_{\alpha=1}^{2} \ell_{\alpha 1} v_\alpha\right)(v_2 - v_1)[1+\bar{c}_2(v_2-v_1)+..]$$

$$+ \left(\sum_{\alpha=1}^{2} \ell_{\alpha 2} v_\alpha\right)(v_2 - v_1)$$

$$\times [(1+\bar{c}_2(v_2-v_1)+..) - (1+\bar{c}_2 v_2+..)] \quad . \qquad (3.88)$$

The phenomenological coefficients L_p, L_{pD}, L_{Dp} and L_D have the same experimental significance as in Kedem-Katchalsky theory.

Since as mentioned before, the integrated phenomenological coefficients $\ell_{\alpha\beta}$ are symmetric, it is obvious from (3.78), (3.79) and (3.88) that only when $v_1 = v_2$ (i.e., when the partial molar volumes of the solvent and solute equal to each other), will the relation $L_{pD} = L_{Dp}$ be valid. However, it is rarely the case that $v_1 = v_2$. Thus, in general $L_{pD} \neq L_{Dp}$.

It can be seen from (3.85) to (3.87) that these lumped transport coefficients depend upon the concentration and pressure distribution within the membrane through $\ell_{\alpha\beta}$, and therefore also depend on the nature of the transport processes taking place and the membrane structure as well as the boundary conditions. In other words L_p, L_{pD}, L_{Dp} and L_D also depend on the applied forces, Δc_2 . The Kedem-Katchalsky equations are thus only apparently linear with respect to the forces. They are ambiguous except in the limit of very small fractional changes in pressure and

composition; this is the fundamental weakness of their discontinuous approach.

We now proceed to estimate the difference between L_{pD} and L_{Dp} for a typical membrane transport experiment. Instead of integrating the local phenomenological coefficients and calculating L_{pD} and L_{Dp} from (3.78) and (3.79) or (3.85) and (3.86), which requires explicit but generally unavailable knowledge of the composition and pressure dependence of the local phenomenological coefficients, we solve for the $\ell_{\alpha\beta}$ from (3.77), (3.78) and (3.80). With the aid of experimental data on L_p, L_{pD} and L_D , we then calculate L_{Dp} from (3.79). The validity of $L_{pD} = L_{Dp}$ can then be checked. There are very few direct experimental tests of the reciprocal relation in membrane transport (Miller, 1960; Lakshminaraianaiah, 1969), and none for L_{pD} and L_{Dp}. Moreover, there are even fewer complete sets of data on L_p, L_D and L_{pD}.

Kaufmann and Leonard (1968) made a careful study of nonelectrolytes transport through cellophane membranes 0.00754 cm thick. The thickness of the unstirred layer was carefully reduced by effective stirring and the determinations were made with 0.1 molar solution on one side and 0.005 molar solution on the other side. Their results are shown in Table 3.1.

In order to find the partial molar volumes for the solutes, we fit the data for concentration dependence of

Table 3.1--Phenomenological coefficients of a cellophane membrane 0.00754 cm thick with 0.1 molar solution on one side and 0.005 molar on the other side. The relation $L_{pD} = L_{Dp}$ was pre-assumed. (Kaufmann and Leonard, 1968).

Solute	Temp.,°C	$L_D \times 10^5$, cm/atm.sec	$L_p \times 10^5$, cm/atm.sec	$L_{pD} \times 10^6$, cm/atm.sec
Glucose	27	11.90	2.00	1.77
	37	15.30	2.44	1.93
	47	17.30	3.05	2.17
Sucrose	27	7.49	1.90	2.00
	37	9.54	2.35	2.28
	47	10.96	3.03	2.72
Raffinose	37	6.56	2.30	2.89

density of various solutes from Timmermans (1960) into polynomials of various degrees, assuming constant amount of solvent--1000 gm of water is used. Somewhat surprisingly, it turns out that a linear fit is the best for the concentration ranges considered here. For Sucrose, at 27°C with molaity from 0 to 0.118,

$$V = 1003.01 + 207.2\ m_2\ , \tag{3.89}$$

and at 47°C with molality from 0 to 0.148,

$$V = 1012.14 + 208.91\ m_2\ . \tag{3.90}$$

For Glucose, at 27°C with molality from 0 to 0.26,

$$V = 1003.04 + 110.6\ m_2\ , \tag{3.91}$$

and at 47°C with molality 0 to 0.78,

$$V = 1009.93 + 115.17\ m_2\ , \tag{3.92}$$

where V is the total volume (in mℓ) of the solution based on 1000 gm of water and m_2 is the molality of the solute. After the explicit expression for the concentration dependence of the volume of the solution is obtained, we calculate, following Klotz (1964), the partial molar volume of the solute and solvent by

$$v_2 = (\partial V/\partial m_2)_{m_1} \tag{3.93}$$

with the molality of solvent, m_1, fixed. The partial molar volume of the solute and solvent obtained (in this case, the data for Raffinose are not available, and the molar volume of water is used in both temperatures) are indeed constant in the concentration range of Kaufmann and Leonard's experiments (but of course $v_1 \neq v_2$). The results are shown in Table 3.2. Because of lack of extensive temperature data, we have used data at 25°C for 27°C and data at 45°C or 50°C for 47°C.

Table 3.2--Partial molar volumes for different solutes, where we have used the molar volume for the solvent water.

Solute	$v_{\alpha,27°C}$, mℓ/mol	$v_{\alpha,47°C}$, mℓ/mol
Sucrose	207.20	208.91
Glucose	110.60	115.17
Water (solvent)	18.01	18.01

After obtaining the partial molar volumes, we solve the simultaneous equation for $\ell_{\alpha\beta}$, and then calculate L_{Dp} from (3.79). The results are shown in Table 3.3.

For the present case, the differences between L_{pD} and L_{Dp} are small. For biological membranes, the experimental uncertainty sometimes might exceed the difference between L_{pD} and L_{Dp}. Therefore, the reciprocal relation in Kedem-Katchalsky theory can be considered approximately valid in membrane transport experiments where quantitative accuracy is of secondary importance. It has to be noted that the difference between L_{pD} and L_{Dp} depends on the nature of the solute as well as on temperature and concentration. The difference increases as the difference in partial molar volumes increases. For large solute molecules such as antibiotics and biopolymers the difference between L_{pD} and L_{Dp} might be large.

E. Discussion

There has been an attack on the discontinuous nonequilibrium thermodynamic membrane theory of Kedem and Katchalsky by Bresler and Wendt (1969). However, their approach is misleading, as pointed out by Smit and Staverman (1970). The main problem considered by Bresler and Wendt (1969) was the Onsager Reciprocal Relation used in the Kedem-Katchalsky theory. They used an example of an

Table 3.3--Comparison of the integrated phenomenological coefficients.

Solute	Temp., °C	$\ell_{11}\times 10^{13}$ cm/atm.sec	$\ell_{21}\times 10^{11}$ cm/atm.sec	$\ell_{11}\times 10^{8}$ cm/atm.sec	Calculated $L_{Dp}\times 10^{6}$ cm/atm.sec	Experimental $L_{pD}\times 10^{6}$ cm/atm.sec	% difference $\frac{(L_{Dp}-L_{pD})\times 100}{L_{pD}}$
Sucrose	27	0.973	3.610	5.774	2.064	2.00	3.2
	47	1.445	5.685	9.208	2.830	2.72	4.0
Glucose	27	1.423	3.759	6.119	1.805	1.77	2.0
	47	2.075	5.641	9.330	2.230	2.17	2.8

open membrane with rapid bulk flow and claimed that the diffusive flow will vanish, and hence $L_{pD} = 0$. However, they retained L_{Dp}. Therefore, they concluded $L_{Dp} \neq L_{pD}$. This is patently incorrect, since we will see in the final chapter, that even in rapid bulk flow across the membrane, the diffusion process is still effective, yet may be small, as long as there is a concentration variation across the membrane. A term can be small compared to another in (3.74) without being small in comparison to other terms in (3.75). Therefore $L_{pD}\Delta\pi$ may be small compared to $L_p\Delta p$ for rapid bulk flow, but may have similar magnitude to $L_{Dp}\Delta p$. Thus the setting of $L_{pD} = 0$ by them is unjustified and the break down of the Onsager Reciprocal Relation by their reasoning is incorrect.

In fact we have obtained a general criteria for the validity of $L_{pD} = L_{Dp}$. We have shown that (1) Kedem-Katchalsky theory is strictly applicable only to homogeneous membranes for thermodynamically ideal binary non-electrolyte solutions; (2) for porous membranes, Kedem-Katchalsky theory can be used only when the barycentric velocity is linearly related to the external forces; (3) for porous membranes in isothermal binary solutions, the reciprocal relation of the local phenomenological coefficients is the natural outcome of the dependence of fluxes; and (4) for homogeneous membranes and for porous membranes satisfying (2), the reciprocal relation $L_{pD} = L_{Dp}$ is strictly valid only when the solution is thermodynamically ideal and the partial molar volumes of solute and solvent are equal. Moreover L_{pD}, L_{Dp} and L_D are independent of the sizes of the gradient Δc_2 only for very small gradients.

Considering again the open membrane with rapid bulk flow described by Bresler and Wendt (1969), the possibilities that $L_{pD} = L_{Dp}$ might break down are the following, (1) nonlinear velocity behavior; (2) local equilibrium assumption break down due to the rapid bulk flow; (3) partial molar volumes of the solute and solvent are different; and (4) thermodynamic nonideality.

Mason, Wendt and Bresler (1972) tested the reciprocal relation $L_{pD} = L_{Dp}$ for ideal gas transport in graphite membranes. Their results show that it is approximately valid only for a limited range and in general the phenomenological coefficients in Kedem-Katchalsky theory depend on the forces. This coincides with our point of view in the last section that the explicit expressions (3.78)--(3.80) and (3.85)--(3.87) have indicated their dependence on the applied forces, on the nature of the transport processes, and on the membrane structure.

As pointed out by Lightfoot (1974), through Stefan-Maxwell equations, the Kedem-Katchalsky theory is only an approximation. This "black box" type theory offers only

lumped experimental parameters which conceal our ignorance of the exact physical nature of the processes. In order to get more insight into the mechanisms involved in transport processes through membranes, it is necessary to employ a continuous approach. We do this in the following chapters.

CHAPTER IV

HYDRODYNAMIC THEORY OF CAPILLARY OSMOSIS OF ELECTROLYTE SOLUTIONS

A. Introduction

In this and the next chapter the continuous approach is utilized in order to examine the mechanisms involved in the transport of electrolyte solutions through charged porous membranes.

One expects that the motion of fluid through porous membranes could be described by a suitable solution of the Navier-Stokes equation. This could be done if one could formulate correctly the boundary conditions at the highly irregular boundaries. Since it is impossible to define the complicated geometry of the solid surface of the porous membrane matrix, one cannot treat the problem at hand, and in fact also the general problem of flow through porous media, in any mathematically exact manner. This difficulty can be circumvented, as in many other physical problems, by replacing the porous membrane with some simplified model. A model will suit this purpose if it (a) explains the phenomena in question; (b) involves parameters which can be measured and related to corresponding properties of the porous membrane; and (c) can be treated by available mathematical tools to yield a macroscopic description of the phenomena with discrepancies which may be neglected for practical purposes.

Among commonly employed models for the porous membrane are: a bundle of circular capillaries; a bundle of parallel plate capillaries; an array of cells (*e.g.*, Kobatake and Fujita, 1964; Kobatake, Toyoshima and Takeguchi, 1966; Philip, 1969). Experimentation is the only way to test the models and to determine the various coefficients which appear in the equations derived from these models; there is no way to obtain numerical values of the coefficients from the mathematical analysis itself.

We use the capillary model here for the discussion of charged porous membranes. The membrane is considered to be composed of bundles of circular capillaries with equal radii and uniform fixed charges on the capillary walls. It is sufficient, therefore, to consider the behavior of only a single charged circular capillary in an electrolyte solution subject to pressure, electrical potential, and concentration variations across the capillary.

The phenomena resulting from externally applied gradients of pressure and electrical potential across a charged capillary are well known, the electrokinetic relationships involved having been discussed by Helmholtz

(1879) and later on reformulated by Smoluchowski (1914). However, the effect due to an externally applied gradient of concentration across a charged capillary has attracted little attention. All refined theories of electrokinetic flow in fine capillaries (e.g., Dresner, 1963; Morrison and Osterle, 1965; Burgreen and Nakache, 1964; Rice and Whitehead, 1965; Hildreth, 1970; Sorensen and Koefoed, 1974) consider only solutions of uniform concentration. Even in the capillary model for charged porous membranes (Kobatake and Fujita, 1964; Kobatake, Toyoshima and Takeguchi, 1966), where an externally applied concentration gradient does exist, only ordinary electrokinetic equations for systems of uniform concentrations are used to obtain the barycentric velocity in the capillary. Gross and Osterle (1968) and Fair and Osterle (1971) have considered the concentration effect on the barycentric velocity in their description of electrodialysis and energy conversion efficiencies in a capillary-model membrane; however, their formulation is valid only for extreme dilution. Moreover, their solution is entirely numerical, so that the explicit significance of the concentration gradient effect is concealed.

It has been predicted theoretically and demonstrated experimentally by Derjaguin, et al. (1947, 1961, 1965, 1969, 1971, 1972, 1974), Milekhina (1961) and Dukhin and Derjaguin that when the adsorption layer on a solid surface in contact with either an ionic or a non-ionic solution is mobile, then the tangential concentration gradient of the solution along the solid surface causes "capillary osmotic slip" in addition to diffusional flow of the liquid. In the case of a porous diaphram separating solutions of different concentration, slip along the pore walls causes convective transfer of the solution--this is named capillary osmosis by Derjaguin, et al. The movement of suspended particles under the effect of an externally imposed solution concentration gradient is called diffusiophoresis. In this thesis we restrict attention to electrolyte solutions, but non-electrolyte solutions also exhibit capillary osmosis and diffusiophoresis (Derjaguin, et al., 1947; Derjaguin and Dukhin, 1974).

The mechanism suggested by Derjaguin, et al. (1947, 1961, 1965, 1969, 1971, 1972, 1974), Milekhina (1961) and Dukhin and Derjaguin (1964) for diffusiophoresis in electrolyte solutions should also be applicable to capillary osmosis. Both phenomena are caused by the polarization of the electrical double layer under the influence of a macrogradient of concentration. A macrogradient of concentration applied from outside causes an uneven concentration distribution of ions in the region adjacent to the outer boundary of the electrical double layer. Since there is equilibrium between ions because there is no flow perpendicular to the solid wall, the double layer rearranges itself to a different thickness according to the given distribution of ion concentration along its outer boundary, and the double layer is polarized. This double layer polarization gives rise both to an additional tangential component of the electric field, and to an additional pressure gradient along the solid surface. The latter is caused by the interaction of the normal electric field and its additional tangential component with the charges in the diffuse double layer. These factors, which are also effective during electroosmosis (the movement of solution in a charged capillary due to the interaction of an external electric potential gradient and the diffuse double layer) and electrophoresis (the movement of suspended colloidal particles under the action of an external electric potential gradient), set in motion either the solution with the mobile part of the double layer or the solid with the immobile part of the double layer, depending on whether the solution phase or the solid phase is mobile. Thus, either the solution moves (capillary osmosis), or the solid particles move (diffusiophoresis).

The relationship between capillary osmosis and diffusiophoresis is the same as that between electroosmosis and electrophoresis. Qualitatively, therefore, capillary osmosis and diffusiophoresis can be characterized respectively as electroosmosis and electrophoresis caused by a microgradient of electrical potential induced by the macrogradient of concentration. This also implies that the theories of capillary osmosis and of electroosmosis (or the theories of diffusiophoresis and of electrophoresis) must be based on the same system of equations and similar boundary conditions. Hence, as pointed out by Derjaguin and Dukhin (1974), the arbitrary inclusion of concentration gradient as an external force term in the equation of motion by Pickard (1961) in the description of the effect of diffusion on electrophoresis is redundant since the concentration influence is already accounted for by the inclusion of the electrical potential and pressure gradient terms in the equation of motion.

Since only capillary osmosis is relevant to the membrane transport in addition to the fact that there have already been extensive investigation on diffusiophoretic mobility and its relation with electrophoretic mobility (see Derjaguin and Dukhin, 1974), we consider only capillary osmosis in this thesis. Derjaguin, et al. (1969), have shown semi-quantitatively that in general the rate of capillary osmosis and of electroosmosis due to diffusion potential are of the same order of magnitude.

Derjaguin, et al. (1947, 1961, 1965, 1969, 1971, 1972, 1974), Milekhina (1961) and Dukhin and Derjaguin

(1964) derived equations for capillary osmotic slip from classical thermodynamic and discontinuous nonequilibrium thermodynamic considerations under various simplifying assumptions. Two such assumptions were (a) the external force field depends only on the coordinate normal to the solid wall; (b) the double layer is very thin compared to other geometric lengths so that a flat geometry can be used for the capillary. Like Smoluchowski's equation for electroosmosis, Derjaguin's formulation is valid strictly only in the limit that the capillary radius or capillary slit width is much greater than the thickness of the electrical double layer. However, in many of the most interesting cases the capillary radius or capillary slit width is comparable to the double layer thickness. This is the case for transport of dilute electrolyte solutions through charged porous membranes.

It is the purpose of this chapter to demonstrate that a general analytical expression for the capillary osmotic velocity due to an axial concentration gradient in a fine charged circular capillary with steady laminar flow of a Newtonian dilute electrolyte solution is a natural outcome of inclusion of the effect of concentration polarization in the simultaneous solution of the set of differential equations which includes the Navier-Stokes equation and the Poisson-Boltzmann equation. In the limit of zero concentration gradient, our barycentric velocity equation reduces to the equation for ordinary electrokinetic flow in capillary tubes (Rice and Whitehead, 1965; Newman, 1973). In the limit of very large ratio of capillary radius to Debye length, our equation for capillary osmotic slip velocity becomes identical to that given by Derjaguin, et al. (1969) and Dukhin and Derjaguin (1964). In the next chapter we develop a theory which successfully describes anomalous osmosis in charged porous membranes. This successful theory requires the theory of the capillary osmotic slip phenomenon presented here.

The system considered here is a dilute, isothermal electrolyte solution contained in a single, long, non-electrically conducting circular capillary with radius a which is large enough to permit a diffuse double layer on the capillary walls but small compared to the length ℓ of the capillary. The capillary connects two compartments which contain well-stirred electrolyte solution maintained at constant but different concentrations. In addition to the fixed concentration gradient, fixed gradients of pressure and electrical potential are imposed across the capillary. We assume that the capillary wall carries a fixed charge density, and that the capillary is readily entered by both solute and solvent. We assume further that there is steady, slow flow. These assumptions are repeated, and further assumptions are stated and used, in their appropriate place below.

In Section B, we use the Navier-Stokes equation and the equation of continuity of total mass density to obtain an integral expression for u_x, the axial component of the barycentric velocity $\underset{\sim}{u}$. In order to obtain the integrated expression for u_x, which is the important result of this chapter, we solve the Poisson-Boltzmann equation for the distribution of electric potential in Section D. Section C contains a discussion and derivation of the Boltzmann equation for the concentration distribution of ions in an electric potential field.

B. Equation of Motion

Under the assumptions (1) constant viscosity coefficients; (2) steady, slow flow that the inertial term $\rho\underset{\sim}{u} \cdot \nabla\underset{\sim}{u}$ is negligible compared to the viscous term $\eta\nabla^2\underset{\sim}{u}$; and (3) negligible density gradient (equivalent to the incompressibility assumption $\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$), the Navier-Stokes equation (2.17) reduces to the so-called creeping motion or Stokes equation, (2.22). For this charged capillary system with only the electric potential gradient, (2.22) has the form

$$\eta\nabla^2\underset{\sim}{u} = \underset{\sim}{\nabla}p + F\left(\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha\right)\underset{\sim}{\nabla}\phi \tag{4.1}$$

where all the parameters have been defined in Chapter II. It should be noted that chemical interactions are included explicitly in (4.1), and it is therefore incorrect to add, as Pickard (1961) did, a further concentration gradient to (4.1) as an additional external force term.

For steady laminar flow; we have, by symmetry, no azimuthal flow; i.e., $u_\theta = 0$. Further, since no transport occurs radially, $u_r = 0$. The incompressibility result, $\underset{\sim}{\nabla} \cdot \underset{\sim}{u} = 0$, then becomes

$$(\partial u_x/\partial x) = 0 \ , \tag{4.2}$$

and therefore the axial velocity u_x is independent of x. It still depends on the radial coordinate r, however, and the radial and axial components of (4.1) become

$$0 = (\partial p/\partial r) + F(\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha)(\partial\phi/\partial r) \tag{4.3}$$

$$(\eta/r)(\partial/\partial r)r(\partial u_x/\partial r) = (\partial p/\partial x) + F\ (\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha)(\partial\phi/\partial x) . \tag{4.4}$$

In order to take account of both (1) applied gradients of pressure and electric potential and (2) induced gradients of pressure and electric potential, we separate p and ϕ according to

$$p(x,r) = P(x) + P'(x,r) \ , \tag{4.5}$$

and

$$\phi(x,r) = \Phi(x) + \psi(x,r) \ , \tag{4.6}$$

where $P(x)$ is the externally applied pressure and $(d\Phi/dx)$ is the externally measurable electric potential gradient between the ends of the capillary. This gradient includes both any applied gradient and any gradient due to diffusion. $P'(x,r)$ and $\psi(x,r)$ are, respectively, the additional pressure and electrical potential due to the fixed wall charge and the concentration polarization of the electrical double layer in the capillary. As the concentration variation vanishes, $\Phi(x)$ is only the externally applied potential and $\psi(x,r)$ and $P'(x,r)$ reduces to $\psi(r)$ and $P'(r)$; which include only the potential and pressure distribution due to the fixed wall charges.

The radial component of the Navier-Stokes equation, (4.3), then becomes

$$0 = (\partial P'/\partial r) + F(\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha)(\partial\psi/\partial r) \ , \tag{4.7}$$

Using (4.5) and (4.6) and integrating (4.4) twice, we obtain

$$u_x = u_p + u_{eo} + u_{co} \ ,$$

$$u_p = (4\eta)^{-1}(r^2-a^2)(dP/dx)$$

$$u_{eo} = (F/\eta)(d\Phi/dx) \int_a^r r^{-1}dr \int_0^r (\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha) rdr$$

$$u_{co} = \eta^{-1} \int_a^r r^{-1}dr \int_0^r [(\partial P'/\partial x) + F(\sum_{\alpha=1}^{\nu} c_\alpha z_\alpha)(\partial\psi/\partial x)] rdr \ , \quad (4.8)$$

where the boundary conditions are such that u_x vanishes at the wall ($r = a$) and is finite at the center ($r = 0$). The double integrals can be evaluated only after $\psi(x,r)$ and $c_\alpha(x,r)$ are obtained. The u_p term is the axial velocity due to an externally applied pressure gradient, the u_{eo} term is the electroosmotic flow velocity, and the u_{co} term is the capillary osmotic flow veloctiy. We show in Section D that u_{co} is proportional to the axial concentration gradient.

C. Boltzmann Equation

We now assume that there is no radial flow of any component within the capillary. This is equivalent to assuming that, for each value of x, the system is in equilibrium in the radial direction. Mechanical equilibrium in the radial direction is represented by (4.3) or (4.7). For equilibrium with respect to movement of component α, it is necessary and sufficient that its chemical potential μ'_α be constant. Thus,

$$(\partial \mu_\alpha / \partial r) = 0 \ , \qquad \alpha=1,\ldots,\nu \ . \tag{4.9}$$

In order to exploit this assumption, we use the explicit formula for the chemical potential by combining (2.32), (2.33), (2.34) and (2.39)

$$\mu'_\alpha = \mu^\infty_\alpha(T,p) + RT \, \ln x_\alpha \, f_\alpha + z_\alpha F\phi \tag{4.10}$$

where the pure solvent standard state is used. We have neglected any polarization effects in the expression for μ'_α because such effects are very small for the application we envisage. Elaboration of this point may be found in Sanfield (1968) and Horne and Chen (1973).

If we now further assume that the activity coefficients are constants in the radial direction, then (4.9) and (4.10) yield, after some algebra (Horne and Chen, 1973),

$$x_\alpha = x^0_\alpha (x_1/x^0_\alpha)^{g_{\alpha 1}} \, [\exp(-\, z_\alpha \Psi)] \ , \qquad \alpha=2,\ldots,\nu \tag{4.11}$$

where $\quad \Psi = F\psi/RT \ ,$ (4.12)

and the ratio $g_{\alpha 1}$ is defined by

$$g_{\alpha 1} = v^\infty_\alpha / v^\infty_1 \ , \qquad \alpha=2,\ldots,\nu \ , \tag{4.13}$$

with v^∞_α the limiting partial molar volume of α at infinite dilution defined by (2.48), and where x^0_α is the mole fraction of α when ψ is zero. We shall show in the next section that this corresponds to zero surface charge density.

For the application at hand, therefore, x_α^0 is the mole fraction of α in the compartments on either side of the capillary. When there is a composition difference between the compartments, then x_α^0 is a function of the axial variable x.

Horne and Chen (1973) have eliminated x_1 from (4.11) by defining a correction parameter ξ by

$$x_1 \equiv x_1^0 \;(1-\xi) \tag{4.14}$$

and using the fact that $\sum_{\alpha=1}^{\nu} x_\alpha = 1$. The found, essentially,

$$\xi = \sum_{\alpha=2}^{\nu} x_\alpha^0[\exp(-z_\alpha\Psi) - 1] + 0\;(I^2) \;, \tag{4.15}$$

where I is the ionic strength,

$$I = (1/2) \sum_{\alpha=2}^{\nu} c_\alpha^0 z_\alpha^2 \tag{4.16}$$

with c_α^0 the molar concentration of α when Ψ is zero. For the case that $z_\alpha\;\Psi < 1$,

$$\xi = -v_1^\infty I\Psi^2 \;. \tag{4.17}$$

For sufficiently dilute solutions, $\xi << 1$, and we have the usual Boltzmann equation,

$$x_\alpha = x_\alpha^0\;[\exp(-\;z_\alpha\Psi)]\;, \qquad \alpha=1,\ldots,\nu\;, \tag{4.18}$$

or, for constant molar volume,

$$c_\alpha = c_\alpha^0\;[\exp(-\;z_\alpha\Psi)2\;, \qquad \alpha=1,\ldots,\;\;. \tag{4.19}$$

The net change per unit volume at any point is then

$$\sum_{\alpha=2}^{\nu} c_\alpha z_\alpha = \sum_{\alpha=2}^{\nu} c_\alpha^0 z_\alpha [\exp(- z_\alpha \Psi)] \ , \tag{4.20}$$

which, for $z_\alpha \Psi << 1$, becomes

$$\sum_{\alpha=2}^{\nu} c_\alpha z_\alpha = -2I\Psi \ . \tag{4.21}$$

For a symmetric binary electrolyte with $z_+ = |z_-| = z$, and $c_+^0 = c_-^0 = c$, (4.20) becomes

$$\sum_{\alpha=2}^{\nu} c_\alpha z_\alpha = - 2cz[\sinh (z\Psi)] \ , \tag{4.22}$$

and this simplifies (to better than 1% accuracy), to

$$\sum_{\alpha=2}^{\nu} c_\alpha z_\alpha = - 2cz^2\Psi \tag{4.23}$$

for $|z\Psi| < 0.245$.

D. Electrical Potential Distribution: Poisson-Boltzmann Equation

The classical treatment of the diffuse double layer relies on the Poisson-Boltzmann equation, which in turn gives rise to the Gouy-Chapman type double layer.

Alhtough this is a relatively simple model, most rigorous quantitative theories are based on it. There are several simplifying physical assumptions involved: (1) the dielectric constant is independent of position; (2) the ions are point charges that interact coulombically with the charged wall; (3) the charges on the capillary wall are uniformly distributed on its surface; and (4) the exponential term in the Boltzmann distribution contains the average potential $\psi(x,r)$ instead of the potential of the mean force.

A number of corrections to these simplifications in the Poisson-Boltzmann equation have been proposed, including corrections for ionic volume, dielectric saturation, ion polarization, self-atmosphere effect of the counterion and the discreteness of surface charge. Haydon (1964) and Overbeek and Wiersema (1967), however, have suggested that these corrections at least partially compensate each other and that it is therefore not advisable to consider one or two corrections and to leave out others. They suggest use of the Poisson-Boltzmann equation inasmuch as refinements in double layer theory are still under development. We follow this suggestion here. Consequently, any experimental test of our final equation is to some extent a test of the Poisson-Boltzmann equation, along with our other assumptions.

For a circular capillary with fixed wall charge density and fixed end concentrations in an electrolyte solution, the potential distribution inside the capillary is governed by Poisson's equation,

$$(\partial^2\phi/\partial x^2) + r^{-1}(\partial/\partial r)r(\partial\phi/\partial r) = -(F/\varepsilon)\sum_{\alpha=2}^{\nu} c_\alpha z_\alpha \ , \quad (4.24)$$

where ε is the dielectric permitivity of the medium. By (4.6) and (4.20), the Poisson-Boltzmann equation is

$$(\partial^2\Psi/\partial x^2) + r^{-1}(\partial/\partial r)r(\partial\Psi/\partial r) = -(F^2/\varepsilon RT)\sum_{\alpha=2}^{\nu} c_\alpha^0 z_\alpha[\exp(-z_\alpha\Psi)] \ , \quad (4.25)$$

where we have required Φ of (4.6) to be linear in x, thus,

$$(d\Phi/dx) = \text{constant} \ . \quad (4.26)$$

The Poisson-Boltzmann equation in the form of (4.25) is quite insoluble. In order to render it tractable, we make two further simplifications. First, we neglect $(\partial^2\Psi/\partial x^2)$--the effect of this can be accessed after an explicit formula for $\Psi(x,r)$ is obtained since the $\bar{c}_\alpha$ are functions of x. Second, we linearize according to (4.21). Then we find the linearized Poisson-Boltzmann equation,

$$r^{-1}(\partial/\partial r)r(\partial\Psi/\partial r) = \kappa^2\Psi \quad (4.27)$$

where the parameter κ, defined by

$$\kappa = F(2I/\varepsilon RT)^{1/2} , \tag{4.28}$$

is the reciprocal of the Debye length. The ionic strength I is defined by (4.16).

The boundary conditions for (4.27) are

$$(\partial\Psi/\partial r)_{r=0} = 0 ,$$

$$(\partial\Psi/\partial r)_{r=a} = (\sigma F/\varepsilon RT) , \tag{4.29}$$

where σ is the surface charge density on the wall. In order to simplify the analysis of flow in charged capillaries, consideration of surface phenomena is minimized by assuming that the surface charge density σ is the charge density of the fluid at some distance from the wall. At this distance from the wall, which is of the order of molecular dimensions, the fluid is assumed to be stationary. The effective capillary radius, a, is then measured from the center up to this stationary layer. The solution of (4.27) is, with (4.29),

$$\Psi = (\sigma F/\kappa\varepsilon RT)[I_0(\kappa r)]/[I_1(\kappa a)] \tag{4.30}$$

where I_0 and I_1 are modified Bessel functions of the first kind of, respectively, order zero and order one.

Much has been written on the validity of (4.27) as the correct form of the Poisson-Boltzmann equation rather than (4.25). We present here a brief analysis of the physical conditions in which (4.25) reduces to (4.27) for a symmetric, binary electrolyte. As our starting point, we note from (4.23) that $\sinh z\Psi = z\Psi$ to better than 1% accuracy as long as $|z\Psi| \lesssim 0.245$. This condition is met for all values of κa such that

$$[I_0(xa)]/[I_1(\kappa a)] \lesssim 0.245\ z(2\varepsilon RT)^{1/2}(c^{1/2}/\sigma) \ ,$$

where we have used (4.30) and (4.28). For T = 298°K, $R = 8.314\text{J mol}^{-1}\text{K}^{-1}$, $z = 1$, and $\varepsilon = 7 \times 10^{-10}\ \text{CV}^{-1}\text{m}^{-1}$, the condition becomes

$[I_0(\kappa a)]/[I_1(\kappa a)] \lesssim 0.456 \times 10^{-3}(c^{1/2}/\sigma)$, with both c and σ in SI units. For $\sigma = 10^{-4}\text{C m}^{-2}$, the condition is met for all concentrations c greater than 5×10^{-3} molar = 5×10^{-2} mol m^{-3} . For $\sigma = 10^{-3}$ C m^{-2} , the condition is met for all concnetrations c greater than 5×10^{-3} molar. For $\sigma = 10^{-2}$ C m^{-2} , the condition is met only for concentrations c greater than 0.5 molar. For a wide range of surface charge densities and concentrations, then, (4.27) is valid regardless of theoretical doubts concerning (4.25). Moreover, for values of κa large enough for (4.21) to hold, the x-derivative term of (4.25) is approximately,

$$(\partial^2\Psi/\partial x^2) \approx -\ \kappa a\Psi\ (d\ell nI/dx)^2\ . \qquad (4.31)$$

Even for large gradients of the ionic strength I, the x-derivative term is very small compared to $\kappa^2\Psi$ because κ is very large, 10^7 to 10^9 m^{-1} .

E. Pressure, Electroosmotic and Capillary Osmotic Flows

In this section we combine the results obtained from previous sections to formulate an analytical expression for the capillary osmosic flow in a charged circular capillary.

Since the presence of the tangential concentration gradient together with the ion distribution (non-electroneutrality) result in the axial polarization of $\psi(x,r)$ and $P'(x,r)$, the following physical conditions should be satisfied:

whenever $\sigma = 0$ or I = constant,

$$(\partial P'(x,r)/\partial x) = 0 \quad \text{and} \quad (\partial\psi(x,r)/\partial x) = 0 \ . \tag{4.32}$$

This implies that whenever the wall charge density is zero or the ionic strength is the same in the compartments on either side of the capillary, the axial polarization effect vanishes.

Combining equations (4.7), (4.19) and (4.20), we find

$$-RT(\partial \sum_{\alpha=2}^{\nu} c_\alpha/\partial r) + (\partial P'/\partial r) = 0 \ , \tag{4.33}$$

this implies

$$P'(x,r) - RT \sum_{\alpha=2}^{\nu} c_\alpha(x,r) = f(x) \;, \qquad (4.34)$$

where f(x) is an unknown function of axial coordinates. Introduction of (4.19) into (4.34) and expansion of the exponential yields

$$P'(x,r) - RT \sum_{\alpha=2}^{\nu} c_\alpha^0(x) - RTI\Psi^2 + O(\Psi^3) = f(x) \;. \qquad (4.35)$$

In (4.5) and (4.6) we have tacitly assumed that the polarization terms $P'(x,r)$ and $\psi(x,r)$ are complicated functions of x and r . They are not further separable in the form of (4.5) and (4.6). This is clearly the case in (4.30). Hence f(x) can be identified from (4.35) as

$$f(x) = - RT \sum_{\alpha=2}^{\nu} c_\alpha^0(x) \qquad (4.36)$$

and (4.34) becomes

$$P'(x,r) - RT \sum_{\alpha=2}^{\nu} c_\alpha(x,r) + RT \sum_{\alpha=2}^{\nu} c_\alpha^0(x) = 0 \;. \qquad (4.37)$$

Differentiating (4.37) with respect to x and utilizing (4.12) and (4.20), we obtain

$$(\partial P'/\partial x) = (F^2\psi^2/RT)(dI/dx) + (2IF^2\psi/RT)(\partial\psi/\partial x) \;, \qquad (4.38)$$

where on the right hand side we retain only up to the square term in ψ.

(4.38) satisfies the physical restriction in (4.32), which further confirms the choice of f(x) in (4.36).

Gross and Osterle (1968) and Fair and Osterle (1971) set f(x) = 0 arbitrarily. Therefore their formulation does not satisfy the physical restrictions in (4.32). Instead, they have an extra term containing $2RT\dot{c}$, (or $RT \sum_{\alpha=2}^{\nu} c_\alpha^0$) which they denote as π, the solute partial pressure given by the Van't Hoff equation for equilibrium osmotic pressure. In fact their results are erroneous since whenever there exists only a concentration variation across an uncharged capillary, their equation predicts a center of mass movement caused by the solute partial pressure gradient (or rather ordinary osmotic pressure gradient from the Van't Hoff equation). This seemingly correct prediction is in fact wrong. For a circular capillary open to both solute and solvent, there can be no ordinary osmotic flow. The only mechanism that can give rise to an osmotic pressure is a momentum deficiency due to a sharp change of solute concentrations at the capillary openings (Mauro, 1957; Longsworth, 1960; Meares, 1966; Philip, 1969). This cannot be taken into account structurally in a continuous theory like this, but it can be taken care of mathematically by a boundary condition as discussed in Chapter III.

For the discussions in this chapter, we stick to our original assumption in Section B that the capillary is open to both solute and solvent so that no ordinary osmotic effect will occur.

(4.38) and (4.21), together with the last of (4.8), gives

$$u_{co} = (F^2/2\eta RT)(dI/dx) \int_a^r (dr)r^{-1} \int_0^r (dr)r\psi^2 \ . \qquad (4.39)$$

Substituting (4.21) and (4.30) into (4.8) and (4.39), and performing the integration we obtain

$$u_x = u_p + u_{eo} + u_{co}$$

$$u_p = (4\eta)^{-1}(r^2-a^2)(dP/dx)$$

$$u_{eo} = [\sigma/\eta\kappa I_1(\kappa a)][I_0(\kappa a) - I_0(\kappa r)](d\Phi/dx)$$

$$u_{co} = [\sigma^2/4\eta\kappa^2\varepsilon I_1^2(\kappa a)]\{(\kappa r)^2[I_0^2(\kappa r)-I_1^2(\kappa r)]-(\kappa r)I_0(\kappa r)I_1(\kappa r) - (\kappa a)^2[I_0^2(\kappa a)-I_1^2(\kappa a)] + (\kappa a)I_0(\kappa a)I_1(\kappa a)\}(d\ell nI/dx) \ . \qquad (4.40)$$

For the first time the general analytical expression of barycentric flow in a charged circular capillary is written down including capillary osmosis. The first term, u_p, represents the well known Poiseville flow due to external pressure gradient. The second term, u_{eo}, represents the capillary osmotic flow caused by the double layer polarization due to an external concentration gradient. It has been shown by Derjaguin, et al. (1969), that in general the rate of capillary osmosis and of electro-osmosis due to diffusion potential are of the same order of magnitude.

We observe that whenever there is no concentration variation, (4.40) reduces to the ordinary electrokinetic flow equation for circular capillaries (Newman, 1973; Sorensen and Koefoed, 1974). Furthermore, if $\sigma = 0$ (zero wall charge) we get the usual pressure flow equation.

The velocity profiles in the capillary for the above mentioned three different cases are shown in Fig. 4.1 to Fig. 4.3. Fig. 4.1 shows the familiar parabolic velocity profile in the capillary due to external pressure gradient. Fig. 4.2 shows the electroosmotic velocity profile due to the external electric field as a function of κa, the ratio of capillary radius to Debye length. Fig. 4.3 shows the capillary osmotic velocity profile due to the electrolyte concentration gradient across the capillary as a function of κa. In the presence of an electrolyte concentration gradient, a diffusion potential will occur, so the capillary osmosis must be accompanied by electroosmosis. Therefore the capillary osmotic velocity can only be measured by short circuiting two reversible electrodes placed at both ends of the capillary. In the most general

Fig. 4.1--Poiseuille Flow

$$Y_1 = -\,4\eta\, u_p(r^2 - a^2)^{-1}(dP/dx)^{-1}$$

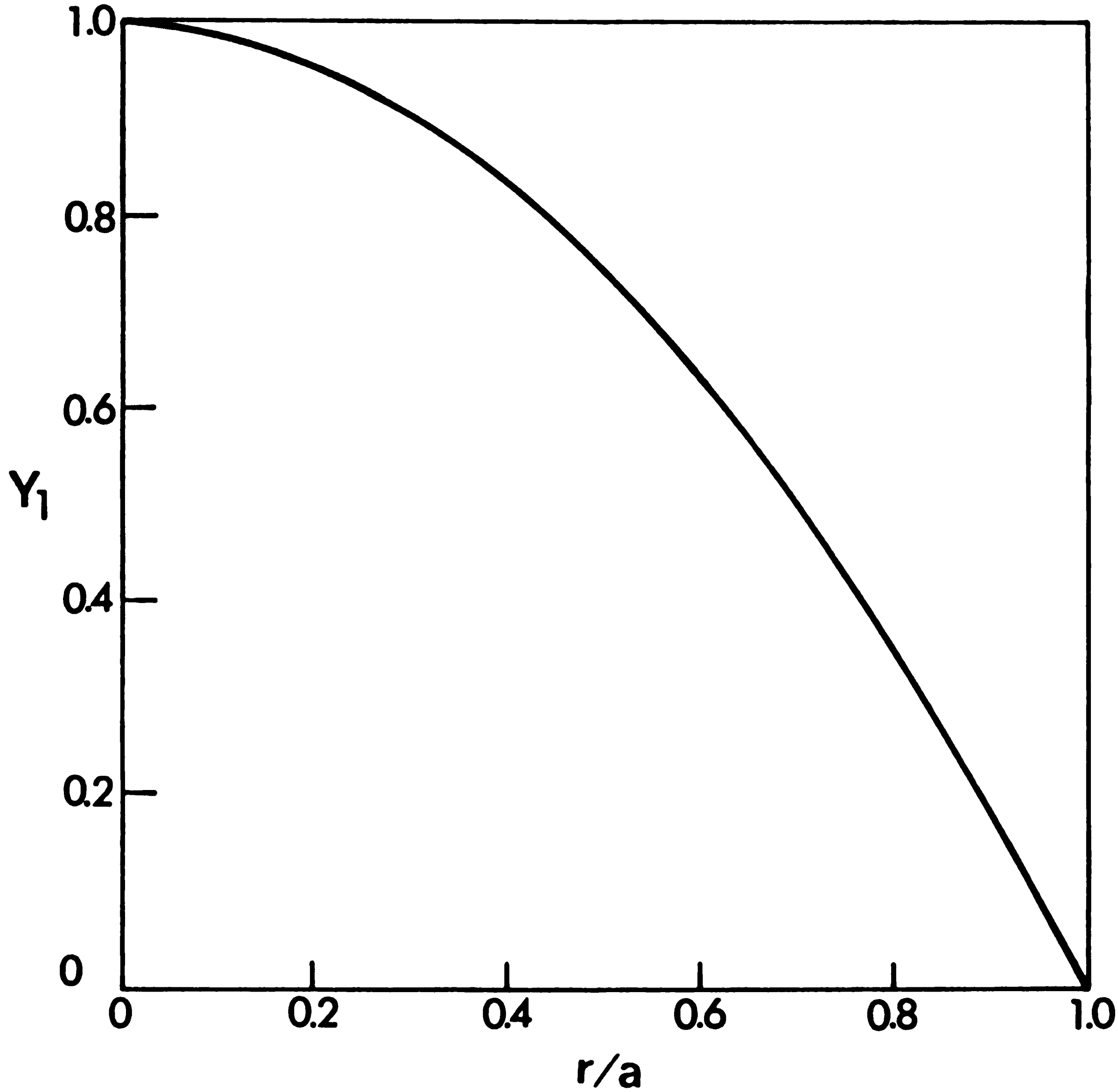

1.0
0.8
0.6
Y1
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1.0
r/a

Fig. 4.2--Electroosmotic Flow

$$Y_2 = \eta \kappa u_{eo}\, \sigma^{-1} (d\Phi/dx)^{-1}$$

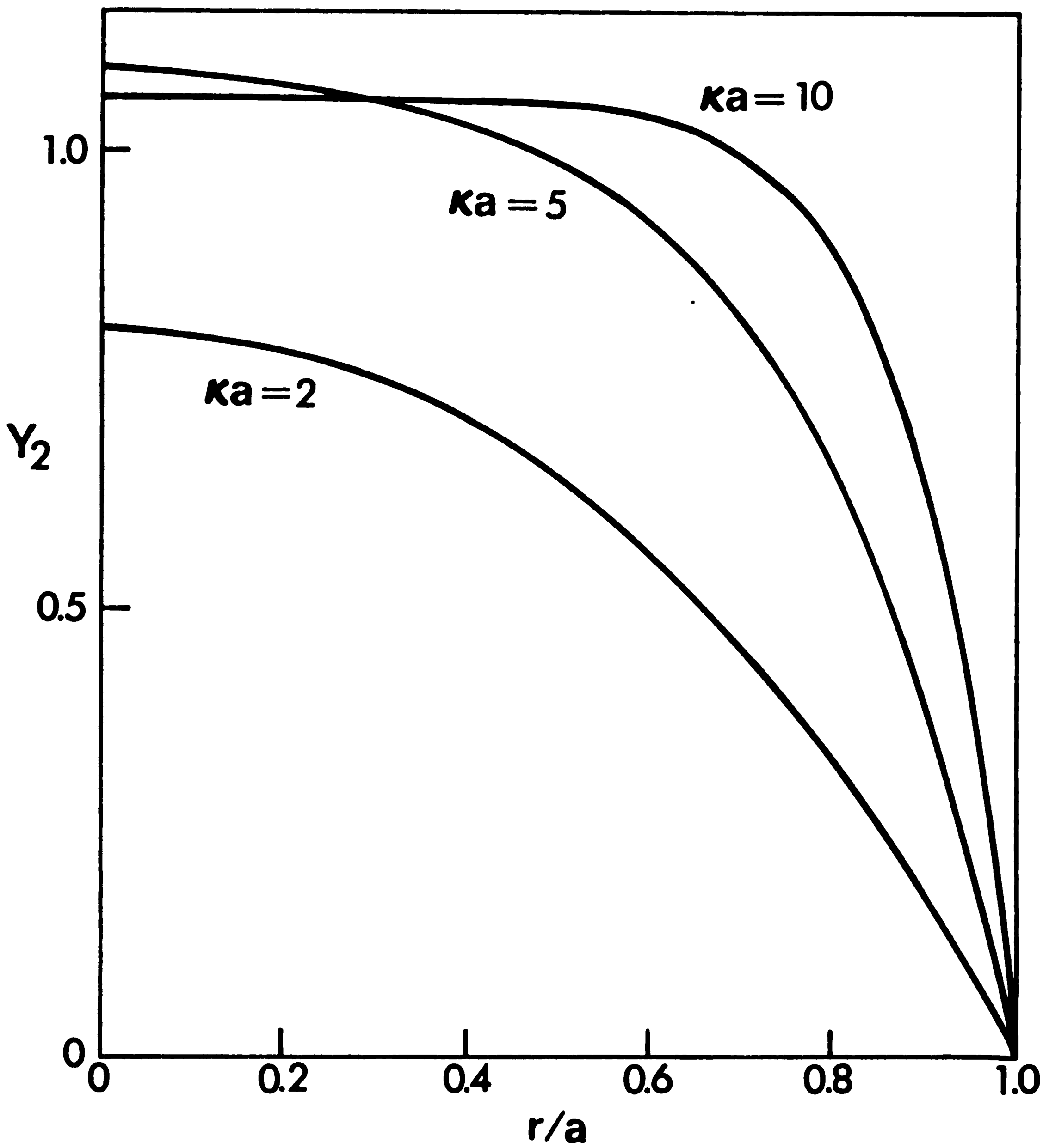
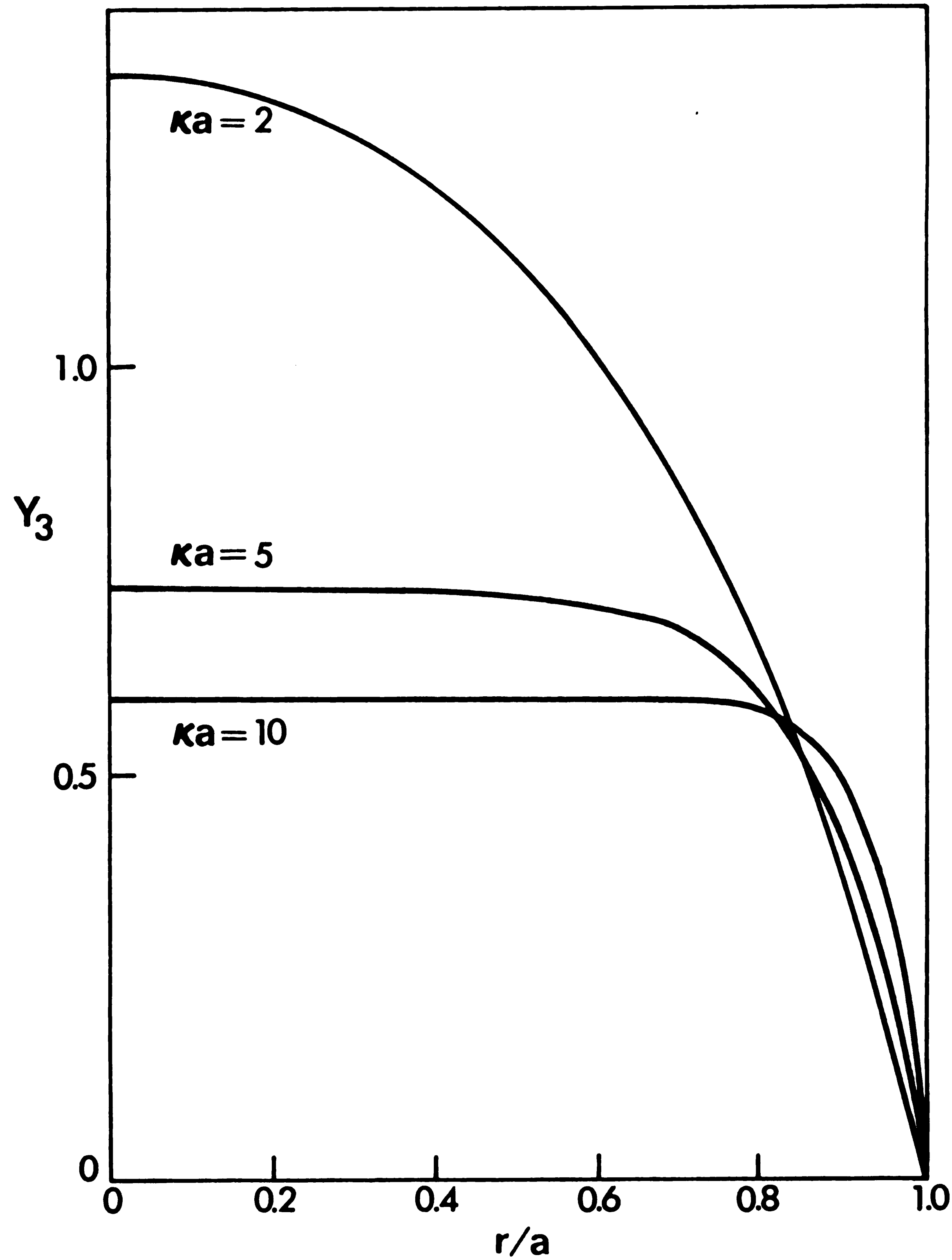

κa = 10
κa = 5
κa = 2
Y2
1.0
0.5
0
0
0.2
0.4
0.6
0.8
1.0
r/a

Fig. 4.3--Capillary Osmotic Flow

$$Y_3 = 4\eta\kappa^2\varepsilon\sigma^{-2}u_{co}\ (d\ell nI/dx)^{-1}$$


κa = 2
κa = 5
κa = 10
1.0
0.5
0
Y3
0
0.2
0.4
0.6
0.8
1.0
r/a

case the barycentric velocity is a mixture of these three aforementioned flows.

For large values of κa, the diffuse double layer is relatively thin, and the velocity variation occurs near the wall where the cylindrical geometry is not important. In this case there tends to be a velocity discontinuity at the wall (see Fig. 4.2 and Fig. 4.3), these are the so called electroosmotic slip and capillary osmotic slip respectively.

Asymptotic expansions for $\kappa a >> 1$ show that $I_0(\kappa r)/I_0(\kappa a)$, $I_0(\kappa r)/I_1(\kappa a)$ and $I_1(\kappa r)/I_1(\kappa a)$ are negligible, except in the double layer region very close to the wall. Asymptotic expansion also yields

$$[I_0(\kappa a)/I_1(\kappa a)] = 1 + (1/2\kappa a) + (3/8\kappa^2 a^2) + \dots \ , \tag{4.41}$$

Hence, in the limit of large κa, the electroosmotic velocity in (4.40) reduces to

$$u_{eo} = (\sigma/\eta\kappa)(d\Phi/dx) \ , \tag{4.42}$$

which is the same as the classical electroosmotic slip velocity given by Helmholtz (1879) and Smoluchowski (1914). The capillary osmotic velocity in (4.40) reduces to, in the limit of large κa,

$$u_{co} = - (\sigma^2/8\eta\kappa^2\varepsilon)(d\ell nI/dx) \ , \tag{4.43}$$

which is consistent with the capillary osmotic slip velocity for flat double layers given by Derjaguin, et al. (1947, 1961, 1965, 1969, 1971, 1972, 1974). This last statement will be justified in the next section.

One thing we like to stress here is that the capillary osmotic velocity contains charge density square term [see (4.40) and (4.43)], which implies that as long as the axial concentration gradient is fixed, the capillary osmotic flow will be in one direction only no matter what the sign of the fixed charges on the capillary wall is. This is also consistent with the results given by Derjaguin, et al. (1969).

F. Comparison with Derjaguin's Formulation

Derjaguin, et al. (1961, 1969) and Dukhin and Derjaguin (1964) derived, by the method of discontinuous nonequilibrium thermodynamics, the formula for capillary osmosis of dilute electrolyte solutions along a flat surface. Their capillary osmotic velocity is expressed as, for a binary electrolyte,

$$u_{co} = - (\nu^+\xi^+ + \nu^-\xi^-)(\frac{c}{\eta}) RT (d\ell nc/dx) \tag{4.44}$$

where ν^+ and ν^- are the number of cations and anions per molecule with $c = (c_+^0/\nu^+) = (c_-^0/\nu^-)$, where c_+^0 and c_-^0 are the ion concnetrations in the bulk. Also

$$\xi^{\pm} = (c_{\pm}^{0}(x))^{-1} \int_0^{\infty} [c_{\pm}(h,x) - c_{\pm}^{0}(x)]hdh \ , \tag{4.45}$$

where $c_{\pm}(h,x)$ are the ion concentrations at a distance h from the slip plane and $c_{\pm}^{0}(x)\xi^{\pm}$ are the moments of adsorption of ions relative to the slip plane with x the coordinate along the flat surface. Combining (4.44) and (4.45), their capillary osmotic velocity on a flat surface becomes

$$u_{co} = -\eta^{-1}RT(d\ell nc/dx) \int_0^{\infty} [\sum_{\alpha=+}^{-} c_{\alpha}(h,x) - \sum_{\alpha=+}^{-} c_{\alpha}^{0}(x)]hdh \ . \tag{4.46}$$

In fact, in our previous derivation, if we use (4.37) and the Boltzmann distribution from (4.19) without expanding the exponentials, we obtain, instead of (4.38),

$$(\partial P'(x,r)/\partial x) = [\sum_{\alpha=2}^{\nu} c_{\alpha}(x,r) - \sum_{\alpha=2}^{\nu} c_{\alpha}^{0}(x)]RT(d\ell nI/dx)$$

$$- F\sum_{\alpha=2}^{\nu} c_{\alpha}z_{\alpha}(\partial\psi(x,r)/\partial x) \ . \tag{4.47}$$

Substituting (4.47) into (4.8), the general form of the capillary osmotic velocity in a circular capillary is obtained

$$u_{co} = \eta^{-1}RT(d\ell nI/dx) \int_a^{r} (dr)r^{-1} \int_0^{r} (dr)r[\sum_{\alpha=2}^{\nu} c_{\alpha}(x,r) - \sum_{\alpha=2}^{\nu} c_{\alpha}(x)] \ . \tag{4.48}$$

This is similar to Derjaguin's formula for flat surface, (4.45). But (4.48) results from the Boltzmann distribution and a hychodynamic approach.

The point we wish to demonstrate here is that when a Boltzmann distribution is assumed and linearization is applied as we did in previous sections, (4.46) due to Derjaguin, et al. (1961, 1969) becomes identical with our limiting equation (4.43).

Similar to (4.19), the Boltzmann distribution for a flat surface is

$$c_\alpha(h,x) = c_\alpha^0 \exp\{- z_\alpha \Psi\} \tag{4.49}$$

with h the distance from the shear plane. According to Overbeek (1952), when linearization is applicable, the potential distribution near a flat surface obtained from solving Poisson-Boltzmann equation with boundary conditions similar to (4.29) reads

$$\Psi(h,x) = (\sigma F/\kappa \varepsilon RT) \exp\{- \kappa h\} \ , \tag{4.50}$$

where κ is still defined by (4.28). Substitution of (4.49) and (4.50) into (4.46) yields the capillary osmotic slip velocity

$$u_{co} = - (\sigma^2/8\eta\kappa^2\varepsilon)(d\ell nI/dx) \ , \tag{4.51}$$

where we have used, for this binary electrolyte case

$$(d\ell nI/dx) = (d\ell n[c(\nu_+z_+^2+\nu_-z_-^2]/dx)/2 = (d\ell nc/dx). \quad (4.52)$$

(4.51) is exactly the same as our limiting equation (4.43). This implies that our equation is consistent with that given by Derjaguin, et al. (1961, 1969) and it serves as a check of the validity of our more general expressions (4.40) and (4.48) for the multicomponent electrolytes capillary osmosis in circular charged capillaries.

G. Conclusion

A general analytical expression for the capillary osmotic velocity of multicomponent electrolyte solution in a charged circular capillary has been derived from hydrodynamic consideration by taking into account the concentration polarization of the electrical double layer near the capillary wall. In the limit of very large radius to Debye length ratio our equation reduces to one which is consistent with that obtained by Derjaguin, et al. (1961, 1969) for flat surfaces from thermodynamic considerations.

It is possible to obtain a similar expression for nonelectrolyte systems by taking into account the concentration polarization of the mobile adsorption layer near the wall, as long as the distribution of surface molecular force field can be formulated. Some experimental evidence of capillary osmosis for nonelectrolytes has been observed by Cleland (1966).

Capillary Osmosis is a general phenomenon whenever there are a mobile ionic or molecular adsorption layer and a tangential concentration gradient present. Study of this process can be valuable for analysis of the structure of ionic double layers and of adsorbed molecular layers at solid and solution interface.

For diffusion through porous media, it is necessary to take into account this capillary osmotic process. It can be very important in cases of transport of electrolyte solutions through porour charged membranes generated only by concentration gradients. A detailed account of its relation with anomalous osmosis in porous charged membrane will be presented in the next chapter.

CHAPTER V

ANOMALOUS OSMOSIS THROUGH CHARGED POROUS MEMBRANES

A. Introduction

Osmotic transport of a nonelectrolyte solution through a membrane or of an electrolyte solution through an uncharged membrane occurs if the membrane acts to some extent as a barrier to the solute (see Chapter III) and if there is a difference of concentration across the membrane. The rate of transport is, in those cases, proportional to the difference in the chemical potential of the solvent; i.e., the rate is roughly proportional to the concentration difference of solute on the two sides of the membrane. Moreover, the direction of transport is toward the more concentrated solution. However, for a charged porous membrane which allows convective transfer of the solution and which separates electrolyte solutions of different concentrations, the rate of osmotic transport appears to be greater and exhibits anomalous behavior.

When the concentration ratio of the two solutions (both maintained at atmospheric pressure) is fixed and flow rate is measured for different mean concentrations, the plot of flow rate against the logarithm of concentration is an N-shaped curve (see Figs. 5.1 and 5.2). The flow rate for medium concentrations is higher than for more concentrated solutions (anomalous positive osmosis). In some cases, the flow occurs toward the less concentrated solution (anomalous negative osmosis). These phenomena, now known collectively as "anomalous osmosis" do not occur in strictly semipermeable membranes.

Anomalous osmosis was first described by Dutrochet (1835) and later by Graham (1854). Since then various transport theories have been developed (cf. Loeb, 1922; Sollner, 1930; Grim and Sollner, 1957; Schlögl, 1955; Kobatake and Fujita, 1964; Toyoshima, Kobatake and Fujita, 1967; Fujita and Kobatake, 1968; Tusaka, et al., 1969; Kedem and Katchalsky, 1961; Dorst, et al., 1964) to describe the mechanism of anomalous osmosis. They are generally of three types:

(a) Loeb (1922), Sollner (1930), Grim and Sollner (1957), and Kobatake and Fujita (1964) recognized the electrochemical nature of this phenomenon. Their theories are based on the idea that electro-osmosis, caused by the diffusion potential across the membrane, is superposed on ordinary osmotic flow which is due to the difference in solute concentration. Grim and Sollner (1957) carried out careful and exact measurements of anomalous osmosis of various electrolyte solutions across oxyhemoglobin-coated collodion membranes, which have clearly defined isoelectric points. By adjusting the PH of the electrolyte solution, the membrane can be negatively or positively charged. The total osmotic flow is composed of a normal component and an abnormal component. The normal flow due to ordinary osmosis was estimated by using the electrolyte as its own reference under conditions of zero net charge on the membrane. Kobatake and Fujita formulated a more quantitative theory by considering a charged capillary model for the porous membrane. They obtained an explicit concentration dependence of the elctroosmotic coefficient. Their theory is successful in predicting the shape of the curve for the anomalous osmosis data obtained by Grim and Sollner (1957). However, their theory cannot cope with the experimental observation that, for KCl solutions, the osmotic flow is in only one direction (toward the more concentrated solution) for both positively and negatively charged membranes. That is they predict (incorrectly) that the direction of flow is determined by the sign of the charge.

(b) Schlögl (1955) and Toyoshima, Kobatake and Fujita (1967) used a one-dimensional treatment and ignored the interactions between ions and solvent. They also made arbitrary assumptions on activity and mobility of ions in the membrane. They assumed that the pressure gradient set up inside the membrane together with the electrostatic potential gradient combine to produce observed flow. Toyoshima, Kobatake and Fujita (1967) succeeded in predicting some experimental observations, but they did not resolve the discrepancy mentioned in (a).

(b) Kedem and Katchalsky (1961), Dorst, et al. (1964) and Tasaka, et al. (1969) used the discontinuous non-equilibrium thermodynamic approach. Anomalous osmosis was attributed to cross terms in the one dimensional phenomenological equations. The observed flow behavior was attributed to frictional interaction between solvent and ions. This "black box" type of theory suffers the same difficulties mentioned in Chapter III.

Although these three types of theories are satisfactory in some respects, they are all inadequate in one way or another. Moreover, the conditions of the numerous experiments so far reported are usually not well defined.

All previous authors have omitted the capillary osmotic contribution described in the last Chapter. The concentration gradient imposed across the membrane in general causes concentration polarization of the electrical double layer along the pore wall and sets up an additional center of mass movement by capillary osmosis. In the absence of externally applied gradients of pressure and electric potential (in fact this is the usual experimental conditions for studying anomalous osmosis), the rate of capillary osmosis is of the same order of magnitude as the rate of electroosmosis due to the diffusion potential. The possible contribution of electroosmosis to the mechanism of anomalous osmosis was realized long ago (Loeb, 1922; Sollner, 1930; Grim and Sollner, 1957; Kobatake and Fujita, 1964), but this is the first time that capillary osmotic contribution has been considered.

In this chapter, we use the continuous approach and the capillary osmosis results of Chapter IV and derive, without recourse to most of the restrictive simplifications required by previous workers, a phenomenological theory for the capillary membrane model which correctly predicts the direction and magnitude of flow for KCl solutions through positively and negatively charged porous membranes.

The system consists of a moderately charged membrane which separates two aqueous uni-univalent electrolyte solutions of different concentrations (with $c^B > c^A$) at the same temperature and in the absence of an external hydrostatic pressure difference. The membrane is assumed to contain a bundle of charged capillaries of equal radius $\underline{a}$ which is large enough to permit a diffuse double layer on the capillary walls but small compared to the thickness $\underline{\ell}$ of the membrane. We assume the unstirred layer thickness on the two sides of the membrane has been minimized by effective stirring and can be ignored here.

B. Phenomenological Equations of Anomalous Osmosis

We confine our discussion to the system which separates two aqueous solutions containing the solvent molecules and the same single uni-univalent electrolyte. Positive ions and negative ions are denoted by + and -, respectively. The solvent (water) is denoted by w.

The one dimensional modified Nernst-Planck equation is, from Appendix A,

$$N_\alpha = -\, z_\alpha \omega_\alpha c_\alpha F(\partial\phi/\partial x) - D_\alpha(\partial c_\alpha/\partial x) - B_\alpha(\partial p/\partial x) + c_\alpha u_x \,, \qquad \alpha=+,- \,. \tag{5.1}$$

As shown in the appendix, this equation is valid only for dilute solutions. The absolute mobility ω_α is related to the ionic conductance λ_α by $\omega_\alpha = (\lambda_\alpha/|z_\alpha|F^2)$. By (A.19),

D_α the diffusion coefficient of α is related to the binary Fickian diffusion coefficient D and to the mobilities by

$$D_\alpha = D + z_\alpha \omega_\alpha RT(\omega_+ - \omega_-)(z_+\omega_+ - z_-\omega_-)^{-1} , \quad \alpha=+,- . \tag{5.2}$$

The pressure term coefficnet is defined by (A.23) as

$$B_\alpha = \nu_\alpha (c_+v_+ + c_-v_-)(D/\nu RT) + c_\alpha z_\alpha \omega_\alpha (v_+\omega_+ - v_-\omega_-)(z_+\omega_+ - z_-\omega_-)^{-1} . \tag{5.3}$$

The electric current and the solute flux of the electrolyte component both relative to the capillary wall are defined by

$$i = F \sum_{\alpha=+}^{-} z_\alpha N_\alpha , \tag{5.4}$$

$$N_s = \sum_{\alpha=+}^{-} N_\alpha . \tag{5.5}$$

The volume flow rate of the liquid which permeates through unit area of the membrane is defined by

$$J_V = N_+v_+ + N_-v_- + N_w v_w \tag{5.6}$$

where v_+, v_- and v_w are the partial molar volumes. With the help of (2.7) and (2.9), (5.6) can be rearranged to

$$J_V = (v_+ - M_+v_w/M_w)(N_+ - c_+u_x) + (v_- - M_-v_w/M_w)(N_- - c_-u_x) + u_x \tag{5.7}$$

By (5.4) and (5.1), for the uni-univalent case,

$$i = -\ (\omega_+ c_+ + \omega_- c_-)F^2(\partial\phi/\partial x)\ -\ FD_+(\partial c_+/\partial x) + FD_-(\partial c_-/\partial x)$$

$$-\ F(B_+ - B_-)(\partial p/\partial x)\ +\ F(c_+ - c_-)u_x\ , \qquad (5.8)$$

with

$$B_+\ -\ B_-\ =\ (c_+\omega_+ - c_-\omega_-)(v_+\omega_+ - v_-\omega_-)(\omega_+ + \omega_-)^{-1}\ . \qquad (5.9)$$

Likewise,

$$N_s\ =\ -\ (c_+\omega_+ - c_-\omega_-)F(\partial\phi/\partial x)\ -\ D_+(\partial c_+/\partial x)\ -\ D_-(\partial c_-/\partial x)$$

$$-\ (B_+ + B_-)(\partial p/\partial x)\ +\ (c_+ + c_-)u_x\ , \qquad (5.10)$$

with

$$B_+ + B_-\ =\ (c_+ v_+ + c_- v_-)(D/RT)\ +\ (c_+\omega_+ + c_-\omega_-)(v_+\omega_+ - v_-\omega_-)(\omega_+ + \omega_-)^{-1}\ . \qquad (5.11)$$

Substitution of the Boltzmann equation (4.19) for the ion concentration with the exponential expanded up to the linear term, separation of the electric potential and pressure according to (4.5) and (4.6) and use of (4.30) and (4.38) for the electrical potential and pressure distribution in the charged capillary transforms (5.8) and (5.10) into

$$
\begin{aligned}
i = & - c\, F^2\{(\omega_+ + \omega_-) - (\omega_+ - \omega_-)\Psi\}(d\Phi/dx) \\
& + \{-F^2[(\omega_+ + \omega_-) - (D_+ + D_-)/RT][rI_1(\kappa r)/I_1(\kappa a) \\
& - aI_0(\kappa r)I_0(\kappa a)/I_1^2(\kappa a)](\sigma/2\varepsilon) - F(D_+ - D_-) \\
& + F(D_+ + D_-)\Psi - FRTC\ [(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} - \Psi](v_+\omega_+ - v_-\omega_-)\Psi^2 \\
& - (F^2 c\ \sigma/\varepsilon)[(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} - \Psi](v_+\omega_+ - v_-\omega_-)\Psi[rI_1(\kappa r)/I_1(\kappa a) \\
& - aI_0(\kappa r)I_0(\kappa a)/I_1^2(\kappa a)]\}(dc\ /dx) \\
& - Fc\ [(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} - \Psi](v_+\omega_+ - v_-\omega_-)(dP/dx) - 2c\ F\Psi u_x\ ,
\end{aligned}
\tag{5.12}
$$

$$
\begin{aligned}
N_s = & - c\ F\{(\omega_+ - \omega_-) - (\omega_+ + \omega_-)\Psi\}(d\Phi/dx) \\
& + \{[(\omega_+ + \omega_-) - (D_+ + D_-)/RT](\sigma\Psi/2\varepsilon)[rI_1(\kappa r)/I_1(\kappa a) \\
& - aI_0(\kappa r)I_0(\kappa a)/I_1^2(\kappa a)] - (D_+ + D_-) + (D_+ - D_-)\Psi \\
& - [Dc\ (v_+ + v_-) - Dc\ (v_+ - v_-)\Psi + RTc[(\omega_+ + \omega_-) - (\omega_+ - \omega_-)\Psi] \\
& \times (v_+\omega_+ - v_-\omega_-)(\omega_+ + \omega_-)^{-1}]\Psi^2 \\
& - (Fc\ \sigma/\varepsilon)[((v_+ + v_-) - (v_+ - v_-)\Psi)D/RT + (\omega_+ + \omega_-) - (\omega_+ - \\
& \omega_-)\Psi](v_+\omega_+ - v_-\omega_-)(\omega_+ + \omega_-)^{-1}\Psi \\
& \times [rI_1(\kappa r)/I_1(\kappa a) - aI_0(\kappa r)I_0(\kappa a)/I_1^2(\kappa a)]\}(dc\ /dx) \\
& - \{Dc\ (v_+ + v_-) - Dc\ (v_+ - v_-)\Psi + RTc\ [(\omega_+ + \omega_-) \\
& - (\omega_+ - \omega_-)\Psi](v_+\omega_+ - v_-\omega_-)(\omega_+ + \omega_-)^{-1}\}(dP/dx) \\
& + 2c\ u_x
\end{aligned}
\tag{5.13}
$$

with

$$\kappa = (2F^2 c\ /\varepsilon RT)^{1/2} \tag{5.14}$$

and

$$\Psi = F\psi/RT = \sigma I_0(\kappa r)/\kappa\varepsilon I_1(\kappa a) \quad , \tag{5.15}$$

where we have used

$$(\partial\psi/\partial x) = (\sigma/2\varepsilon)[rI_1(\kappa r)/I_1(\kappa a) - aI_0(\kappa r)I_0(\kappa a)/I_1^2(\kappa a)](d\ell nc\ /dx) \quad . \tag{5.16}$$

For this uni-univalent electrolyte, the center of mass velocity u_x is given by (4.40)

$$\begin{aligned} u_x = {} & (4\eta)^{-1}(r^2-a^2)(dP/dx)+[\sigma/\eta\kappa I_1(\kappa a)][I_0(\kappa a)-I_0(\kappa r)](d\Phi/dx) \\ & + [\sigma^2/4\eta\kappa^2\varepsilon I_1^2(\kappa a)]\{(\kappa r)^2[I_0^2(\kappa r)-I_1^2(\kappa r)] \\ & - (\kappa r)I_0(\kappa r)I_1(\kappa r)-(\kappa a)^2[I_0^2(\kappa a)-I_1^2(\kappa a)] \\ & + (\kappa a)I_0(\kappa a)I_1(\kappa a)\}(d\ell nc\ /dx) \quad . \end{aligned} \tag{5.17}$$

The use of (4.30) for the electric potential tacitly implies that κa, the ratio of capillary radius to Debye length, is larger than unity. Equations (5.12), (5.13) and (5.17) constitute the phenomenological description of local membrane-referenced fluxes along a particular streamline in the capillary tube. It is important to note that after the substitution of (5.14) and (5.15), the coefficient matrix of (5.12), (5.13) and (5.17) is not symmetric simply because the sum of product of the fluxes and forces are chosen in this way only for experimental convenience. One must not forget, however, that the local phenomenological coefficient matrix of (A.7) is still symmetric.

C. Practical Equation for the Volume Flow

In this section, we average the steady state fluxes over the capillary cross section, combine the phenomenological equations of the last section, solve the resulting equations subject to the appropriate boundary conditions and derive a practical equation for the volume flow across charged capillary membranes.

The fluxes are averaged over the capillary cross section by means of the relations

$$\bar{u}_x = \int_0^a 2\pi r u_x dr / \int_0^a 2\pi r dr \ , \tag{5.18}$$

$$\bar{i} = \int_0^a 2\pi r i dr / \int_0^a 2\pi r dr \ , \tag{5.19}$$

$$\bar{N}_s = \int_0^a 2\pi r N_s dr / \int_0^a 2\pi r dr \ , \tag{5.20}$$

$$\bar{J}_V = \int_0^a 2\pi r J_V dr / \int_0^a 2\pi r dr \ . \tag{5.21}$$

Introduction of (5.17) into (5.18) leads to

$$\bar{u}_x = A_{11}(dP/dx) + A_{12}(d\Phi/dx) + A_{13}(d\ell nc\ /dx) \ , \tag{5.22}$$

where the coefficients are

$$A_{11} = -\ a^2/8\eta \ ,$$

$$A_{12} = \sigma(\kappa\eta)^{-1}\{[I_0(\kappa a)/I_1(\kappa a)]-2\kappa a\} \ ,$$

$$A_{13} = \sigma^2(12\eta\varepsilon\kappa^2)^{-1}\{(\kappa a)[I_0(\kappa a)/I_1(\kappa a)]$$
$$-\ (\kappa a)^2[I_0^2(\kappa a)/I_1^2(\kappa a)] + (\kappa a)^2-1\} \ , \tag{5.23}$$

and where we have used integration formulas from the literature (Hildebrand, 1962)

$$\int_0^x xI_0(x)\,dx = xI_1(x) \ ,$$

$$\int_0^x xI_0^2(x)\,dx = \frac{1}{2}\, x^2[I_0^2(x)-I_1^2(x)] \ ,$$

$$\int_0^x x^2I_0(x)I_1(x)\,dx = \frac{1}{2}\, x^2I_1^2(x) \ , \qquad (5.24)$$

and some previously unpublished formulas derived by us (see Appendix B)

$$\int_0^x x^3I_1^2(x)\,dx = (1/3)\{\tfrac{1}{2}x^4[I_0^2(x)-I_1^2(x)]+x^3I_0(x)I_1(x)-x^2I_1^2(x)\} \ , \qquad (5.25)$$

$$\int_0^x x^3I_1^2(x)\,dx = (1/3)\{2x^3I_0(x)I_1(x)-2x^2I_1^2(x)-\tfrac{1}{2}x^4[I_0^2(x)-I_1^2(x)]\} \ . \qquad (5.26)$$

It is interesting to note that the electroosmotic coefficient A_{12} and the capillary osmotic coefficient A_{13} are complicated functions of salt concentration through the concentration dependence of κ. Among existing theories only Kobatake and Fujita (1964) take the concentration dependence of the electroosmotic coefficient into account. None consider the capillary osmotic coefficient, which might have the same order of magnitude as the electro-osmotic coefficient. As we see later, both effects are essential to describe anomalous osmotic flow behavior observed in charged porous membranes.

Substitution of (5.12) into (5.19) and utilization of (5.22) yields

$$\bar{I} = A_{21}(dP/dx) + A_{22}(d\Phi/dx) + A_{23}(d\ell nc\ /dx), \qquad (5.27)$$

with the coefficients

$$A_{21} = \sigma(\kappa\eta)^{-1}[(I_0(\kappa a)/I_1(\kappa a))-2\kappa a]-(Fc^0a^2/2)(\omega_+-\omega_-)(v_+\omega_+-v_-\omega_-)(\omega_++\omega_-)$$
$$+ \sigma a(v_+\omega_+-v_-\omega_-)/2 \ ,$$

$$A_{22} = (\omega_+-\omega_-)(\sigma F/a) - F^2c\ (\omega_++\omega_-)+\sigma^2\eta^{-1}[I_0^2(\kappa a)/I_1^2(\kappa a)]$$
$$- \sigma^2\eta^{-1}[1+2\kappa a(I_0(\kappa a)/I_1(\kappa a))] \ ,$$

$$A_{23} = [F^2(\omega_++\omega_-)-F^2(D_++D_-)/RT](\sigma/Fa)-Fc\ (D_+-D_-)+(D_++D_-)(\sigma/a)$$
$$- c\ (\sigma RTa^2/2\kappa\varepsilon)(v_+\omega_+-v_-\omega_-)\{[I_0^2(\kappa a)/I_1^2(\kappa a)]-1\}(\omega_+-\omega_-)(\omega_++\omega_-)^{-1}$$
$$+ [F^2\sigma^3c\ /a^2RT\kappa^3\varepsilon^2I_1^3(\kappa a)]\int_0^{\kappa a} xI_0^3(x)\,dx$$
$$- (F\sigma^2c\ /2\varepsilon)(\omega_+-\omega_-)(\omega_++\omega_-)^{-1}(\omega_+v_+-\omega_-v_-)\{1-\kappa a[I_0^3(\kappa a)/I_1^3(\kappa a)$$
$$- (I_0(\kappa a)/I_1(\kappa a))]\}$$
$$+[F^2\sigma^3c\ /a^2RT\kappa^3\varepsilon^2I_1^3(\kappa a)][\int_0^{\kappa a} x^2I_0^2(x)I_1(x)\,dx$$
$$- (\kappa aI_0(\kappa a)/I_1(\kappa a))\int_0^{\kappa a} xI_0^3(x)\,dx]$$
$$- [2\eta\varepsilon\kappa I_1^3(\kappa a)]^{-1}(\kappa a)^{-2}[(\kappa a)^2I_0(\kappa a)I_1^2(\kappa a)$$
$$- (\kappa a)^3I_0(\kappa a)I_1(\kappa a) + (2/3)(\kappa a)^3I_1^3(\kappa a)$$
$$- \int_0^{\kappa a} x^3I_0^3(x)\,dx - \int_0^{\kappa a} x^2I_0^2(x)I_1(x)\,dx \ , \qquad (5.28)$$

where in addition to (5.24) - (5.26) we have used the additional integration formulas derived by us (see Appendix B)

$$\int_0^x x^2 I_1(x)\,dx = x^2 I_0(x) - 2xI_1(x) \ , \tag{5.29}$$

$$\int_0^x x^3 I_1^2(x) I_0(x)\,dx = [x^3 I_1^3(x)]/3 \ , \tag{5.30}$$

$$\int_0^x x^3 I_0(x)\,dx = x^3 I_1(x) + 4xI_1(x) - 2x^2 I_0(x) \ , \tag{5.31}$$

$$\int_0^x x^4 I_0(x) I_1(x)\,dx = x^4 I_0^2(x)/6 + x^4 I_1^2(x)/3 - 2x^3 I_1(x) I_0(x)/3 + 2x^2 I_1^2(x)/3 \ . \tag{5.32}$$

Successful calculation of the remaining definite integrals in (5.28) has so far eluded us, except for large κa..

The averaged solute flux is obtained by substituting (5.13) into (5.20)

$$\overline{N}_s = A_{31}(dP/dx) + A_{32}(d\Phi/dx) + A_{33}(d\ell nc\ /dx) \ , \tag{5.33}$$

where the coefficients are

$$A_{31} = Dc\ (RT)^{-1}(v_+ + v_-) + c\ (v_+\omega_+ - v_-\omega_-) + [(v_+ - v_-)D(RT)^{-1} - (\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1}(v_+\omega_+ - v_-\omega_-)](\sigma/Fa) - c\ a^2/4\eta \ ,$$

$$A_{32} = (\sigma/a)(\omega_+ - \omega_-) - Fc(\omega_+ + \omega_-) - 2c\ (\eta\kappa)^{-1}\sigma[2\kappa a - I_0(\kappa a)/I_1(\kappa a)] \ ,$$

$$
\begin{aligned}
A_{33} = {} & (F\sigma^2 c\ /4\varepsilon)\,[(\omega_+ + \omega_-) - (D_+ + D_-)/RT]\{1 - \kappa a[I_0^3(\kappa a)/I_1^3(\kappa a) \\
& - (I_0(\kappa a)/I_1(\kappa a))]\} - c\ (D_+ + D_-) + (D_+ - D_-)\sigma/Fa \\
& - (\sigma RTc\ /4Fa)\,[D(v_+ + v_-) + RT(v_+\omega_+ - v_-\omega_-)] \\
& + [D(v_+ - v_-)/RT - (\omega_+ - \omega_-)(\omega_+ v_+ - \omega_- v_-)(\omega_+ \\
& \quad + \ \omega_-)^{-1}](F\sigma^3 c\ /RT\varepsilon^2\kappa^3 a^2 I_1^3(\kappa a)) \int_0^{\kappa a} x I_0^3(x)\,dx \\
& - (\sigma^2 c\ /2\varepsilon)\,[D(v_+ + v_-)/RT + (v_+\omega_+ - v_-\omega_-)]\{1 - \kappa a[I_0^3(\kappa a)/I_1^3(\kappa a) \\
& - (I_0(\kappa a)/I_1(\kappa a))]\} \\
& + (F\sigma^3/RT\kappa^3\varepsilon^2 I_1^3(\kappa a)\,a^2)\,[(v_+ - v_-)D/RT \\
& + (\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1}(v_+\omega_+ - v_-\omega_-)]\,[\int_0^{\kappa a} x^2 I_0^2 I_1\,dx \\
& - (\kappa a I_0(\kappa a)/I_1(\kappa a)) \int_0^{\kappa a} x I_0^3(x)\,dx]\ . \qquad (5.34)
\end{aligned}
$$

Once again, the coefficient matrix of $A_{\alpha\beta}$ is not symmetric because the fluxes and forces do not preserve the entropy production. They are defined instead for experimental convenience.

At the steady state, the conservation of mass and electricity and the incompressibility of the fluid yield, for the one-dimensional flow considered here, the conditions:

$$d\rho u_x/dx = 0\ ,\ di/dx = 0\ ,\ dN_s/dx = 0\ .$$

These imply that u_x , i and N_s , and hence the averaged flows $\bar{u}_x$, $\bar{I}$ and $\bar{N}_s$, are constant in the x direction across the membrane. In addition if there is no external electric field applied across the membrane, then condition on the electric current $\bar{I} = 0$ must also be applied.

At this point we note that there are no externally applied electrical potential and pressure gradients in the anomalous osmosis experiment. However, the (dP/dx) and (dΦ/dx) terms do not disappear from (5.22), (5.27) and (5.33). The pressure gradient term in these equations now should be the pressure gradient generated by the sharp concentration change at the membrane solution interface. This osmotic pressure gradient drives the solution through the membrane even when there is no hydrostatic pressure difference across the membrane. The fluid inside the membrane pores cannot distinguish between the osmotic pressure gradient and the external hydrostatic pressure gradient, because these two appear together as a single hydrodynamic pressure gradient. Therefore, in the case of anomalous osmosis, (dP/dx) includes only the osmotic pressure gradient. The elctrical potential term includes a diffusion potential caused by the concentration gradient in the membrane. Moreover, Donnan potentials occur at the two membrane-solution interfaces due to the partial impermeability of ions (Helfferich, 1962). As stated in

Section B of Chapter III, the continuous capillary membrane model cannot describe the osmotic effect and the Donnan potential which arise from the concentration discontinuity at the interface (the end of the capillary). However, one can take these effects into account as boundary conditions at the ends of the capillary. We do this in the next section for KCl solution transport through the oxyhemoglobin collodion membrane. If the distribution coefficients, which define the relation between the solute concentrations just inside and outside the membrane boundaries, are the same on both sides of the membrane (This implies constant distribution coefficients.), then the Donnan potential contribution cancel each other, and the electric potential gradient can be approximated by the diffusion potential alone. We assume this.

Accordingly, the appropriate boundary conditions are

$$c = c_A' \text{ at } x = 0^+ \quad \text{and } c = c_B' \text{ at } x = \ell^- \tag{5.35}$$

where 0^+ and ℓ^- indicate the locations just inside the ends of the capillary. The distribution coefficients due to the presence of charge on the capillary are defined by

$$\frac{c_A'}{c_A} = \frac{c_B'}{c_B} = \gamma \tag{5.36}$$

where γ is the distribution coefficient and c_A and c_B are the concentrations just outside the ends of the capillary. The osmotic pressure is defined by

$$\Delta\pi = P(x=\ell^-) - P(x=0^+) = \bar{\sigma}RT(c_B-c_A) \ , \tag{5.37}$$

where $\bar{\sigma}$ is the reflection coefficient defined in Chapter III, which is an experimental parameter measured for an uncharged membrane. As we mentioned in Chapter III, ordinary osmosis is still effective in charged membranes, and the charge produces effects superimposed on it.

Utilizing the asymptotic expansion formula (4.41) together with (cf. Abramowitz and Stegun, 1964)

$$I_0(\kappa a) = (2\pi\kappa a)^{-1/2}\exp(\kappa a)\{1+(8\kappa a)^{-1}+9(2!)^{-1}(8\kappa a)^{-2}+\ldots\}$$

$$I_1(\kappa a) = (2\pi\kappa a)^{-1/2}\exp(\kappa a)\{1-3(8\kappa a)^{-1}-15(2!)^{-1}(8\kappa a)^{-2}+\ldots\} \tag{5.38}$$

for large κa values, expanding those definite integrals in (5.28) which do not have explicit forms, by the mean value theorem, and retaining leading terms, we find that (5.27) reduces to, with the condition $i = 0$,

$$\begin{aligned} d\Phi/dx = [&a^{-1}(D_+ + D_-)\sigma - (D_+ - D_-)Fc - (\sigma RTac\ /2\kappa^2\varepsilon)(v_+\omega_+ - \\ &\quad v_-\omega_-)(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} \\ &- (2\eta\varepsilon\kappa)^{-1}(\kappa a)^2][(\omega_+ + \omega_-)F^2c \\ &- (\omega_+ - \omega_-)\sigma F/a + \sigma^2(\eta\kappa a)^{-1}](d\ell nc\ /dx) \ , \end{aligned} \tag{5.39}$$

where we neglect the small pressure contribution. Eliminating $(d\Phi/dx)$ from (5.22) by (5.39) and using (4.41) and (5.38) again, we obtain

$$\bar{u}_x = A_{11}(dP/dx) + B_1(d\ell nc\ /dx)\ , \tag{5.40}$$

where A_{11} is given by (5.23) and where

$$\begin{aligned} B_1 = {} & \sigma(\kappa\eta)^{-1}[1-3(2\kappa a)^{-1}+3(8\kappa a)^{-2}][a^{-1}(D_+ + D_-) - (D_+ - D_-)Fc \\ & - (\sigma RTac\ /2\kappa\varepsilon^2)(v_+\omega_+ - v_-\omega_-)(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} \\ & - (2\eta\varepsilon\kappa)^{-1}(\kappa a)^2][(\omega_+ + \omega_-)F^2c - (\omega_+ - \omega_-)\sigma F/a + \sigma^2(\eta\kappa a)^{-1}]^{-1} \\ & + \sigma^2(8\eta\varepsilon\kappa^2)^{-1}[(4\kappa a)^{-1} - 1]\ . \end{aligned} \tag{5.41}$$

(5.41) can be integrated across the capillary subject to boundary conditions (5.35), (5.36) and (5.37). This gives

$$\begin{aligned} \bar{u}_x\ell = {} & -(8\eta)^{-1}a^2\Delta\pi + (2\sigma KRT/\eta)\{0.5A\ell n\beta + B(c_B\gamma)^{-1/2}[\beta^{-1/2}-1] \\ & + (2c_B\gamma)^{-1}\bar{D}[\beta^{-1}-1] + E(c_B\gamma)^{3/2}[\beta^{3/2}-1]/3 \\ & + (\bar{F}/2f)\ell n[(fc_B\gamma - g)/(fc_B\gamma\beta - g)] + \Omega\} \\ & + (48\eta\varepsilon a)^{-1}(c_B\gamma)^{-3/2}\sigma^2K^3[\beta^{-3/2}-1] - (8\eta\varepsilon c_B\gamma)^{-1}\sigma^2K^2[\beta^{-1}-1] \end{aligned} \tag{5.42}$$

with

$$\Omega = \bar{F}(-fg)^{-1/2}[\tan^{-1}[-\sqrt{-c_B\gamma fg}\ g^{-1}]-\tan^{-1}[-\sqrt{-c_B\gamma fg}\ g^{-1}] \quad g < 0$$

$$\Omega = (G/2\sqrt{fg})\,\ell n[(\sqrt{fc_B\gamma} - \sqrt{g})(\sqrt{fc_B\gamma\beta}$$

$$+ \sqrt{g})/(\sqrt{fc_B}\gamma+\sqrt{g})(\sqrt{fc_B\gamma\beta} - \sqrt{g})] \quad g > 0 \qquad (5.43)$$

where $K = \sqrt{c}\ \kappa^{-1}$, $\beta = c_A/c_B$

$$b = (D_+ + D_-)\sigma - (2\eta\varepsilon\kappa)^{-1}(\kappa a)^2 ,$$

$$d = (D_+ - D_-)Fa + (\sigma RTa^2/2\kappa^2\varepsilon)(v_+\omega_+ - v_-\omega_-)(\omega_+ - \omega_-)(\omega_+ + \omega_-)^{-1} ,$$

$$f = (\omega_+ + \omega_-)F^2 a ,$$

$$g = (\omega_+ - \omega_-)\sigma F - \sigma^2(\eta\kappa)^{-1} ,$$

$$A = -(3K/2ag)[(bf/g)-d] ,$$

$$B = -(3K^2/8a^2g)[(bf/g)-d]-b/f ,$$

$$\bar{D} = 3Kb/2af ,$$

$$E = -\ 3K^2b/8a^2g ,$$

$$\bar{F} = -\ 3Kb/2ag[(bf/g)-d] ,$$

$$G = -\ d+(3K^2b/8a^2g)[(bf/g)-d]+bf/g . \qquad (5.44)$$

For the case of KCl , $D_+ - D_- = RT(\omega_+ - \omega_-) \approx 0$, and the above procedure yields

$$\bar{u}_x \ell = -(8\eta)^{-1}a^2\Delta\pi + (2\sigma KRT/\eta)\{b(3f)^{-1}(c_B\gamma)^{-3/2}(\beta^{-3/2}-1) - (3Kb/8af)(c_B\gamma)^{-2}(\beta^{-2}-1) + (3K^2b/40af)(c_B\gamma)^{-5/2}(\beta^{-5/2}-1)\} + (\sigma^3K^3/48\eta\varepsilon a)(c_B\gamma)^{-3/2}(\beta^{-3/2}-1) - (\sigma^2K^2/8\eta\varepsilon)(c_B\gamma)^{-1}(\beta^{-1}-1) \quad . \tag{5.45}$$

The volume flow rate through the capillary can be calculated by combining (5.6), (5.7) and (5.21) and then integrating across the capillary from 0 to ℓ , there follows

$$\bar{J}_V \ell = \{bj'(fc_B\gamma)^{-1}(\beta^{-1}-1) + \ell k' f^{-1} \ell n\beta\} - j'' \ell n\beta - k'' c_B\gamma(1-\beta) + \bar{u}_x \ell \quad , \tag{5.46}$$

where

$$j' = [\omega_+(v_+ - M_+ v_w/M_w) - \omega_-(v_- - M_- v_w/M_w)](\sigma/a) \quad ,$$

$$k'' = F[\omega_+(v_+ - M_+ v_w/M_w) + \omega_-(v_- - M_- v_w/M_w)] \quad ,$$

$$j'' = [D_+(v_+ - M_+ v_w/M_w) - D_-(v_- - M_- v_w/M_w)](\sigma/aF) \quad ,$$

$$k'' = D_+(v_+ - M_+ v_w/M_w) + D_-(v_- - M_- v_w/M_w) \quad , \tag{5.47}$$

and where we have neglected the pressure term from (5.1) because of its smallness compared to the pressure contribution from $\bar{u}_x$. The true volume folw rate $\bar{J}'_V$ across membrane of unit area is then given by

$$\bar{J}'_V = \bar{\varepsilon}\,\bar{J}_V \tag{5.48}$$

where $\bar{\varepsilon}$ is the porosity of the membrane.

It is interesting to note that for equal or nearly equal cation and anion diffusivities and mobilities, the averaged center of mass velocity depends on σ^2 , the charge density squared, as shown in (5.45) (the parameter b is proportion to σ). This implies that for uni-univalent electrolytes of equal ion diffusivities, the averaged center of mass velocity is independent of the sign of the charge on the wall. This has an important bearing on the concentration dependence of the volume flow rate of KCl solution through charged porous membranes.

Before considering the experimental data of Grim and Sollner (1957) we remark that they determined osmotic flow rates from the volume changes of liquid transported through the membrane in an intervals of time in which the solution concentrations on the two sides of the membrane were maintained effectively constant. There has been some misuse of the averaged center of mass movement as the volume flow (Gross and Osterle, 1968; Fair and Osterle, 1971); however, only the volume flux defined by (5.46) and (5.48) is experimentally measurable.

D. Comparison with Grim and Sollner's Experimental Data

Grim and Sollner (1957) made careful measurements of anomalous osmosis of various electrolyte solutions across oxyhemoglobin-coated, highly porous, collodion membranes which had clearly defined isoelectric points. By adjusting the pH of the electrolyte solution, the membrane can be put into a negatively or a positively charged state. The total osmotic flow is composed of a normal component and an abnormal component. The normal flow due to ordinary osmosis was estimated by the use of the electrolyte as its own reference under conditions of zero net charge on the membrane. We are interested in interpreting their observations on KCl solutions. Their data on KCl show that the volume flow is in the positive direction only (toward the more concentrated solution) for both positively and negatively charged membranes. This was not explainable by previous theories.

According to their study for 25°C, the measured volume flow rates were of the order of 10 to 100 microliters/ cm^2-hr. The membranes were about 10^{-2} cm thick, the water content was 60 to 75 volume percent and the porosity of the membrane was approximately 0.6 to 0.75. The average pore radius was not given; instead, they did filtration rate studies. With 10 cm of water pressure head, the average rate of filtration was 12.3 microliters/cm^2-hr. Both the Poiseville volume flow formula for straight capillaries

$$\bar{J}_V = \bar{\varepsilon} a^2 \Delta p / 8 \eta \ell \tag{5.49}$$

and the Konzey-Carman law for porous media (Carman, 1948)

$$a = \frac{1}{2} \sqrt{(80 J_V \eta \ell / \bar{\varepsilon} \Delta p)} \tag{5.50}$$

yield values for the pore radius of the order of 10^{-8} m, or 100 Å (generally, the Konzey-Carman law gives value lower than those given by Poiseville's law). The data obtained for ordinary osmosis of KCl through uncharged membranes is used together with (5.37) to determine the reflection coefficient $\bar{\sigma}$. From the plot of the observed volume flow J_V vs. the osmotic gradient for a single capillary, $a^2 RT(c_B - c_A)/4\eta\ell$, the reflection coefficient is $\bar{\sigma} = .08 \times 10^{-3}$. The smallness of this reflection coefficient indicates that only a small amount of solute molecules is rejected by the uncharged membrane. This is due to the presence of relatively large pores. The diffusion coefficients of K^+ ion and Cl^- ion in aqueous solution and similarly their mobilities are almost equal (Miller, 1966; Haase, 1969), $D_{K^+} \cong D_{Cl^-} = 2.01 \times 10^{-9}$ m^2/s. However, there is ample evidence that the values of diffusion coefficients in membranes are 1/5 to 1/20 lower than the corresponding coefficients in water (Lakshiminarayanaiah, 1969; Beck and Schultz, 1972). For purposes of estimation, we assume that they are 10 times smaller than the diffusion coefficients in free solution. We also assume that $D_+ + D_- \approx RT(\omega_+ + \omega_-)$ for estimation. Since the membrane charge comes from the coated oxyhemoglobin, we approximate its value from the electrokinetic charge of the human blood cell (Cook, et al., 1961); it ranges from 10^{-3} to 10^{-2} c/m^2. The viscosity coefficient of the KCl solution and its absolute permitivity are approximated by the values of water at 25°C. They are $\eta = 10^{-3}$ N · s/m^2 and $\varepsilon = 7 \times 10^{-10}$ C/V · m respectively. In summary, the values of the parameters used in the present calculation are:

$$D_+ = D_- = 2.01 \times 10^{-10} m^2/s \;, \qquad \sigma = 2.2 \times 10^{-3}\ C/m^2 \;,$$

$$\beta = c_A/c_B = 0.5 \;, \qquad \eta = 10^{-3}\ N \cdot s/m^2 \;,$$

$$F = 96500\ C/mol \;, \qquad \varepsilon = 7 \times 10^{-10}\ C/V \cdot m$$

$$\ell = 10^{-4}\ m \;, \qquad a = 10^{-8}\ m \;,$$

$$\bar{\sigma} = 0.8 \times 10^{-3} \;, \qquad \gamma = c_A^0/c_A = c_B^0/c_B = 0.25 \;,$$

$$R = 8.314\ J\ K^{-1}\ mol^{-1} \;, \qquad T = 298°K \;, \quad \bar{\varepsilon} = 0.75 \;.$$

The distribution coefficient has been chosen so that the shift on the abscissa will make the maximum data point coincide with that of the theoretical curve. We do this because there are no available data to estimate γ in this system. These values together with (5.45) - (5.48) yield the true volume flow through charged porous oxyhemoglobin collodion membranes, both negatively and positively charged. They are plotted in Fig. 5.1 and Fig. 5.2 as a function of the KCl concentration on the higher concentration side. The true volume flow is positive, which means that the flow is toward the more concentrated solution.

It can be seen from these two figures that the experimental data of Grim and Sollner agree well with the theoretical values calculated from (5.45) - (5.48). The values of $\bar{J}_V$ below $2c_B = 0.0125$ mol/ℓ are not shown because in that region, when $\kappa a \sim 1$, the asymptotic expansions of Bessel function used in obtaining (5.39) - (5.48) fail. The use of (5.45) - (5.48) in this region therefore gives incorrect values. The larger deviation in the middle range of the concentration [about $O(10^{-1})$] might be attributed to the approximate nature of the electric potential distribution (4.30) obtained for a Gouy-Chapman type double layer. It has been shown by Krylov and Levich (1963) by a statistical mechanical derivation allowing for the short-range interaction between ions in the diffuse part of the double layer in a concentrated solution and also allowing for the discrete structure of the charge of specifically adsorbed ionic layers that in a moderate

Fig. 5.1--Volume flow of solution across an Oxyhemoglobin coated collodion membrane as a function of concentration, with a concentration ratio of 1:2. Points are Grim and Sollner's experimental data, solid curve is the present theoretical result. Charge of membrane: negative.

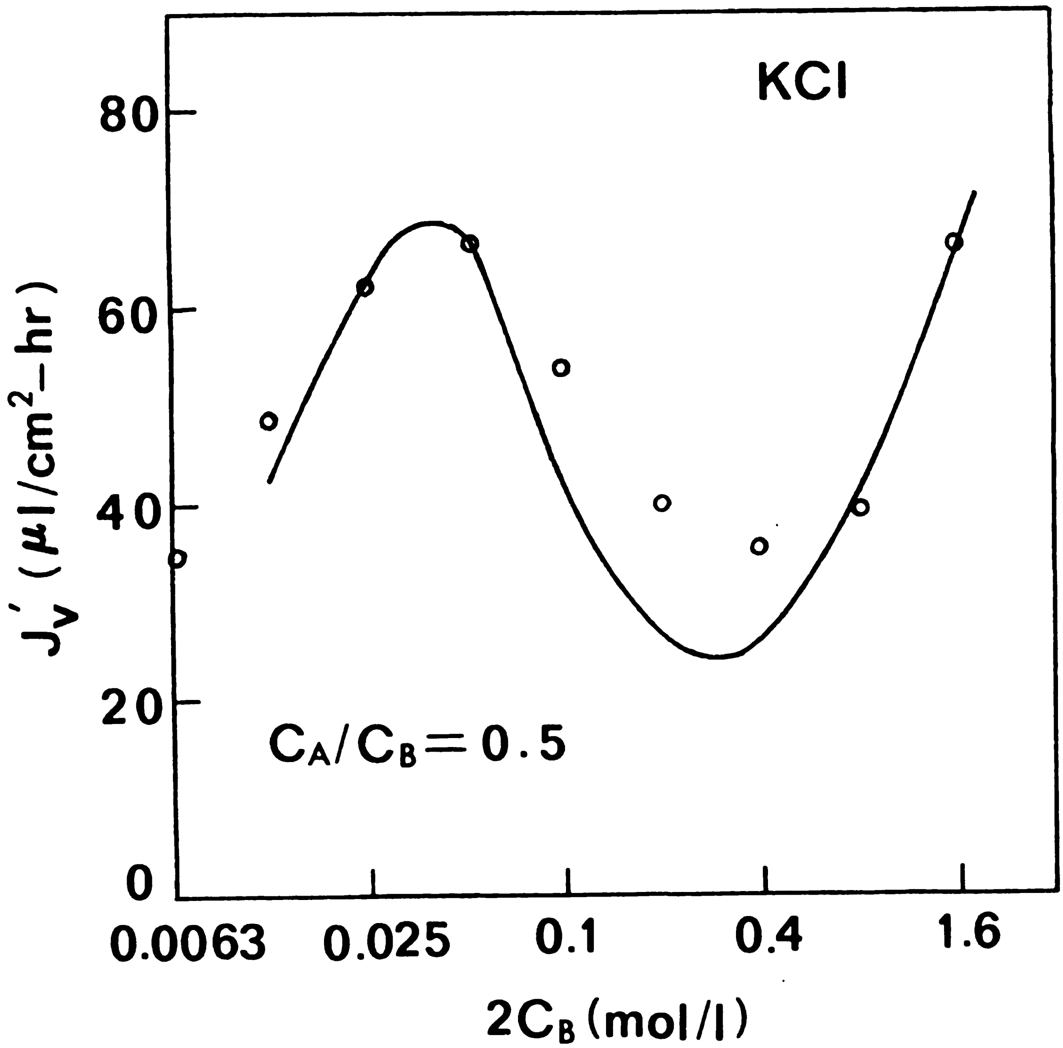
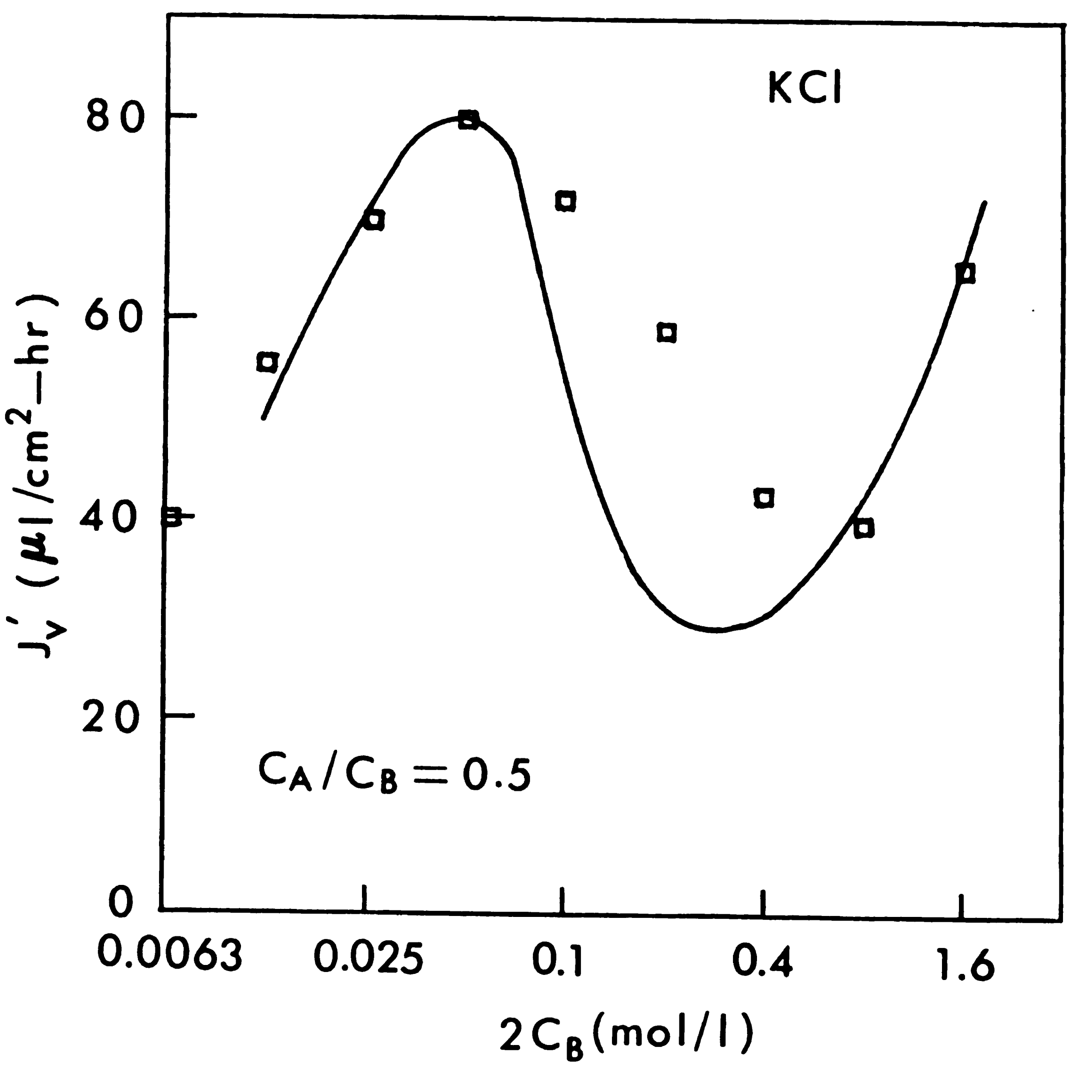

KCl
80
60
40
20
0
J_v' (μl/cm^2-hr)
$C_A/C_B = 0.5$
0.0063
0.025
0.1
0.4
1.6
$2C_B$ (mol/l)

Fig. 5.2--Volume flow rate of solution across an Oxyhemoglobin coated collodion membrane as a function of concentration with a concnetration ratio of 1:2. Points are Grim and Sollner's experimental data, solid curve is the present theoretical result. Charge of membrane: positive.


KCl
80
60
40
20
0
J_v' (μl/cm^2—hr)
$C_A/C_B = 0.5$
0.0063
0.025
0.1
0.4
1.6
$2C_B$(mol/l)

bulk concentration (0.1 ~ 0.75) the potential in the diffuse part of the double layer decreases in the bulk of the solution more rapidly than predicted by Guoy-Chapman theory. They have shown that for a solution of 0.75 molar the decreases in the potential in the diffuse part of the double layer occurs over a distance of the order of two ionic diameters. There may also be other factors contributing to the deviation in this concentration range, such as the neglect of the nonideality at higher concentrations, the concentration dependence of parameters, and the real pore size distribution. The good fit at very high concentrations is due to the dimunition of the abnormal component and the domination of ordinary osmotic flow. Nevertheless, considering the approximations and assumptions introduced in our derivation together with the lack of precise values of parameters from independent measurements, this agreement between theory and experiment is quite satisfactory. The most important fact we have demonstrated is that for ions with almost equal diffusivities the volume flows across a negatively or a positively charged porous membranes not only have the same direction but also similar magnitudes and composition dependence due to the fact that the center of mass velocities are the same for both charges. We have also shown that with the inclusion of the capilliary osmotic contribution, which was ignored by other authors, and with suitable values of parameters it is possible to achieve a quantitative description of the anomalous osmotic phenomena.

E. Conclusion

We have derived, with the inclusion of the capillary osmotic contribution which is usually in effective and was ignored by other authors, a general analytical formula for anomalous osmosis through charged capillary membranes. The formula applies to any uni-univalent electrolyte. In particular, for KCl solutions, the volume flows through the membrane are in the same direction (toward the concentrate solution) and are of almost the same magnitude and composition dependence. This is due to the facts that (a) cation and anion mobilities are nearly equal and (b) the averaged center of mass velocity depends on the charge density squared. This is demonstrated by the good agreement between our theoretical and Grim and Sollner's experimental results for KCl solution, as shown in Fig. 5.1 and Fig. 5.2. For uni-univalent electrolytes with different ion diffusivities our equation (5.42) describes the negative anomalous behavior. For other binary electrolytes, similar expressions can be derived. However, before satisfactory quantitative double layer theory for concentrated solutions is developed, we expect the present theory to be a good approximation in the high concentration range.

Furthermore, until precise values of membrane and solution parameters are determined by independent experiments, a rigorous test of the present theory cannot be performed.

CHAPTER VI

CONVECTIVE-DIFFUSIVE FLOW IN A TUBULAR MEMBRANE WITH AXIAL DIFFUSION AND NONUNIFORM VELOCITY PROFILE

A. Introduction

The solution for the capillary membrane model discussed in the previous chapters did not require explicit knowledge of the concentration distribution inside the capillary. However, it is advantageous, especially for understanding the concnetration dependence of phenomenological coefficients, to acquire such knowledge in order to develop further membrane transport theory. We investigate in this chapter a capillary with not only axial transport of solution (by diffusion and convection) but also radial transport (by diffusion) through the capillary wall. The wall is at least partially permeable to both the solvent and the solute. When the wall permeability vanishes, the capillary membrane model of the previous chapter is recovered.

Membranes of tubular geometry and different permeabilities with both laminar and fully developed liquid flow have various applications in various fields.

Among these are: (a) electrolysis with flowing solution in a porous or tubular electrode (e.g., Sioda, 1968; Wroblowa and Razumney, 1974; Flanagan and Marcoux, 1974; Newman, 1973); (b) artificial kidneys (Stewart, et al., 1966; Cooney, Kim and Davis, 1974); (c) vascular flow in plants (Eschrich, et al., 1972); (d) microtubules (Olmsted and Borisy, 1973); and (e) gas separation (Bird, Stewart and Lightfoot, 1960). Because of the similarity of the heat transport equations to the mass transport equations, the formalism for convective diffusion in tubular membranes is also applicable to convective heat transfer by laminar flow in tubes. In fact most previous analyses were restricted to heat transfer problems.

A major assumption usually made in the analysis of both problems is the neglect of axial diffusion or axial heat conduction. With such an assumption and the boundary condition of uniform wall temperature, the heat transfer problem is the well-known classical Graetz problem (Graetz, 1883, 1885). Neglect of axial diffusion or heat transfer leads to a parabolic partial differential equation whose radial eigenfunctions are orthogonal. Graetz calculated only the first two eigenvalues. Since then a great deal of effort has been spent on calculating more accurate eigenvalues and eigenfunctions, and improving the convergence of the eigenfunction expansion by various orthogonal trial functions. The Graetz problem with the boundary condition of constant wall temperature or constant concentration has been treated by, e.g., Sellars, Tribus and Klein (1956), Singh (1958), Bodnarescu (1955), Brown (1960), Sparraw and Siegel (1960), Sideman, Luss and Peck (1965), Worsøe-Schmidt (1967), and Davis and Parkinson (1970). The most exact computation performed to date are those of Brown (1960), who, by using a computer capable of manipulating 50 digits, computed the first ten eigenvalues and other constants. The Graetz problem with the boundary condition of constant wall heat flux or constant wall mass flux has been treated by Sellars, Tribus and Klein (1956), Siegel, Sparraw and Hallmant (1958), and Worsøe-Schmidt (1967). For the boundary condition of constant wall resistance or permeability, the Graetz problem has been investigated by Schenk (1954), Schenk and Dumore (1954), Sideman, Luss and Peck (1965), Davis and Parkinson (1970), and Cooney, Kim and Davis (1974).

The assumption of negligible axial diffusion or heat conduction, however, is not always valid. It can lead to significant errors for fluids of high diffusivities (e.g., gases) or high termal conductivities (e.g., liquid metals). Using the simplifying assumption of a flat velocity profile, Schneider (1957) analyzed the effect of axial conduction on entrance region heat transfer and concluded that it is appreciable if the Peclet number (which describes the ratio of convective to diffusive effects) is smaller than 100. This was confirmed by Hsu (1967) through a refined analysis. It is necessary on both theoretical and practical grounds to have a general treatment which takes into account the effects of both non-uniform velocity profiles and axial diffusion or axial heat conduction.

Inclusion of axial diffusion or axial heat conduction causes the partial differential equation for the problem to become elliptic and the eigensolutions are no longer orthogonal. This has been one of the reasons for the neglect of axial diffusion or axial heat conduction in the traditional Graetz problem since non-orthogonality inhibits mathematical manipulations. It is customary to solve the partial differential equation as accurate as possible by numerical methods and subsequently to use tabulated results in similar problems. For the constant wall temperature boundary condition, Singh (1958) proposed a Bessel function expansion method. However, his method does not readily yield higher eigenvalues and eigenfunctions. Jones (1971) considered this problem, still with a constant wall temperature boundary condition, by a Laplace Transform method followed by a Frobenius approach. Rapid convergence of his final result is not assured, and errors in the linear combination coefficients tend to build up rapidly due to the use of a recurrence relation which relates the higher coefficient to previous coefficients. Tamir and Taitel (1973) and Taitel, Bentwich and Tamir (1973) considered the effect of upstream and downstream boundary conditions on heat or mass transfer with axial conduction or diffusion, but they used a simplified flat velocity profile. Hsu (1967) and Tan and Hsu (1970) treated this problem (with constant wall heat flux) carefully and determined the first 20 eigenvalues and the corresponding eigenfunctions by a Runge-Kutta numerical scheme. Hsu (1971) extended this to an infinite tube half insulated and half at a constant temperature. The nonorthogonal eigenfunctions were expanded in sets of orthogonal functions by a Gram-Schmidt orthogonalization procedure. This numerical scheme is unnecessarily complicated, especially since no increase in accuracy is obtained by use orthogonal eigenfunctions. Michelsen and Villadsen (1974) use a method of orthogonal collocation and matrix diagonalization to solve the Graetz problem with axial heat conduction. The partial differential equation is changed to 2N algebraic equations by collocating it to zero residure at N points; these N points are chosen as the zeros of an Nth degree orthogonal polynomial (they use Legendre polynomial). This method has the advantage of accuracy in the entrance region, but the higher eigenvalues deviates enormously (e.g., for the classical Graetz problem the 7th eigenvalue is 15% larger than its accurate value and the 10th eigenvalue is almost ten times bigger than its accurate value). Moreover, the partial differential equation is solved only numerically.

In this chapter we analyze a mass transfer system in a tubular membrane with axial diffusion. The result can easily be applied to heat transfer systems. We solve this problem in terms of confluent hypergeometric functions (CHF). The eigenvalues are obtained as the zeros of a transcendental equation expressed in terms of the CHF, and asymptotic forms of the CHF are used to obtain expressions for higher eigenvalues. Concentration distributions are calculated for various values of the Peclet number and wall permeability. The linear combination coefficients in the solution are found by an "Overdetermined Collocation" numerical scheme which involves a least-squares-type collocation of the boundary condition equations and a matrix inversion to solve for the coefficients. The most obvious advantage in expressing solutions in terms of well-known tabulated functions is that the properties of the functions (e.g., derivatives, recurrence relations, convergence properties) are known and the asymptotic solutions are available. In addition, explicit expressions in tabulated functions obviates the need for a totally numerical scheme to obtain eigenvalues from the differential equation and the boundary conditions. Application of the CHF to the Graetz problem without axial diffusion or heat conduction was reviewed by Davis (1973) and extended by Cooney, Kim and Davis (1974) to the case of the hemodialyzer. However, this is the first time that the "Overdeterined Collocation" method and CHF have been applied to Graetz problem with axial diffusion. In the case of no axial diffusion, the overdetermined collocation method reduces to the usual method of finding the linear combination coefficients in an orthogonal system. Although our method is simpler, it has the same accuracy as more sophisticated ones. To our knowledge, no results corresponding to the boundary condition considered here (finite wall permeability) are avilable in the literature. We also demonstrate that the solution obtained by neglecting axial diffusion may be regarded as a special case of a more general solution in which the axial diffusion is included. The methods given here are also applicable to parallel plate membrane systems with axial diffusion.

B. Basic Equations and Boundary Conditions

For economy of language, we use the terminology for the artificial kidney system, which consists of hollow fiber membranes. The results can of course be used for analogous heat or mass transfer processes as well.

We consider mass transfer between two flowing fluids (solution, dialysate) separated by a membrane which is permeable to the species being exchanged but is impermeable to all other species. The permeability of the tubular membrane is constant however can have different values. The dialyzer system (artificial kidney) consists of solvent with an evenly distributed solute flowing from left to right in the tubular membrane. At a certain point in the tubular membrane system, the fluid contacts a portion of the wall that is permeable to the solute. The length of the impermeable portion is assumed to be long enough that the flow is laminar and fully developed before the fluid contacts the section of the wall that is permeable, and the dimensions of the tubular membrane are such that it can be considered to be semi-infinite. The dialysate flow is turbulent, with flow rate high enough that mass transfer resistance on the dialysate side can be neglected. The dialysate is assumed to have a constant bulk concentration at all axial positions in the dialyzer. This is shown schematically in Fig. 6.1. We also assume:

(1) The solution is Newtonian, homogeneous and has constant physical properties.

(2) Only purely diffusive transport occurs across the membrane. Convection across the membrane and hence the hydrostatic and osmotic pressure differences between the fluids are considered to be negligible.

(3) Steady state has been reached.

(4) The solute distribution coefficients for both solution-membrane and dialysate-membrane interface are equal.

(5) Axial diffusion in the tubular membrane is not negligible.

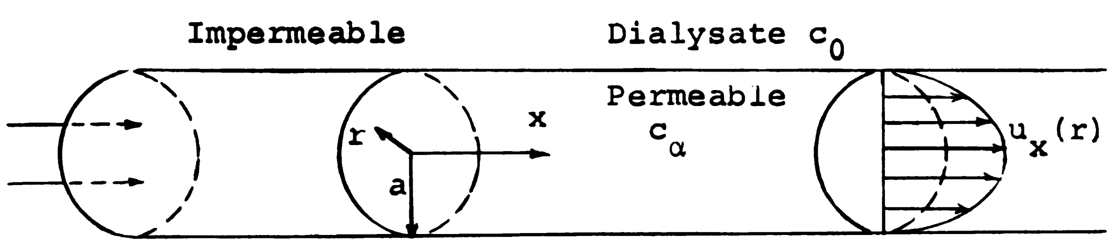


Fig. 6.1--Schematic diagram of tubular membrane.

For a binary nonelectrolyte solution without pressure gradients, the flux equation (5.2) becomes

$$\underset{\sim}{N}_\alpha = - D_\alpha \underset{\sim}{\nabla} c_\alpha + c_\alpha \underset{\sim}{u} \quad (6.1)$$

This is also applicable to electrolyte solutions containing enough supporting electrolyte that the contribution of ionic migration may be neglected. Substitution of (6.1) into the continuity equation, with the understanding from assumption (3) that the steady state has been reached, yields

$$D_\alpha \nabla^2 c_\alpha = \underset{\sim}{u} \cdot \underset{\sim}{\nabla} c_\alpha \; , \tag{6.2}$$

where we have used the constant physical properties assumption. This is the so called convective diffusion equation (Bird, Stewart and Lightfoot, 1960; Levich, 1962; Kays, 1966; Newman, 1973). For the tubular membrane considered here, the solution of the Navier-Stokes equation under the condition of steady laminar flow has the form

$$u_r = u_\theta = 0 \; ,$$

$$u_x = 2u^0[1-(r/a)^2] \; , \tag{6.3}$$

where the average velocity over the tube cross section is

$$u^0 = \left(\int_0^a u_x r dr / \int_0^a r dr \right) = a^2(4\eta)^{-1}(\partial p/\partial x) \; . \tag{6.4}$$

The equation of convective diffusion then becomes

$$2u^0[1-(r/a)^2](\partial c_\alpha/\partial x) = D_\alpha[r^{-1}(\partial/\partial r)r(\partial c_\alpha/\partial r) + (\partial^2 c_\alpha/\partial x^2)] \; . \tag{6.5}$$

The boundary conditions are

$$\text{BCI} \quad c_\alpha = c_b \quad \text{at } x = 0 \quad \text{for } 0 \le r \le a , \tag{6.6}$$

$$\text{BCII} \quad c_\alpha = c_0 \quad \text{when } x \to \infty \quad \text{for } 0 \le r \le a , \tag{6.7}$$

$$\text{BCIII} \quad (\partial c_\alpha/\partial r) = 0 \quad \text{at } r = 0 \quad \text{for } x > 0 , \tag{6.8}$$

$$\text{BCIV} \quad -D_\alpha(\partial c_\alpha/\partial r) = P_m(c_\alpha - c_0) \text{ at } r = 0 \text{ for } x > 0 , \tag{6.9}$$

where c_b is the inlet concentration, c_0 is the dialysate concentration, P_m is the permeability coefficient of the tubular membrane, and where the derivative is zero at the center of the tube by symmetry. BCII indicates that for downstream the concentration of the solution approaches the dialysate concentration and BCIV serves as a definition of the permeability coefficient. The dimensionless variables

$$c = (c_\alpha - c_0)/(c_b - c_0) , \tag{6.10}$$

$$\zeta = r/a , \tag{6.11}$$

$$z = x/aPe \text{ where } Pe = 2u^0 a/D_\alpha , \tag{6.12}$$

$$N_{sh_w} = P_m a/D_\alpha , \tag{6.13}$$

transform the convective diffusion equation (6.5) and the boundary conditions (6.6)-(6.8) to

$$(1-\zeta^2)(\partial c/\partial z) = \zeta^{-1}(\partial/\partial\zeta)\zeta(\partial c/\partial\zeta) + Pe^{-2}(\partial^2 c/\partial z^2) , \tag{6.14}$$

BCI $\quad c = 1$ at $z = 0$ for $0 \leq \zeta \leq 1$, (6.15)

BCII $\quad c = 0$ when $z \to \infty$ for $0 \leq \zeta \leq 1$, (6.16)

BCIII $\quad (\partial c/\partial \zeta) = 0$ at $\zeta = 0$ for $z > 0$, (6.17)

BCIV $\quad -(\partial c/\partial \zeta) = N_{sh_w} c$ at $\zeta = 1$ for $z > 0$, (6.18)

where the Peclet number is a measure of convective to diffusive effects and the wall Sherwood number N_{sh_w} describes the transport conductance of the membrane.

C. The Graetz Problem and Its Extension

On the assumption that the Peclet number is large, which implies that axial convection dominates over axial diffusion since the Peclet number is the ratio of convective to diffusive effects, the second derivative with respect to z in (6.14) is usually neglected. This neglect is equivalent to the neglect of the contribution of axial diffusion. (6.14) then reduces to

$$(1-\zeta^2)(\partial c/\partial z) = \zeta^{-1}(\partial/\partial \zeta)\ (\partial c/\partial \zeta) \ . \tag{6.19}$$

Neglect of axial diffusion changes the problem considerably. Firstly, there are no dimensionless parameters in the problem. Secondly, the original partial differential equation is elliptic, while without axial diffusion the equation becomes parabolic. In the elliptic problem, all boundary conditions including the one at $x \to \infty$ have to be specified.

In the parabolic problem, there is no upstream propagation of effects, and the boundary condition (6.16) is not necessary. Furthermore, if constant wall concentration obtains, then the Sherwood number $N_{sh_w} \to \infty$, and the boundary conditions reduce to

BCI $\quad c = 1$ at $z = 0 \quad$ for $0 \leq \zeta \leq 1$ $\quad$ (6.20)

BCII $\quad (\partial c/\partial \zeta) = 0$ at $\zeta = 0 \quad$ for $z > 0$ $\quad$ (6.21)

BCIII $\quad c = 0$ at $\zeta = 1 \quad$ for $z > 0$. $\quad$ (6.22)

(6.19)-(6.22) constitute the classical Graetz problem.

Graetz (1883, 1885) treated this problem by the method of separation of variables:

$$c(\zeta,z) = R(\zeta)Z(z) \quad . \tag{6.23}$$

Substitution of (6.23) into (6.19) gives

$$(1-\zeta^2)R(dZ/dz) = (Z/\zeta)(d/d\zeta)\zeta(dR/d\zeta)$$

or

$$Z^{-1}(dZ/dz) = [(1-\zeta^2)\zeta R]^{-1}(d/d\zeta)\zeta(dR/d\zeta) = -\lambda^2 \tag{6.24}$$

where λ are the eigenvalues.

The function $Z(z)$ can be determined from

$$(dZ/dz) = -\lambda^2 Z \tag{6.25}$$

with the solution (apart from a multiplicative constant)

$$Z = \exp(-\lambda^2 z) \tag{6.26}$$

The function $R(\zeta)$ can be determined from

$$\zeta^{-1}(d/d\zeta)\zeta(dR/d\zeta) + \lambda^2(1-\zeta^2)R = 0 \tag{6.27}$$

and the boundary conditions

$$\begin{aligned} (dR/d\zeta) &= 0 \qquad && \text{at } \zeta = 0 \ , \\ R &= 0 && \text{at } \zeta = 1 \ . \end{aligned} \tag{6.28}$$

(6.27) and (6.28) constitute a Sturm-Liouville problem because the linear, second-order, ordinary differential equation (6.27) is self-adjoint with homogeneous boundary conditions (6.28). The eigenfunctions of the Sturm-Liouville problem are orthogonal,

$$\int_0^1 \zeta(1-\zeta^2)R_n(\zeta)R_m(\zeta)\,d\zeta = \begin{cases} 0 & n \neq m \\ 1 & n = m \ , \end{cases} \tag{6.29}$$

where R_n and R_m are eigenfunctions corresponding to eigenvalues λ_n and λ_m. The general solution is then

$$c = \sum_{n=1}^{\infty} A_n[\exp(-\lambda_n^2 z)]R_n(\zeta) \ . \tag{6.30}$$

This is known as the Graetz series, with A_n the linear combination coefficient corresponding to the nth eigenvalue and eigenfunction.

Only two boundary conditions have been used. The remaining one, (6.20), together with (6.30), gives

$$1 = \sum_{n=1}^{\infty} A_n R_n(\zeta) \ . \tag{6.31}$$

With the use of the orthogonality property (6.29), the coefficients can be obtained by

$$A_n = \int_0^1 \zeta(1-\zeta^2) R_n(\zeta) d\zeta / \int_0^1 \zeta(1-\zeta^2) R_n^2(\zeta) d\zeta \ . \tag{6.32}$$

This completes the solution of the classical Graetz problem. From this solution one can calculate other related quantities for the problems of interest.

Inspection of the solution (6.30) shows that fewer terms are needed for large z and more terms for small z in order to obtain proper convergence. Lévêque (1928) used a boundary layer treatment (which is equivalent to singular perturbation) to obtain a simple equation valid for small z. For more detailed discussion of the Lévêque solution and its extension see Newman (1973). Other extensions of the Graetz problem involve constant mass flux or finite wall permeability boundary conditions, which require extra mathematical manipulations. However, the forms of the solution are still the same as (6.30). The references for these extensions have been given in Section A. The most important extension of the Graetz problem, however, is the inclusion of axial diffusion. This is the topic of the next section.

D. Exact Solution with Axial Diffusion

As pointed out in Section A, it is not always justifiable to neglect the axial diffusion. Schneider (1957) analyzed the effect of axial conduction on entrance-heat transfer and concluded that it is appreciable if the Peclet number $Pe < 100$. This was confirmed later by Singh (1958) and Hsu (1967). The axial diffusion effect can be very important in gases, for which the diffusion coefficients are usually of the order of 10^{-1} cm^2/sec and the Peclet number may well be much smaller than 100. This can make the last term on the right hand side of (6.14) comparable to or greater than the other terms. Consequently, the axial diffusion contribution cannot be neglected. Tan and Hsu (1970) recognized the necessity of including axial diffusion for gas flow problems, but they solved the differential equation by a Runge-Kutta numerical scheme for a constant wall concentration boundary condition.

The starting equations are (6.14)-(6.18). With the inclusion of the axial diffusion term, the method of separation of variables no longer works.

Nevertheless, we can seek a solution of the same form as in the case of no axial diffusion, i.e.

$$c(\zeta,z) = \sum_{n=1}^{\infty} B_n[\exp(-\beta_n^2 z)]\; Y_n(\zeta) \;, \tag{6.33}$$

where β_n and $Y_n(\zeta)$ are the eigenvalues and eigenfunctions of

$$\zeta^{-1}(d/d\zeta)\zeta(dY_n/d\zeta) + \beta_n^2[1-\zeta^2 + (\beta_n/Pe)^2]\; Y_n = 0 \tag{6.34}$$

with boundary conditions

$$(\partial Y_n/\partial\zeta) = 0 \text{ at } \zeta = 0$$

$$-(\partial Y/\partial\zeta) = N_{sh_w} Y_n \text{ at } \zeta = 1 \;. \tag{6.35}$$

By the transformation

$$\xi = \beta_n\zeta^2 \quad\text{and } W_n(\xi) = Y_n(\zeta)\; \exp\;(\beta_n\zeta^2/2) \;, \tag{6.36}$$

we obtain the CHF equation (or Kummer's equation)

$$\xi(d^2W_n/d\xi^2) + (1-\xi)(dW_n/d\xi)-\{\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2]\}W_n = 0 \;. \tag{6.37}$$

This has the solution (apart from a multiplcation constant), under the boundary condition (6.17),

$$W_n = M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2] \;,\; 1 \;,\; \beta_n\zeta^2) \;, \tag{6.38}$$

where M is Kummer's function, defined by (see, e.g., Abramowitz and Stegun, 1964)

$$M(a,b,y) = 1 + \frac{ay}{b} + \frac{(a)_2 y^2}{(b)_2 2!} + \ldots + \frac{(a)_n y^n}{(b)_n n!} + \ldots \qquad (6.39)$$

with $(a)_n = a(a+1)(a+2)\ldots(a+n-1)$, $(a)_0 = 1$

$$(b)_n = b(b+1)(b+2)\ldots(b+n-1) \ , \ (b)_0 = 1 \ . \qquad (6.40)$$

Instead of $M(a,b,y)$, the notation ${}_1F_1\,(a,b,y)$ is also widely used.

The advantages of expressing the solution to this problem in terms of Kummer function are

(1) The properties of the functions (e.g., derivatives, recurrence relations, convergence properties) are well known, and the numerical values of the function are tabulated.

(2) The asymptotic forms of the function are available.

(3) Direct power series solutions obtained by the Frobenius method suffer from rapid error build-up due to recurrence relations which evaluate coefficients from previous coefficients. Moreover, fast convergence is not guaranteed. (Both these remarks apply only in the case that the general term cannot be found).

(4) The Kummer function can be evaluated quickly, and its convergence properties are known.

When the eigenvalue β_n is sufficiently large, the following asymptotic form can be used instead of the series from

$$M(a,b,y) = \Gamma(b)\sin(a\pi)\exp[(b-2a)(\tfrac{1}{2}\sinh 2\theta - \cosh^2\theta)]$$
$$\times [(b-2a)\cosh\theta]^{1-b}[\pi(\tfrac{1}{2}b-a)\sinh 2\theta]^{-1/2}[1+O(|\tfrac{1}{2}b-2|^{-1})] \tag{6.41}$$

where $\cosh^2\theta = y/(2b-4a)$.

Combination of (6.36) and (6.38) gives

$$Y_n = \exp(-\beta_n\zeta^2/2)\ M(\tfrac{1}{2}-\beta_n/4)[1+(\beta_n/Pe)^2],\ 1,\beta_n\zeta^2)\ . \tag{6.42}$$

Applying the boundary conditions (6.35) to (6.42), we obtain the transcendental equation

$$\{1+\tfrac{1}{2}\beta_n[1-(\beta_n/Pe)^2]-N_{sh_w}\}M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],\ 1,\beta_n)$$
$$= \{1-\tfrac{1}{2}\beta_n[1+(\beta_n/Pe)^2]\}M(\tfrac{3}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],\ 1,\beta n)\ . \tag{6.43}$$

The eigenvalues are those values of β_n which satisfy this equation. We have solved this equation by a half-interval method (Carnahan, et al., 1969) for various values of Pe and N_{sh_w}. Eigenvalues up to the 10th have been calculated to an accuracy of at least 9 significant figures on a CDC 6500 computer. In the range of parameters considered here, computer calculations show that function converges to the 9th decimal place in less than 50 terms, and for some parameters convergence is achieved in less than ten terms. In order to assure convergence, we used 100 terms for every Kummer function calculated. Sideman, Luss and Peck (1965), who used a Frobenius method for the no axial diffusion case, had to calculate 300 terms in order to assure convergence. It has not been necessary in our work to use the asymptotic formula (6.41) because the computation time needed for evaluating the more general expression is reasonably short. Eigenvalues calculated for different values of Pe and N_{sh_w} are tabulated in Table 6.1. For the case of Pe = ∞ (no axial diffusion) and $N_{sh_w} = 0$ (constant wall concentration), our eigenvalues are exactly the same as the most accurate ones reported by Brown (1960). This serves as a check on the accuracy of our calculations and the solution of the transcendental equation (6.43).

The solution to this problem is, then

$$c = \sum_{n=1}^{\infty} B_n \exp(-\beta_n^2 z) \exp(-\beta_n \zeta^2/2) M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2], 1, \beta_n \zeta^2) \ . \tag{6.43}$$

Application of boundary condition (6.15) leads to the requirement that

TABLE 6.1--EIGENVALUES AND LINEAR COMBINATION COEFFICIENTS WHERE PE IS THE PECLET NO., NSHW IS THE WALL SHERWOOD NO.

PE = ∞ (NO AXIAL DIFFUSION), NSHW = 0

N	EIGENVALUE	L.C.COEFFICIENT
1	.0	.100000000E+01
2	.506750550E+01	.348369938E-04
3	.915760643E+01	.174746389E-03
4	.131972247E+02	.530178988E-03
5	.172202294E+02	.122157932E-02
6	.212355173E+02	.240628066E-02
7	.252465312E+02	.433019997E-02
8	.292549056E+02	.702668270E-02
9	.332615237E+02	.139603654E-01
10	.372669082E+02	.211231428E-01

PE = ∞ (NO AXIAL DIFFUSION), NSHW = 1

N	EIGENVALUE	L.C.COEFFICIENT
1	.164124968E+01	.120134311E+01
2	.547830896E+01	-.292880993E+00
3	.943596343E+01	.146817052E+00
4	.134152429E+02	-.923853264E-01
5	.174025912E+02	.673316688E-01
6	.213939242E+02	-.477366962E-01
7	.253875496E+02	.439236392E-01
8	.293826286E+02	-.237851960E-01
9	.333786940E+02	.459593159E-01
10	.373754628E+02	-.335526867E-02

PE = ∞ (NO AXIAL DIFFUSION), NSHW = 3

N	EIGENVALUE	L.C.COEFFICIENT
1	.217867110E+01	.134642180E+01
2	.592089914E+01	-.536460461E+00
3	.980170980E+01	.315483558E+00
4	.137298094E+02	-.215478660E+00
5	.176807495E+02	.162207347E+00
6	.216447120E+02	-.123473279E+00
7	.256168956E+02	.105851973E+00
8	.295946445E+02	-.731838145E-01
9	.335763588E+02	.100732189E+00
10	.375610109E+02	-.429037063E-01

TABLE 6.1 (CONTINUED)

PE = ∞ (NO AXIAL DIFFUSION), NSHW = 5

N	EIGENVALUE	L.C.COEFFICIENT
1	.235665282E+01	.139577409E+01
2	.613503977E+01	-.631419626E+00
3	.100134767E+02	.399538242E+00
4	.139317598E+02	-.286155912E+00
5	.178717951E+02	.221912122E+00
6	.218253916E+02	-.174246906E+00
7	.257881427E+02	.149305796E+00
8	.297574214E+02	-.109080029E+00
9	.337315471E+02	.143786719E+00
10	.377093872E+02	-.723413142E-01

PE = ∞ (NO AXIAL DIFFUSION), NSHW = 20

N	EIGENVALUE	L.C.COEFFICIENT
1	.200000000E+01	.129610764E+01
2	.574392286E+01	-.447068839E+00
3	.964505993E+01	.246781000E+00
4	.135903285E+02	-.162705427E+00
5	.175548018E+02	.120291970E+00
6	.215295463E+02	-.893566792E-01
7	.255104998E+02	.775797876E-01
8	.294955269E+02	-.504121527E-01
9	.334833878E+02	.748985002E-01
10	.374733093E+02	-.245815355E-01

PE = ∞ (NO AXIAL DIFFUSION), NSHW = ∞

N	EIGENVALUE	L.C.COEFFICIENT
1	.270436440E+01	.147643749E+01
2	.667903145E+01	-.805975194E+00
3	.106733795E+02	.588738876E+00
4	.146710785E+02	-.474356718E+00
5	.186698719E+02	.404894166E+00
6	.226691434E+02	-.348975091E+00
7	.266686620E+02	.313868161E+00
8	.306683233E+02	-.259458827E+00
9	.346680738E+02	.363943064E+00
10	.386678833E+02	-.212763768E+00

TABLE 6.1 (CONTINUED)

PE = 10, NSHW = 0

N	EIGENVALUE	L.C.COEFFICIENT
1	.0	.100001757E+01
2	.433450605E+01	.320928527E-04
3	.674077170E+01	.197994361E-03
4	.863291810E+01	.226416718E-03
5	.102294108E+02	.825692094E-03
6	.116291065E+02	.949272593E-03
7	.128875272E+02	.229775554E-02
8	.140389783E+02	.277996852E-02
9	.151061298E+02	.523893021E-02
10	.161047775E+02	.611224263E-02

PE = 10, NSHW = 1

N	EIGENVALUE	L.C.COEFFICIENT
1	.160693886E+01	.123362606E+01
2	.461293884E+01	-.351899078E+00
3	.686810618E+01	.187279846E+00
4	.870307867E+01	-.112100394E+00
5	.102737014E+02	.737358617E-01
6	.116598825E+02	-.499819499E-01
7	.129103779E+02	.395951659E-01
8	.140567625E+02	-.260779613E-01
9	.151204598E+02	.269040363E-01
10	.161166343E+02	-.103561920E-01

PE = 10, NSHW = 3

N	EIGENVALUE	L.C.COEFFICIENT
1	.211152461E+01	.140789505E+01
2	.493894340E+01	-.667468723E+00
3	.706887800E+01	.430911217E+00
4	.882833085E+01	-.286993624E+00
5	.103570071E+02	.198235391E+00
6	.117191847E+02	-.141649188E+00
7	.129549665E+02	.108884553E+00
8	.140917169E+02	-.809130356E-01
9	.151487520E+02	.685755495E-01
10	.161401131E+02	-.425261138E-01

TABLE 6.1 (CONTINUED)

PE = 10, NSHW = 5

N	EIGENVALUE	L.C.COEFFICIENT
1	.227689655E+01	.146653127E+01
2	.510707389E+01	-.796814137E+00
3	.720686024E+01	.568671807E+00
4	.892995632E+01	-.409917070E+00
5	.104306446E+02	.297777052E+00
6	.117740015E+02	-.220690662E+00
7	.129972248E+02	.171344366E+00
8	.141253452E+02	-.131867503E+00
9	.151762335E+02	.107874478E+00
10	.161630672E+02	-.734508076E-01

PE = 10, NSHW = 20

N	EIGENVALUE	L.C.COEFFICIENT
1	.194469705E+01	.134716874E+01
2	.480500760E+01	-.548532172E+00
3	.697747135E+01	.326716618E+00
4	.876854786E+01	-.206942774E+00
5	.103164082E+02	.139238737E+00
6	.116899962E+02	-.973835464E-01
7	.129329049E+02	.750617002E-01
8	.140743695E+02	-.539480010E-01
9	.151346842E+02	.480081132E-01
10	.161284238E+02	-.265724011E-01

PE = 10, NSHW = ∞

N	EIGENVALUE	L.C.COEFFICIENT
1	.259693069E+01	.154482887E+01
2	.554688364E+01	-.992091824E+00
3	.771384879E+01	.834827499E+00
4	.945921128E+01	-.743207154E+00
5	.109532010E+02	.664788758E+00
6	.122780443E+02	-.610516342E+00
7	.134795640E+02	.550461082E+00
8	.145862171E+02	-.519711963E+00
9	.156170643E+02	.423382882E+00
10	.165855906E+02	-.434981778E+00

TABLE 6.1 (CONTINUED)

PE = 5, NSHW = 0

N	EIGENVALUE	L.C.COEFFICIENT
1	.0	.100000000E+01
2	.359888760E+01	.511043564E-05
3	.528431362E+01	.159575484E-04
4	.658343386E+01	.250003578E-04
5	.767466503E+01	.642649052E-04
6	.863236148E+01	.100127941E-03
7	.949549026E+01	.182994130E-03
8	.102872754E+02	.284646152E-03
9	.110228168E+02	.429543747E-03
10	.117125652E+02	.611398838E-03

PE = 5, NSHW = 1

N	EIGENVALUE	L.C.COEFFICIENT
1	.152643054E+01	.124916617E+01
2	.378783563E+01	-.361985691E+00
3	.536175412E+01	.173585363E+00
4	.662568139E+01	-.978889917E-01
5	.770179016E+01	.636071853E-01
6	.865156326E+01	-.433999813E-01
7	.950997227E+01	.348500880E-01
8	.102986897E+02	-.231611648E-01
9	.110321083E+02	.244289195E-01
10	.117203174E+02	-.957047041E-02

PE = 5, NSHW = 3

N	EIGENVALUE	L.C.COEFFICIENT
1	.196825988E+01	.143898809E+01
2	.402627138E+01	-.695702306E+00
3	.549158476E+01	.412792041E+00
4	.670346995E+01	-.258459766E+00
5	.775359230E+01	.175204603E+00
6	.868886593E+01	-.125589855E+00
7	.953836580E+01	.975508840E-01
8	.103211912E+02	-.734888110E-01
9	.110504894E+02	.638259916E-01
10	.117356897E+02	-.405635149E-01

TABLE 6.1 (CONTINUED)

PE = 5, NSHW = 0

N	EIGENVALUE	L.C.COEFFICIENT
1	.0	.100000000E+01
2	.359888760E+01	.511043564E-05
3	.528431362E+01	.159575484E-04
4	.658343386E+01	.250003578E-04
5	.767466503E+01	.642649052E-04
6	.863236148E+01	.100127941E-03
7	.949549026E+01	.182994130E-03
8	.102872754E+02	.284646152E-03
9	.110228168E+02	.429543747E-03
10	.117125652E+02	.611398838E-03

PE = 5, NSHW = 1

N	EIGENVALUE	L.C.COEFFICIENT
1	.152643054E+01	.124916617E+01
2	.378783563E+01	-.361985691E+00
3	.536175412E+01	.173585363E+00
4	.662568139E+01	-.978889917E-01
5	.770179016E+01	.636071853E-01
6	.865156326E+01	-.433999813E-01
7	.950997227E+01	.348500880E-01
8	.102986897E+02	-.231611648E-01
9	.110321083E+02	.244289195E-01
10	.117203174E+02	-.957047041E-02

PE = 5, NSHW = 3

N	EIGENVALUE	L.C.COEFFICIENT
1	.196825988E+01	.143898809E+01
2	.402627138E+01	-.695702306E+00
3	.549158476E+01	.412792041E+00
4	.670346995E+01	-.258459766E+00
5	.775359230E+01	.175204603E+00
6	.868886593E+01	-.125589855E+00
7	.953836580E+01	.975508840E-01
8	.103211912E+02	-.734888110E-01
9	.110504894E+02	.638259916E-01
10	.117356897E+02	-.405635149E-01

TABLE 6.1 (CONTINUED)

PE = 5, NSHW = 5

N	EIGENVALUE	L.C.COEFFICIENT
1	.211136940E+01	.150313133E+01
2	.415661177E+01	-.838094691E+00
3	.558724175E+01	.558657114E+00
4	.676947642E+01	-.379188813E+00
5	.780055467E+01	.268789765E+00
6	.872385417E+01	-.198842025E+00
7	.956551654E+01	.155460142E+00
8	.103429643E+02	-.121140671E+00
9	.110684138E+02	.101648250E+00
10	.117507602E+02	-.705874212E-01

PE = 5, NSHW = 20

N	EIGENVALUE	L.C.COEFFICIENT
1	.182316661E+01	.137232406E+01
2	.392596792E+01	-.567953153E+00
3	.543117391E+01	.307861770E+00
4	.666590535E+01	-.183504353E+00
5	.772819648E+01	.121618552E+00
6	.867044635E+01	-.855375845E-01
7	.952429049E+01	.667373781E-01
8	.103100105E+02	-.486082485E-01
9	.110413424E+02	.442833400E-01
10	.117280321E+02	-.251519533E-01

PE = 5, NSHW = ∞

N	EIGENVALUE	L.C.COEFFICIENT
1	.238530388E+01	.157994866E+01
2	.451094012E+01	-.104878236E+01
3	.597652591E+01	.863096477E+00
4	.715791311E+01	-.750045375E+00
5	.817439447E+01	.662905828E+00
6	.907984008E+01	-.604807520E+00
7	.990399756E+01	.547676176E+00
8	.106653498E+02	-.513836928E+00
9	.113763062E+02	.433982795E+00
10	.120456724E+02	-.391516345E+00

TABLE 6.1 (CONTINUED)

PE = 5, NSHW = 5

N	EIGENVALUE	L.C.COEFFICIENT
1	.211136940E+01	.150313133E+01
2	.415661177E+01	-.838094691E+00
3	.558724175E+01	.558657114E+00
4	.676947642E+01	-.379188813E+00
5	.780055467E+01	.268789765E+00
6	.872385417E+01	-.198842025E+00
7	.956551654E+01	.155460142E+00
8	.103429643E+02	-.121140671E+00
9	.110684138E+02	.101648250E+00
10	.117507602E+02	-.705874212E-01

PE = 5, NSHW = 20

N	EIGENVALUE	L.C.COEFFICIENT
1	.182316661E+01	.137232406E+01
2	.392596792E+01	-.567953153E+00
3	.543117391E+01	.307861770E+00
4	.666590535E+01	-.183504353E+00
5	.772819648E+01	.121618552E+00
6	.867044635E+01	-.855375845E-01
7	.952429049E+01	.667373781E-01
8	.103100105E+02	-.486082485E-01
9	.110413424E+02	.442833400E-01
10	.117280321E+02	-.251519533E-01

PE = 5, NSHW = ∞

N	EIGENVALUE	L.C.COEFFICIENT
1	.238530388E+01	.157994866E+01
2	.451094012E+01	-.104878236E+01
3	.597652591E+01	.863096477E+00
4	.715791311E+01	-.750045375E+00
5	.817439447E+01	.662905828E+00
6	.907984008E+01	-.604807520E+00
7	.990399756E+01	.547676176E+00
8	.106653498E+02	-.513836928E+00
9	.113763062E+02	.433982795E+00
10	.120456724E+02	-.391516345E+00

TABLE 6.1 (CONTINUED)

PE = 2, NSHW = 0

N	EIGENVALUE	L.C.COEFFICIENT
1	.0	.100000000E+01
2	.254697750E+01	.646672617E-05
3	.357449546E+01	.130149210E-04
4	.436655654E+01	.284188287E-04
5	.503530538E+01	.501644084E-04
6	.562497585E+01	.107553912E-03
7	.615837293E+01	.149088178E-03
8	.664907748E+01	.296987771E-03
9	.710595219E+01	.362321253E-03
10	.753516030E+01	.637470698E-03

PE = 2, NSHW = 1

N	EIGENVALUE	L.C.COEFFICIENT
1	.126747377E+01	.124858768E+01
2	.265204155E+01	-.348002793E+00
3	.361672134E+01	.152076969E+00
4	.439020129E+01	-.853040789E-01
5	.505083399E+01	.563963979E-01
6	.563615069E+01	-.390983069E-01
7	.616690304E+01	.318698728E-01
8	.665586196E+01	-.212798631E-01
9	.711151414E+01	.227957120E-01
10	.753982692E+01	-.903712763E-02

PE = 2, NSHW = 3

N	EIGENVALUE	L.C.COEFFICIENT
1	.157656037E+01	.145069445E+01
2	.279636097E+01	-.687947992E+00
3	.369040639E+01	.377202919E+00
4	.443446256E+01	-.232199087E+00
5	.508072123E+01	.158593813E+00
6	.565795033E+01	-.115106352E+00
7	.618366851E+01	.904670590E-01
8	.666925762E+01	-.688773930E-01
9	.712252871E+01	.607340730E-01
10	.754908674E+01	-.399002727E-01

TABLE 6.1 (CONTINUED)

PE = 2, NSHW = 5

N	EIGENVALUE	L.C.COEFFICIENT
1	.167684193E+01	.152236493E+01
2	.288080189E+01	-.841660575E+00
3	.374750313E+01	.524959013E+00
4	.447301082E+01	-.348220229E+00
5	.510818961E+01	.246972677E+00
6	.567855713E+01	-.184245043E+00
7	.619977674E+01	.145388889E+00
8	.668225994E+01	-.114486330E+00
9	.713329256E+01	.975734380E-01
10	.755818143E+01	-.700613747E-01

PE = 2, NSHW = 20

N	EIGENVALUE	L.C.COEFFICIENT
1	.147508528E+01	.137772448E+01
2	.273400989E+01	-.554581736E+00
3	.365561244E+01	.275920727E+00
4	.441295106E+01	-.162595708E+00
5	.506602382E+01	.109079648E+00
6	.564716792E+01	-.778469718E-01
7	.617534921E+01	.615476307E-01
8	.666259728E+01	-.452639255E-01
9	.711704512E+01	.418542721E-01
10	.754447266E+01	-.245115077E-01

PE = 2, NSHW = ∞

N	EIGENVALUE	L.C.COEFFICIENT
1	.186754496E+01	.160224005E+01
2	.312312007E+01	-.107462507E+01
3	.400195773E+01	.863029319E+00
4	.472062018E+01	-.742327533E+00
5	.534393020E+01	.654614886E+00
6	.590201686E+01	-.597334076E+00
7	.641185041E+01	.543205374E+00
8	.688411546E+01	-.509680162E+00
9	.732605580E+01	.444028110E+00
10	.774285050E+01	-.376076193E+00

$$\sum_{n=1}^{\infty} B_n \exp(-\beta_n\zeta^2/2)M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],1,\beta_n\zeta^2) = 1 \ . \qquad (6.44)$$

do not constitute a Sturm-Liouville system, and the eigenfunctions (6.42) are therefore not orthogonal. The usual way of finding the linear combination coefficients B_n fails. We demonstrate in the next section that by employing an "Overdetermined Collocation" method the values of B_n can easily be calculated. The advantages of this "Overdetermined Collocation" have been described in Section A.

E. Overdetermined Collocation Method--
Least Square Scheme

In this section we utilize an approximate but direct method to evaluate the linear combination coefficients in (6.44) where the eigenfunctions are not orthogonal. Of several different methods for obtaining approximate solutions, the "Overdetermined Collocation" (Lee, 1966) is applied here, not only because of its simplicity but also because it is formulated in such a way that the boundary conditions pertinent to the problem are satisfied particularly well on the boundaries. This is similar to the least-squares method often used in solving integral equations (Hildebrand, 1965).

The usual method of collocation consists in using a truncated series solution of the differential equation to satisfy the boundary conditions at a selected finite set of boundary points. It is hoped that the solution thus found will also meet the boundary conditions at boundary points between those of the selected set. The accuracy of the solution found in this way depends on how well the boundary conditions are met at the intermediate boundary points. Usually, the solution satisfies only the selected collocation points and oscillates between them. It is therefore desirable to have a solution which minimizes the difference between the real and the mathced boundary values. The method of Overdetermined Collocation is an extension of the usual method of collocation. It involves writing more boundary equations than there are unknown coefficients and solving the overdetermined system of equations by a least-squares scheme. We illustrate this method by solving (6.44) for B_n.

After truncation of the infinite series at the Nth term and division of the dimensionless radial coordinate into m-1 divisions such that

$$0 \leq \zeta_1 < \zeta_2 < \ldots < \zeta_m \leq 1 \quad \text{with } m > N , \tag{6.45}$$

(6.44) reduces to

$$\sum_{n=1}^{N} B_n \exp(-\beta_n \zeta_i^2/2) M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],\ 1, \beta_n \zeta_i^2) = 1 , \quad i=1,2,\ldots,m \tag{6.46}$$

or

$$\sum_{n=1}^{N} Y_{in}B_n = 1 \ , \tag{6.47}$$

where

$$Y_{in} = \exp(-\beta_n\zeta_i^2/2)M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],\ 1,\ \beta_n\zeta_i^2) \ . \tag{6.48}$$

Define the residue as

$$S_i = \sum_{n=1}^{N} Y_{in}B_n -1 \ , \tag{6.49}$$

and also define the residue squares by

$$g(B_1,B_2,\ldots,b_N) = \sum_{i=1}^{m} S_iS_i \ . \tag{6.50}$$

Minimizing g by

$$(\partial g/\partial B_k) = 0 \ , \tag{6.51}$$

we obtain

$$\sum_{n=1}^{N}\sum_{i=1}^{m} Y_{ki}Y_{in}B_n = \sum_{i=1}^{m} Y_{ki} \ , \quad k=1,2,\ldots,N \ . \tag{6.52}$$

This is similar to the Galerkin method used in elasticity problems (Sokolinkoff, 1956). The difference is that the weighting functions in (6.52) are the Y_{in} themselves. (6.52) is the required system of N equations for determining the N unknowns B_n. The final result is in a form which is very convenient for computer calculations. The solutions B_n obtained minimize the residues in the least-square sense.

(6.52) was solved on a CDC 6500 computer for various values of Pe and N_{sh_w} with a Gauss-Jordan reduction algorithm to invert the matrix. We have used N = 10 and m = 8. All the B_n are calculated to nine significant figures. They appear in Table 6.1.

F. Physical Analysis

From the results of Sections D and E, particularly (6.43), the local radial concentration distributions at certain fixed axial coordinates are calculable. These are shown in Fig. 6.2 to Fig. 6.3.

The local bulk concentration is defined as

$$\bar{c}(\zeta,z) = \int_0^1 u_x c(\zeta,z)\zeta d\zeta / \int_0^1 u_x \zeta d\zeta \ . \tag{6.53}$$

Substitution of (6.3) into (6.53) yields

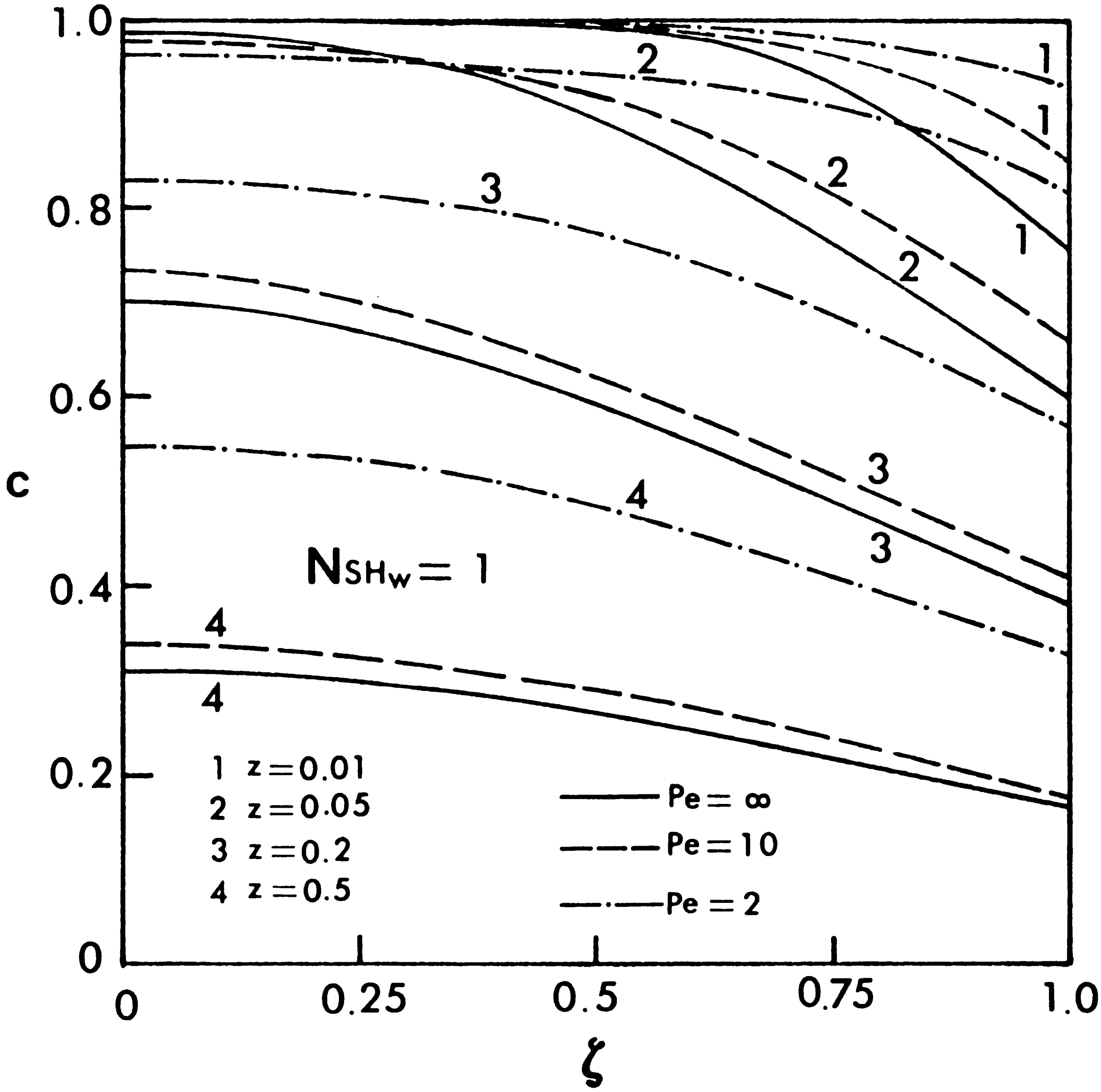
$$\bar{c}(\zeta,z) = \int_0^1 (1-\zeta^2) c(\zeta,z)\zeta d\zeta / \int_0^1 (1-\zeta^2)\zeta d\zeta \ , \tag{6.54}$$

which can be further simplified by the use of (6.43) with truncation

$$\bar{c}(\zeta,z) = \sum_{n=1}^{N} B_n \exp(-\beta_n^2 z) \int_0^1 \zeta(1-\zeta^2)\exp(-\beta_n\zeta^2/2)$$

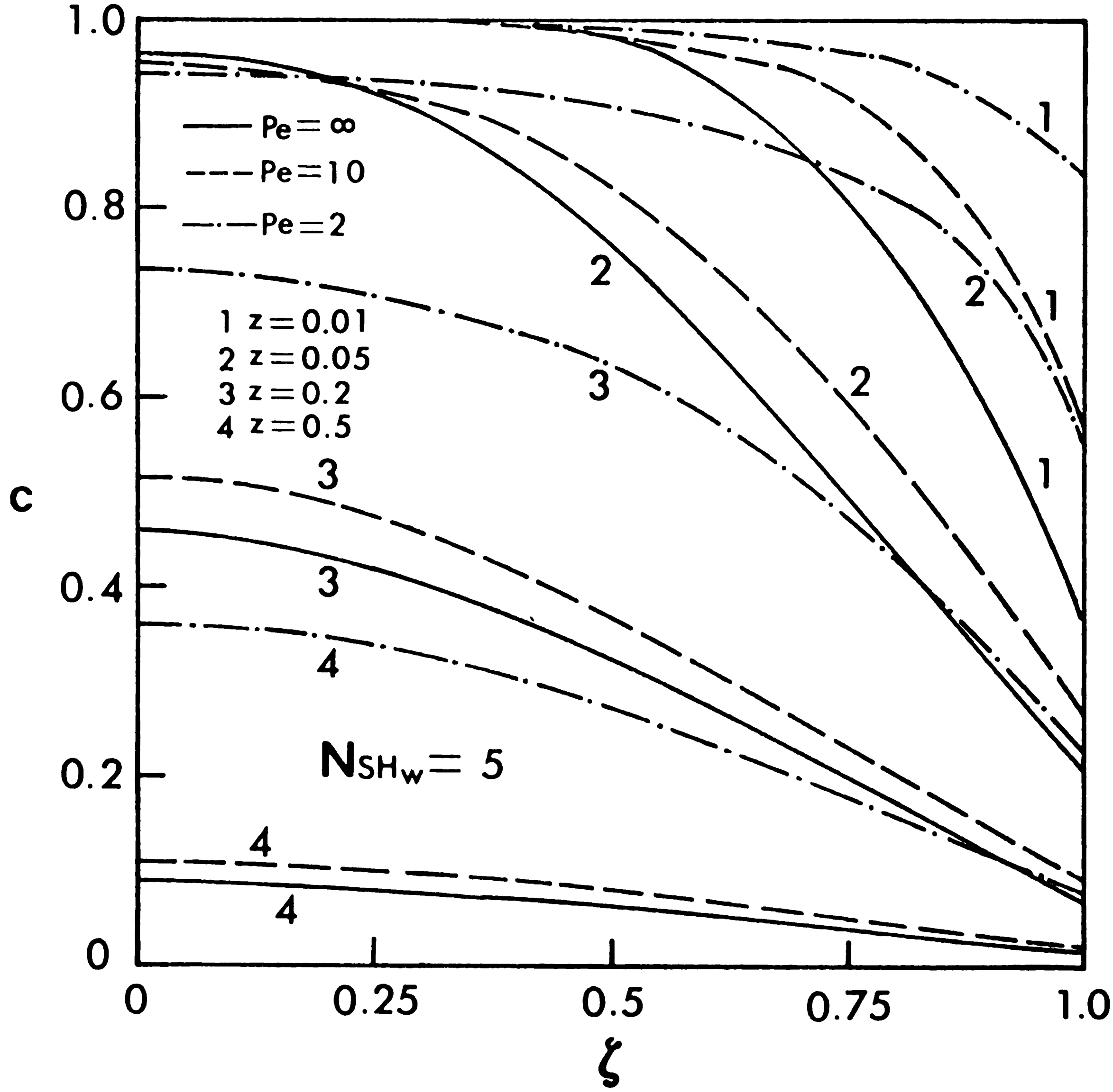
$$\times M(\tfrac{1}{2}-(\beta_n/4)[1+(\beta_n/Pe)^2],\ 1,\ \beta_n\zeta^2)d \ . \tag{6.55}$$

Fig. 6.2--Radial concentration distribution for $N_{sh_w} = 1$.



1.0
0.8
0.6
0.4
0.2
0
c
0
0.25
0.5
0.75
1.0
ζ
$N_{SH_w} = 1$
1 z = 0.01
2 z = 0.05
3 z = 0.2
4 z = 0.5
Pe = ∞
Pe = 10
Pe = 2

Fig. 6.3--Radial concentration distribution for $N_{sh_w} = 5$.


1.0
0.8
0.6
0.4
0.2
0
c
0
0.25
0.5
0.75
1.0
ζ
Pe = ∞
Pe = 10
Pe = 2
1 z = 0.01
2 z = 0.05
3 z = 0.2
4 z = 0.5
N_SHw = 5
1
2
3
4

The local bulk concentrations have also been calculated. The integrals in (6.55) were computed by the use of a 15-point Gauss-Legendre quadrature formula (Carnahan, 1969). The results are shown in Fig. 6.4 to Fig. 6.6. As expected the local bulk concentrations decrease with axial distance and with increasing Peclect number. We observe that if axial diffusion is neglected for small Peclect number, the local bulk concentration may have up to 400% error near the netrance region (i.e., small z). In general neglect of axial diffusion usually lends to underestimation of the local bulk concentration.

One can also define an overall Sherwood number by use of a total mass transport coefficient:

$$N_{sh} = (h_D a/D) = -\ (\partial c/\partial \zeta)_{\zeta=1}/\bar{c} \tag{6.56}$$

where the total mass transfer coefficient is defined as

$$h_D = N_{\zeta w}/(\bar{c}-0) = -\ D(\partial c/\partial \zeta)_{\zeta=1}/\partial \bar{c} \tag{6.57}$$

with $N_{\zeta w}$ the radial diffusional flux at the wall. Again, the overall Sherwood number is a dimensionless mass transfer coefficient which characterizes the rate of mass transport for the whole system. Substitution of (6.43) into (6.56) gives

Fig. 6.4--Local bulk concentration as a function of reduced axial distance from the entrance for $N_{sh_w} = 1$, Pe = 2, 5, and ∞.

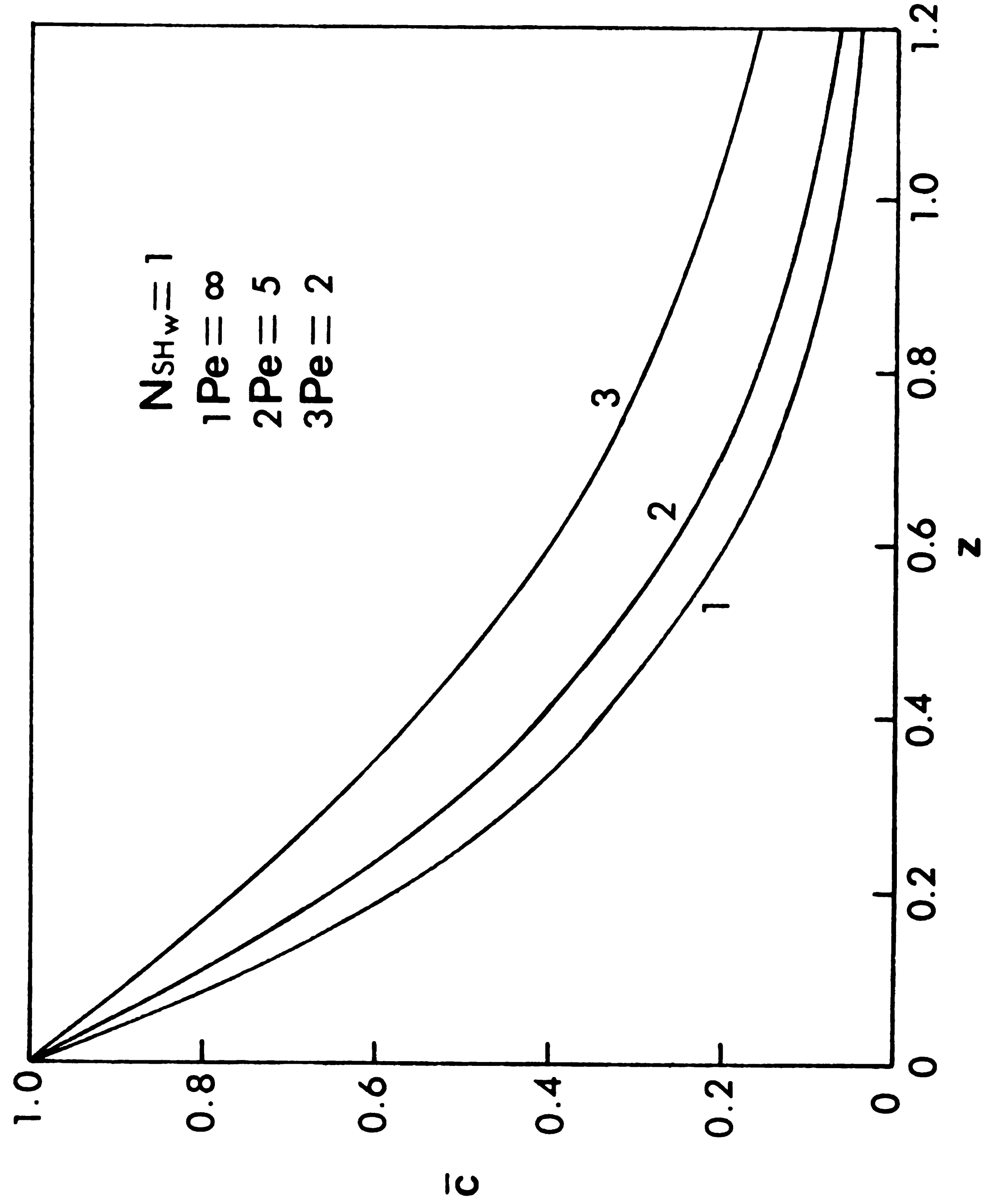

$N_{SH_w} = 1$
1 Pe = ∞
2 Pe = 5
3 Pe = 2
1
2
3
z
$\bar{c}$
0
0.2
0.4
0.6
0.8
1.0
1.2

Fig. 6.5--Local bulk concentration as a function of reduced axial distance from the entrance for $N_{sh_w} = 5$, Pe = 2, 5, and ∞.

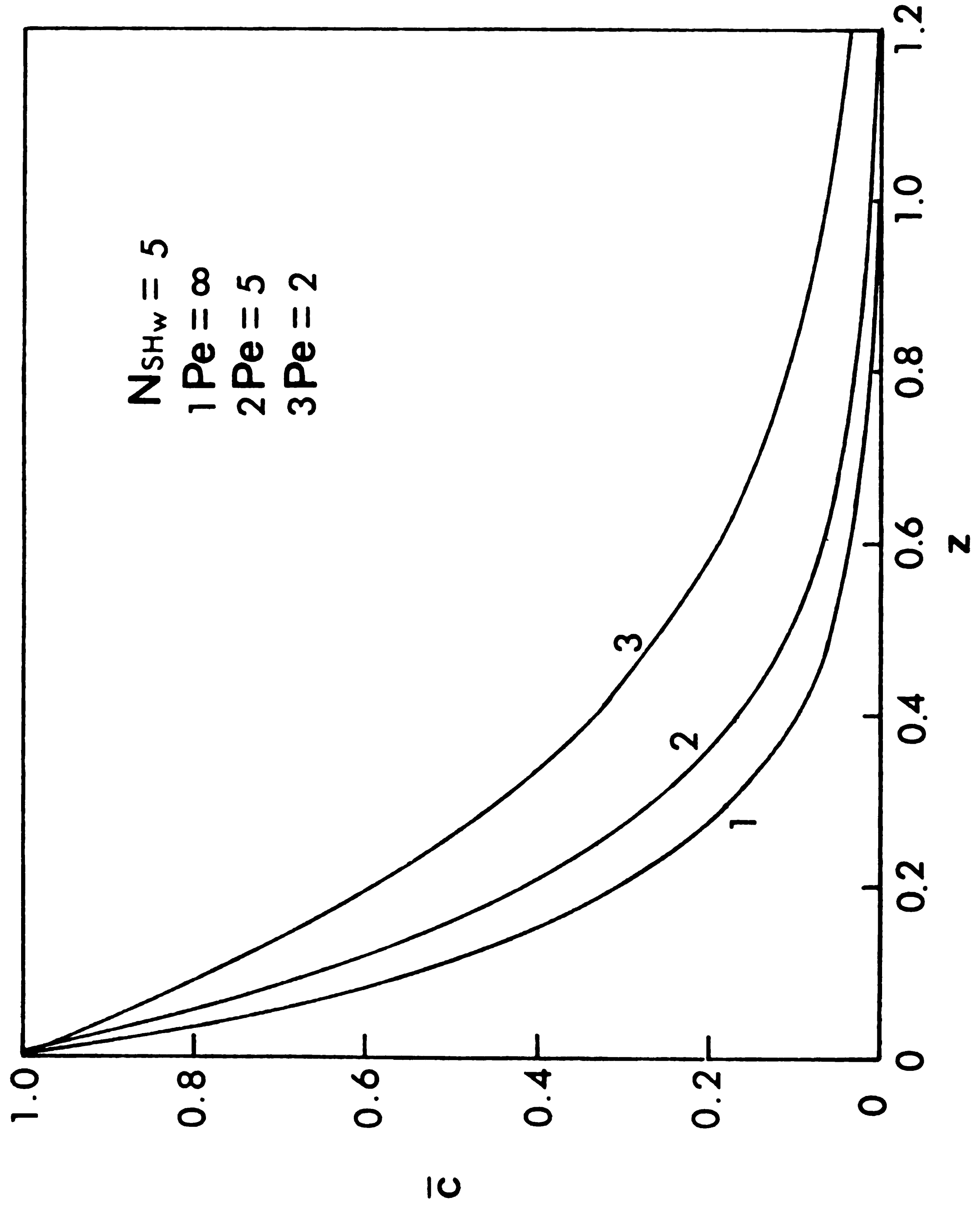
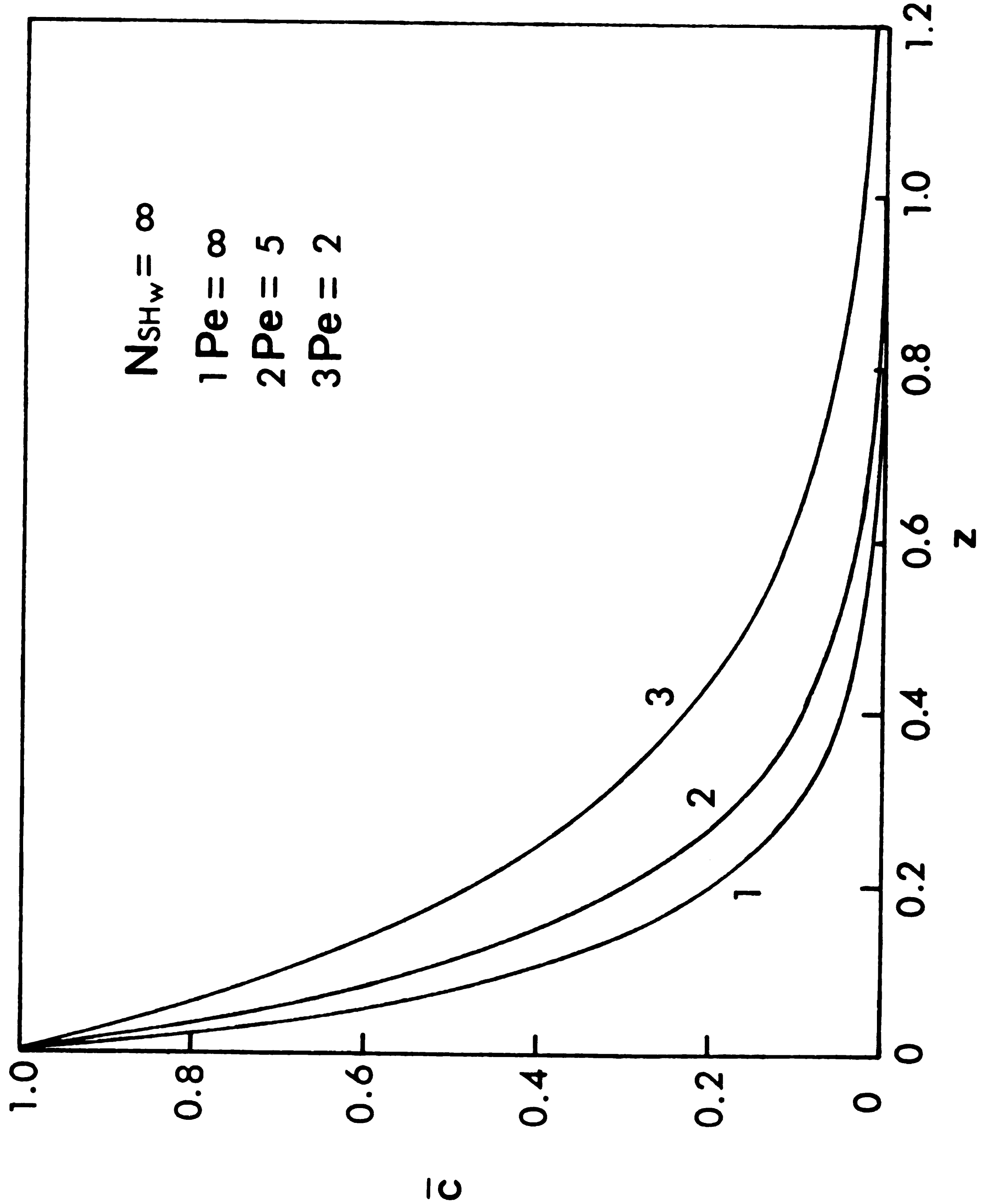

$N_{SH_w} = 5$
1 Pe = ∞
2 Pe = 5
3 Pe = 2
1
2
3
$\bar{c}$
z
0
0.2
0.4
0.6
0.8
1.0
1.2

Fig. 6.6--Local bulk concentration as a function of reduced axial distance from the entrance for $N_{sh_w} = \infty$, Pe = 2, 5, and ∞.


$N_{SH_w} = \infty$
1 Pe = ∞
2 Pe = 5
3 Pe = 2
1
2
3
$\bar{c}$
1.0
0.8
0.6
0.4
0.2
0
z
0
0.2
0.4
0.6
0.8
1.0
1.2

$$N_{sh} = \sum_{n=1}^{N} B_n \exp(-\beta_n^2 z) \exp(-\beta_n/2) [2kM(k+1,1,\beta_n) - (2k+\beta_n) M(k,1,\beta_n)] /$$

$$2 \sum_{n=1}^{N} B_n \exp(-\beta_n^2 z) \int_0^1 \zeta (1-\zeta^2) \exp(-\beta_n \zeta^2/2) M(k,1,\beta_n \zeta^2) d\zeta \tag{6.58}$$

with

$$k = \frac{1}{2} - (\beta_n/4)[1+(\beta_n/Pe)^2] \quad , \tag{6.59}$$

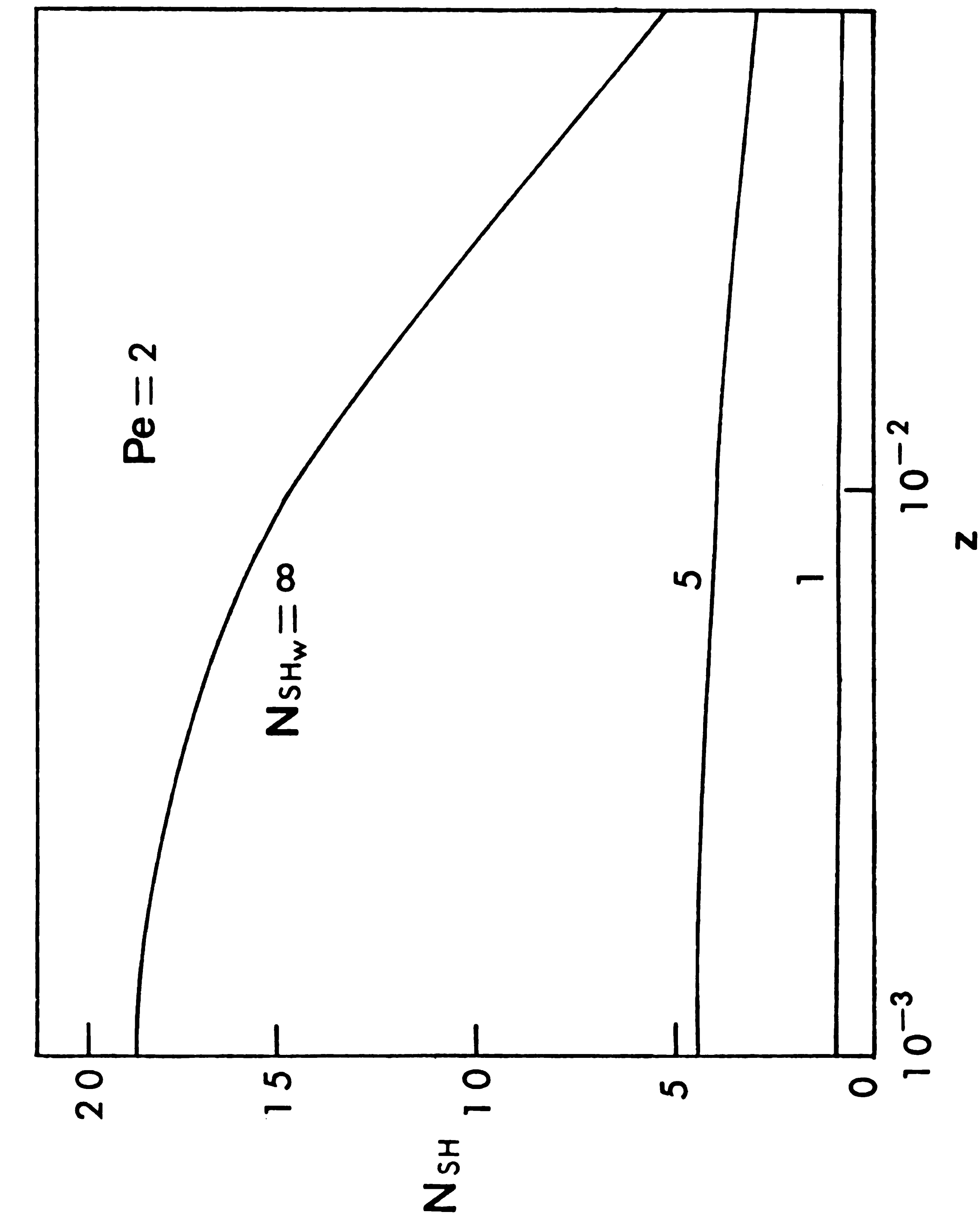
where we have truncated the infinite series to N terms for the numerical calculation. The overall Sherwood numbers are calculated for various Pe and N_{sh_w} values and are shown in Fig. 6.7 to Fig. 6.9. It is seen that the Sherwood number increases with increasing Peclect number for a fixed wall Sherwood number and, not surprisingly, increases with increasing wall Sherwood number for fixed Peclet number. The figures also indicate that the mass transfer rate is highest near the entrance region and generally decreases to a constant value.

The overall picture can be summarized qualitatively:

(1) Whenever the membrane permeability increases (increasing N_{sh_w}) the total mass tansfer rate through the membrane also increases (increasing overall Sherwood number N_{sh}).

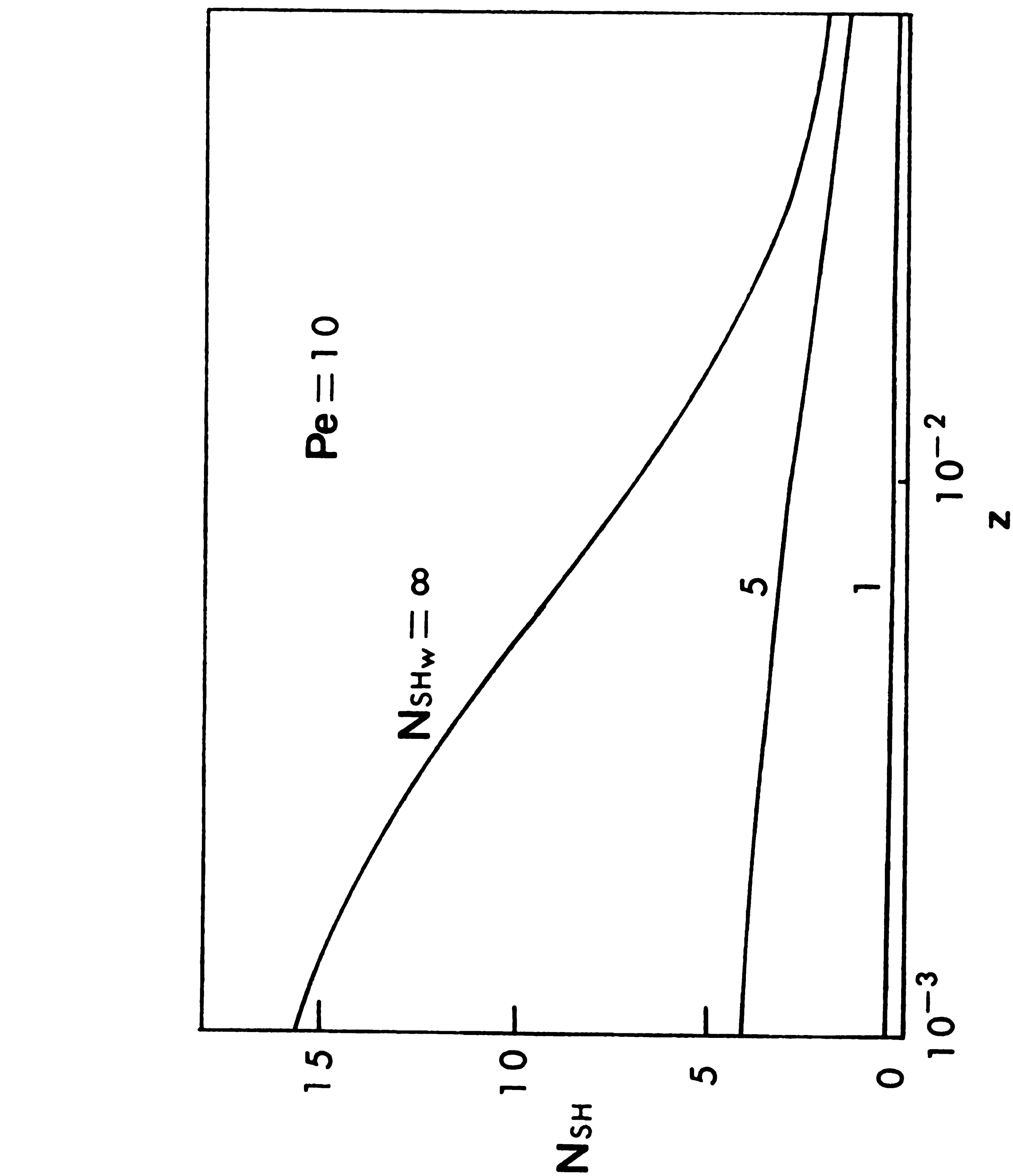
(2) The local bulk concentration decreases with axial coordinates due to the fact that solutes are

Fig. 6.7--Overall Sherwood number as a function of reduced axial distance from the entrance for $Pe = 2$, $N_{sh_w} = 1, 5, \infty$.



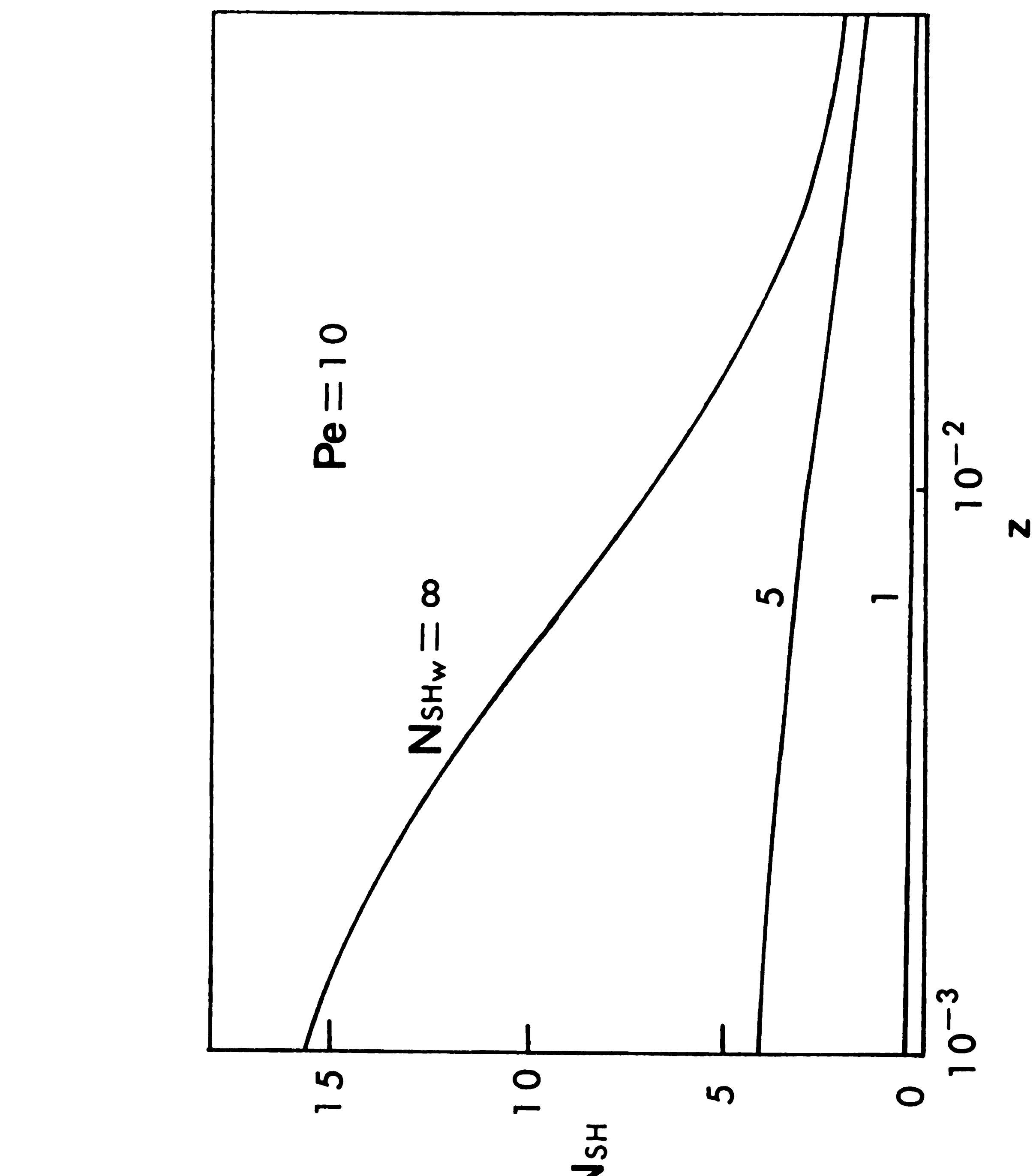
Pe = 2
$N_{SH_w} = \infty$
5
1
N_{SH}
20
15
10
5
0
10^{-3}
10^{-2}
z

Fig. 6.8--Overall Sherwood number as a function of reduced axial distance from the entrance for Pe = 10, N_{sh_w} = 1, 5, ∞.



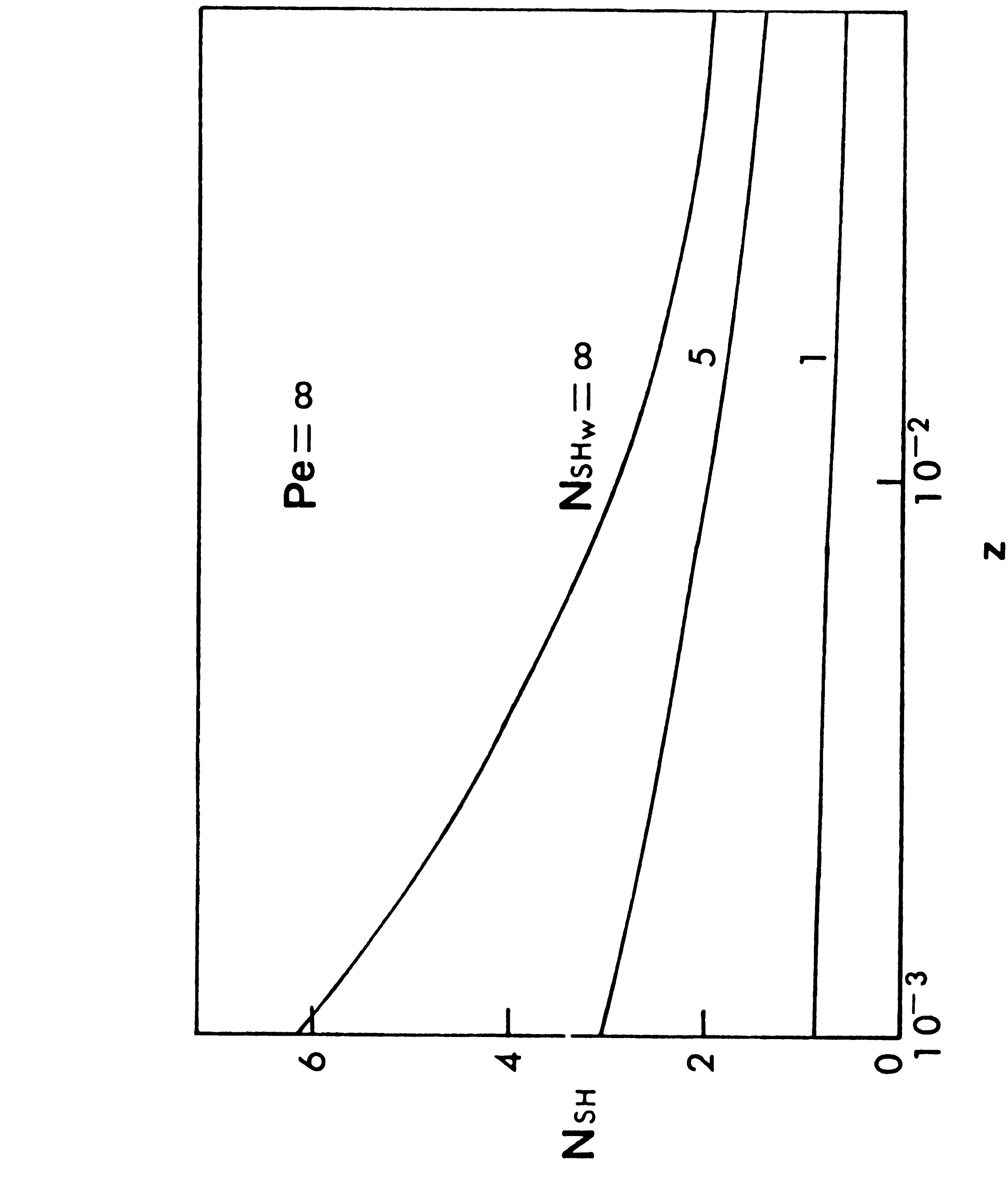
Pe = 10
N_{SH_w} = 8
5
1
N_{SH}
15
10
5
0
10^{-3}
10^{-2}
z

Fig. 6.8--Overall Sherwood number as a function of reduced axial distance from the entrance for Pe = 10, N_{sh_w} = 1, 5, ∞.



N_{SH}
0
5
10
15
10^{-3}
10^{-2}
z
Pe = 10
$N_{SH_w} = \infty$
5
1

Fig. 6.9--Overall Sherwood number as a function of reduced axial distance from the entrance for $Pe = \infty$, $N_{sh_w} = 1, 5, \infty$.



Pe = ∞
N_SHw = ∞
5
1
N_SH
6
4
2
0
10^-3
10^-2
z

diffusing through the membrane into the dialysate along the membrane wall.

(3) The presence of axial diffusion (small Pe) tends to decrease the overall mass transfer rate (decreasing N_{sh}) along the tabular membrane and also tends to reduce the size of local concentration gradients.

G. Discussion

In this chapter we have treated tubular membrane transport with axial diffusion and with a boundary condition of finite wall permeabilities. The solutions are expressed terms of Kummer functions, and numerical values are obtained by the use of an "Overdetermined Collocation" method.

In addition we have used a boundary condition of finite wall permeability which is more general than the constant wall concentration and the constant wall mass flux conditions. In fact these are the limiting cases of our boundary condition. We have also used the boundary condition that the entrance concentration is uniform over the cross section of the tubular membrane. Rigorously, the axial diffusion effect, which tends to propagate upstream, will change the entrance concentration profile. Nevertheless under some experimental conditions (*e.g.*, in hollow-fiber artificial kidney), the uniform entrance concentration condition can be considered as a very good approximation.

Although only selected results for only a few values of Pe and N_{sh_w} are presented here, they suffice to demonstrate the general trends. For other values of Pe and N_{sh_w}, one can use the method developed here systematically.

From the results in previous sections it is clear that axial diffusion is important for small Peclet numbers. This effect is significant for the prediction of performance in artificial kidney systems operated at low blood flow rate or in gas separation through tubular glass membranes.

Further extensions of this approach can be made by taking into consideration of chemical reactions at the membrane surface. This should be a good model for the hollow-fiber membrane/enzyme reactor operated at low flow rate such that $Pe < 100$ (Waterland, et al., 1974; Lewis and Middleman, 1974). Further improvement in the results can be attained by considering non-uniform entrance concentrations and extending the problem to an infinite domain instead of the semi-infinite one considered here. One can also extend the approach to non-Newtonian flows (which do not have parabolic velocity profile) such as polymer solutions. Moreover, one could take into account osmotic pressure and convection across the membrane in the radial direction. In either case the neglect of axial diffusion can only be justified when the Peclet number is very large.

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APPENDICES

APPENDIX A

THE MODIFIED NERNST-PLANCK EQUATION

Equation (5.1) repeated here,

$$\underset{\sim}{N}_\alpha = - z_\alpha \omega_\alpha c_\alpha F \underset{\sim}{\nabla} \phi - D_\alpha \underset{\sim}{\nabla} c_\alpha - \beta_\alpha \underset{\sim}{\nabla} p + c_\alpha \underset{\sim}{u} \qquad \text{(A.1)}$$

is useful, but it is correct only for extreme dilution. Our use of it in Chapter V is justifiable because our chief purpose there was to obtain the form (particularly the sign) of the concentration gradient contribution to anomalous osmosis. Better numerical estimates of the contribution can be obtained by starting with the more exact equation of this Appendix.

Most common transport properties for electrolyte solutions (mobility, transference number, conductance) are defined and measured in the Hittorf frame of reference, where the diffusion fluxes are defined by

$$\underset{\sim}{j}_\alpha^H \equiv c_\alpha (\underset{\sim}{u}_\alpha - \underset{\sim}{u}_w) \ , \qquad \text{(A.2)}$$

where u_w is the velocity of the solvent, water. The absolute molar fluxes,

$$\underset{\sim}{N}_\alpha \equiv c_\alpha \underset{\sim}{u}_\alpha \ , \qquad \text{(A.3)}$$

are related to the Hittorf fluxes by

$$\underset{\sim}{N}_\alpha = c_\alpha \underset{\sim}{u} + \underset{\sim}{j}_\alpha^H - (x_\alpha/\overline{M}) \sum_{\beta=1}^{w-1} M_\beta \underset{\sim}{j}_\beta^H \ , \qquad \alpha=1,\ldots,w-1$$

$$\underset{\sim}{N}_w = c_w \underset{\sim}{u} - (x_w/\overline{M}) \sum_{\beta=1}^{w-1} M_\beta \underset{\sim}{j}_\beta^H \ , \tag{A.4}$$

where $\overline{M}$ is the mean molecular weight,

$$\overline{M} = \sum_{\beta=1}^{w} x_\beta M_\beta \ , \tag{A.5}$$

and the velocity $\underset{\sim}{u}$ of the center of mass is given by

$$\underset{\sim}{u} = (v/\overline{M}) \sum_{\beta=1}^{w} M_\beta \underset{\sim}{N}_\beta \ , \tag{A.6}$$

where v is the molar volume of the solution.

For an isothermal single strong electrolyte, the linear flux equations in the Hittorf frame are (Haase, 1969; Katchalsky and Curran, 1965)

$$\underset{\sim}{j}_+^H = - a_{++} \underset{\sim}{\nabla} \mu'_+ - a_{+-} \underset{\sim}{\nabla} \mu'_-$$

$$\underset{\sim}{j}_-^H = - a_{-+} \underset{\sim}{\nabla} \mu'_+ - a_{--} \underset{\sim}{\nabla} \mu'_- \tag{A.7}$$

where the $a_{\alpha\beta}$ are Onsager coefficients and the μ'_α include external potentials. For an ideal solution (or for a sufficiently dilute solution),

$$\underset{\sim}{\nabla}\mu'_\alpha = v_\alpha \underset{\sim}{\nabla} p + RT\underset{\sim}{\nabla}\ell n x_\alpha + z_\alpha F \underset{\sim}{\nabla}\phi \ . \tag{A.8}$$

Moreover,

$$\underset{\sim}{\nabla}\ell n x_+ = \underset{\sim}{\nabla}\ell n x_- \approx \{1+\nu c[v_w-(z_-v_+-z_+v_-)(z_--z_+)^{-1}]\}^{-1}\underset{\sim}{\nabla}\ell n c_+ \ , \tag{A.9}$$

where, for an electrolyte of molarity c which contains ν_+ moles of cation and ν_- moles of anion per mole of electrolyte,

$$c_+ = \nu_+ c \ , \qquad c_- = \nu_- c \ ,$$

$$\nu = \nu_+ + \nu_- \ , \quad z_+\nu_+ + z_-\nu_- = 0 \ . \tag{A.10}$$

In terms of more accessible experimental quantities, the Onsager coefficients are, when $a_{+-} = a_{-+}$,

$$a_{++} = (c_+\lambda_+^2/z_+F^2\Lambda) + (\nu_+c_+D/\nu RT)$$

$$a_{+-} = a_{-+} = (c_+\lambda_+\lambda_-/z_-F^2\Lambda) + (\nu_-c_+D/\nu RT)$$

$$= -(c_-\lambda_+\lambda_-/z_+F^2\Lambda) + (\nu_+c_-D/\nu RT)$$

$$a_{--} = -(c_-\lambda_-^2/z_-F^2\Lambda) + (\nu_-c_-D/\nu RT) \ . \tag{A.11}$$

The λ_α in these formulas are the single ionic conductances, which are related to the Hittorf transference number t_α by

$$\lambda_\alpha = \Lambda t_\alpha \;, \qquad \alpha=+,- \tag{A.12}$$

where Λ is the equivalent conductance,

$$\Lambda = \lambda_+ + \lambda_- \tag{A.13}$$

and the transference numbers sum to one,

$$t_+ + t_- = 1 \;. \tag{A.14}$$

The diffusion coefficient D in (A.11) is the Fickian mutual diffusion coefficient for the binary system. Instead of conductances, earlier workers used mobilities ω_α defined by

$$\omega_+ = \lambda_+/z_+F^2 \qquad \omega_- = -\lambda_-/z_-F^2$$

$$\omega_- = c(\nu_-\lambda_- + \nu_+\lambda_+)\omega_+ \;. \tag{A.15}$$

Thus,

$$z_+\omega_+ - z_-\omega_- = \Lambda/F^2 \tag{A.16}$$

and

$$\omega_+ - \omega_- = [(\lambda_+/z_+) + (\lambda_-/z_-)/F^2$$

$$= [(t_+/z_+) + (t_-/z_-)](z_+\omega_+ - z_-\omega_-) \;. \tag{A.17}$$

Combining (A.7) through (A.17), we find

$$
\begin{aligned}
\underset{\sim}{j}_+^H = & - \{1+\nu c[v_w-(z_-v_+-z_+v_-)(z_--z_+)^{-1}]\}^{-1} \\
& \times [D_++z_+RT\omega_+(\omega_+-\omega_-)(z_+\omega_+-z_-\omega_-)^{-1}]\underset{\sim}{\nabla}c_+ \\
& - c_+z_+\omega_+F\underset{\sim}{\nabla}\phi \\
& - [c_+z_+\omega_+(v_+\omega_+-v_-\omega_-)(z_+\omega_+-z_-\omega_-)^{-1} \\
& + \nu_+(c_+v_++c_-v_-)(D/\nu RT)]\underset{\sim}{\nabla}p
\end{aligned}
$$

$$
\begin{aligned}
\underset{\sim}{j}_-^H = & - \{1+\nu c[v_w-(z_-v_+-z_+v_-)(z_--z_+)^{-1}]\}^{-1}[D \\
& + z_-RT\omega_-(\omega_+-\omega_-)(z_+\omega_+- z_-\omega_-)^{-1}]\underset{\sim}{\nabla}c \\
& - c_-z_-\omega_-F\underset{\sim}{\nabla}\phi \\
& - [c_-z_-\omega_-(v_+\omega_+-v_-\omega_-)(z_+\omega_+-z_-\omega_-)^{-1} \\
& + \nu_-(c_+v_++c_-v_-)(D/\nu RT)]\underset{\sim}{\nabla}p \ . \qquad \text{(A.18)}
\end{aligned}
$$

Now define D_α by

$$D_\alpha = D + z_\alpha\omega_\alpha RT(\omega_+-\omega_-)(z_+\omega_+-z_-\omega_-)^{-1} \ , \ \alpha=+,- \ . \qquad \text{(A.19)}$$

In order to make contact with the Nernst-Planck equation rearrange the middle two parts of (A.11)

$$
\begin{aligned}
D &= (\nu RTa_{+-}/\nu_+c_-) + (\nu RT\lambda_+\lambda_-/\nu_+z_+F^2\Lambda) \\
&= (\nu RTa_{+-}/\nu_-c_+) - (\nu RT\lambda_+\lambda_-/\nu_-z_-F^2\Lambda) \\
&= (\nu RT/\nu_+c_-)a_{+-} + (\nu RTt_-/\nu_+)\omega_+ \\
&= (\nu RT/\nu_-c_+)a_{+-} + (\nu RTt_+/\nu_-)\omega_- \ . \qquad \text{(A.20)}
\end{aligned}
$$

(A.20) and (A.19) yield

$$D_\alpha = RT\omega_\alpha + (\nu RT/\nu_+\nu_- c)a_{+-} \ , \qquad \alpha=+,- \ . \qquad (A.21)$$

Thus, the Einstein Relation $RT\omega_\alpha = D_\alpha$ is valid only when $a_{+-}=0$. Katchalsky and Curran (1965) have calculated a_{++} , a_{--} and a_{+-} for Nacl Solutions. They find that for 0.01 M solutions, a_{+-} is about 4% of a_{++} and about 3% of a_{--} ; for 0.1 M solutions, a_{+-} is about 11% of a_{++} and about 7% of a_{--} ; for 1.0 M solution a_{+-} is about 21% of a_{++} and about 14% of a_{--} . For greatest accuracy, the a_{+-} term should be retained in (A.21). However, for <u>estimating</u> effects, it is satisfactory to use Einstein Relation.

With (A.19) and the further definitions

$$RT\omega_\alpha = D'_\alpha \ , \qquad \alpha=+,- \qquad (A.22)$$

and

$$B_\alpha = c_\alpha z_\alpha \omega_\alpha (v_+\omega_+ - v_-\omega_-)(z_+\omega_+ - z_-\omega_-)^{-1}$$

$$+ \nu_\alpha (c_+v_+ + c_-v_-)(D/\nu RT) \ , \qquad (A.23)$$

and

$$D^c_\alpha = \{1+\nu c[v_w - (z_-v_+ - z_+v_-)(z_- - z_+)^{-1}\}^{-1} D_\alpha \ , \qquad (A.24)$$

The Hittorf diffusion fluxes become

$$\underset{\sim}{j}^H_+ = - D^C_+\underset{\sim}{\nabla}c_+ - c_+z_+\omega_+F\underset{\sim}{\nabla}\phi - B_+\underset{\sim}{\nabla}p$$

$$\underset{\sim}{j}^H_- = - D^C_-\underset{\sim}{\nabla}c_- - c_-z_-\omega_-F\underset{\sim}{\nabla}\phi - B_-\underset{\sim}{\nabla}p \ . \qquad (A.25)$$

Note that $D^C_\alpha = D_\alpha$ for dilute solutions.

Substitution of these into (A.4) yields

$$\underset{\sim}{N}_+ = c_+\underset{\sim}{u} - \{D^C_+ - (x_+/\overline{M})[M_+D^C_+ + (\nu_-/\nu_+)M_-D^C_-]\}\underset{\sim}{\nabla}c_+$$

$$- [c_+z_+\omega_+ - (x_+/\overline{M})(M_+c_+z_+\omega_+ + M_-c_-z_-\omega_-)]F\underset{\sim}{\nabla}\phi$$

$$- [B_+ - (x_+/\overline{M})(M_+B_+ + M_-B_-)]\underset{\sim}{\nabla}p$$

$$\underset{\sim}{N}_- = c_-\underset{\sim}{u} - \{D^C_- - (x_-/\overline{M})[M_+D^C_+(\nu_+/\nu_-) + M_-D^C_-]\}\underset{\sim}{\nabla}c_-$$

$$- [c_-z_-\omega_- - (x_-/\overline{M})(M_+c_+z_+\omega_+ + M_-c_-z_-\omega_-)]F\underset{\sim}{\nabla}\phi$$

$$- [B_- - (x_-/\overline{M})(M_+B_+ - M_-B_-)]\underset{\sim}{\nabla}p \ . \qquad (A.26)$$

For high dilution $x_+ << 1$ and $x_- << 1$ and we have

$$N_\alpha = c_\alpha\underset{\sim}{u} - D_\alpha\underset{\sim}{\nabla}c_\alpha - c_\alpha z_\alpha\omega_\alpha F\underset{\sim}{\nabla}\phi - B_\alpha\underset{\sim}{\nabla}p \ , \qquad (A.27)$$

the modified Nernst-Planck Equation.

APPENDIX B

DERIVATION OF SOME INTEGRALS INVOLVING MODIFIED BESSEL FUNCTIONS OF THE FIRST KIND

In the following we drive equations (5.25), (5.26), (5.29), (5.30), (5.31) and (5.32) which are not available in published tables. We utilize the known relations

$$\int_0^x xI_0(x)\,dx = xI_1(x) \quad ,$$

$$\int_0^x xI_0^2(x)\,dx = x^2[I_0^2(x)-I_1^2(x)]/2 \quad , \tag{5.24}$$

$$\int_0^x x^2I_0(x)I_1(x)\,dx = x^2I_1^2(x)/2 \quad ,$$

and

$$(dI_0(x)/dx) = I_1(x) \quad ,$$

$$(dI_1(x)/dx) = I_0(x) - (I_1(x)/2) \quad . \tag{B.1}$$

We also employ integration by parts,

$$\int_a^b udV = uV|_a^b - \int_a^b Vdu \quad . \tag{B.2}$$

(1)

Let $u = x^2[I_0^2(x) - I_1^2(x)]/2$ and $dV = 2xdx$.

Integration by parts yields

$$\int_0^x x^3 I_0^2(x)\,dx - \int_0^x x^3 I_1^2(x)\,dx = \int_0^x 2x\{x^2[I_0^2(x)-I_1^2(x)]/2\}dx$$
$$= x^4[I_0^2(x)-I_1^2(x)]/2 - \int_0^x x^3 I_0^2(x)\,dx$$

or

$$2\int_0^x x^3 I_0^2(x)\,dx - \int_0^x x^3 I_1^2(x)\,dx = x^4[I_0^2(x)-I_1^2(x)]/2 \ . \qquad (B.3)$$

Similarly, letting $u = x^3 I_1(x)$ and $dV = I_1(x)dx$ and integrating, by parts, we obtain

$$\int_0^x x^3 I_1^2(x)\,dx = x^3 I_1(x) I_0(x) - 2\int_0^x x^2 I_0(x) I_1(x)\,dx - \int_0^x x^3 I_0^2(x)\,dx$$

or

$$\int_0^x x^3 I_0^2(x)\,dx + \int_0^x x^3 I_1^2(x)\,dx = x^3 I_1(x) I_0(x) - x^2 I_1^2(x) \qquad (B.4)$$

where we have used (5.24). Solving (B.3) and (B.4) together, we find

$$\int x^3 I_0^2(x)\,dx = (1/3)\{x^4[I_0^2(x)-I_1^2(x)]/2 + x^3 I_1(x) I_0(x) - x^2 I_1^2(x)\} \quad (5.25)$$

and

$$\int_0^x x^3 I_1^2(x)\,dx = (1/3)\{2x^3 I_1(x) I_0(x) - 2x^2 I_1^2(x) - x^4[I_0^2(x) - I_1^2(x)]/2\} \ . \qquad (5.26)$$

(2)

Integration by parts with $u = x^2$ and $dV = I_1(x)dx$ yields

$$\int_0^x x^2 I_1(x)\,dx = x^2 I_0(x) - 2\int_0^x x I_0(x)\,dx$$

$$= x^2 I_0(x) - 2x I_1(x) \;, \qquad (5.29)$$

where we have used (5.24).

(3)

Letting $u = x^2 I_1^2(x)$ and $dV = xI_0(x)dx$ and integrating by parts we obtain

$$\int_0^x x^3 I_1^2(x) I_0(x)\,dx = x^3 I_1^3(x) - 2\int_0^x x^3 I_1^2(x) I_0(x)\,dx$$

or

$$\int_0^x x^3 I_1^2(x) I_0(x)\,dx = x^3 I_1^3(x)/3 \;. \qquad (5.30)$$

(4)

Integration by parts with $u = x^2$ and $dV = xI_0(x)dx$ yields

$$\int_0^x x^3 I_0(x)\,dx = x^3 I_1(x) - 2\int_0^x x^2 I_1(x)\,dx$$

$$= x^3 I_1(x) = 4x I_1(x) - 2x^2 I_0(x) \;, \qquad (5.31)$$

where (5.29) has been used.

(5)

Let $u = x^4 I_0(x)$ and $dV = I_1(x)dx$. Integration by parts yields

$$\int_0^x x^4 I_0(x) I_1(x)\,dx = x^4 I_0^2(x) - 4 \int_0^x x^3 I_0^2(x)\,dx - \int_0^x x^4 I_1(x) I_0(x)\,dx$$

or

$$\int_0^x x^4 I_0(x) I_1(x)\,dx = (x^4 I_0^2(x)/6) + (x^4 I_1^2(x)/3) - (2x^3 I_1(x) I_0(x)/3) + (2x^2 I_1^2(x)/3) \quad , \qquad (5.32)$$

where (5.25) has been used.

APPENDIX C

COMPUTER PROGRAMS

The three primary computer programs used in Chapter VI are listed in this appendix. Program ROOTS uses the half-interval method to calculate eigenvalues from (6.43). Program OCM utilizes the "Overdetermined Collocation" method to evaluate linear combination coefficients for non-orthogonal functions. Program BULCON calculates local axial bulk concentrations and overall Sherwood numbers according to (6.55) and (6.58). A 15-point Gauss-Legendre quadrature formula is included in BULCON to evaluate integrals.

PROGRAM ROOTS

```
C     PROGRAM TO FIND ROOTS OF THE FUNCTION Y(W.X.Z)
      PROGRAM ROOTS (INPUT,OUTPUT,TAPE55=INPUT,TAPE65=OUTPUT,PUNCH)
      DIMENSION BL(13),BR(13),BT(13)
      PRINT 99
   99 FORMAT (1H1,* BT(L) IS THE L≠TH EIGENVALUE WITH PARAMETERS XR$ZR
     1YHALF IS THE VALUE OF THE FUNCTION Y AT BT(L) WHICH SHOULD BE *)
      PRINT 98
   98 FORMAT (* ZERO. THE CLOSER IT TO ZERO THE BETTER THE ACCURACY OF
     1BT(L).*)
      DO 3 K=1,4
      AK=K
      XR=(AK+1.)*0.1
      DO 11 J=1,11
      AJ=J
      ZR=(AJ-1.)*0.5
      N=0
      YS=0.
      DO 17 M=1,160
      AM=M
      BS=AM*0.1
      YY=Y(BS,XR,ZR)
      IF (M .EQ. 1) GO TO 16
      IF (YY*YS .LE. 0.0) GO TO 15
      GO TO 16
   15 N=N+1
      BL(N)=BS-0.1
      BR(N)=BS
   16 YS=YY
      IF (N .EQ. 13) GO TO 20
   17 CONTINUE
   20 DO 13 L=1,13
      AL=L
      YBL=Y(BL(L),XR,ZR)
      ITER=25.+(2.*AL)
C     BEGIN HALF-INTERVAL ITERATION
      DO 18 M=1,ITER
      BHALF=(BR(L)+BL(L))/2.
      YHALF=Y(BHALF,XR,ZR)
C     CHOOSE THE SUB-INTERVAL CONTAINING THE ROOT
      IF (YHALF*YHALF .LT. 2.5E-15) GO TO 32
      IF (YHALF*YBL .LT. 0.0) GO TO 19
      BL(L)=BHALF
      YBL=YHALF
      GO TO 18
   19 BR(L)=BHALF
   18 CONTINUE
   32 BT(L)=(BL(L)+BR(L))/2.
      PRINT 77,XR,ZR,L,BT(L),YHALF
   77 FORMAT (*   XR    = *,F8.3,*     ZR    = *,F8.3,*     BT(*,I2,*)    = *,
     1E16.9,*  YHALF   = *,E16.9)
   13 CONTINUE
      PUNCH 97,BT
   97 FORMAT (5E16.9)
   11 CONTINUE
    3 CONTINUE
      END


C     FUNCTION FOR EVALUATING EIGENVALUES OF ARTIFICAL KIDNEY PROBLEM
      FUNCTION Y(W,X,Z)
      S=1.
      B=W
      T=0.5-((X*X*W*W*W+W)/4.)
      TP=T+1.
      DI=T
      DL=TP
      XX=(1.+0.5*(W-X*X*W*W*W))*Z-1.
      XY=(1.-0.5*(X*X*W*W*W+W))*Z
      Y=(1.+T*W)*XX-(1.+TP*W)*XY
```

```
      DO 13 I=1,100
      AI=I
      T=T*(AI+DI)
      TP=TP*(AI+DL)
      B=B*W
      S=S*(AI+1.)
      Y=(T*B/(S*S))*XX-(TP*B/(S*S))*XY+Y
   13 CONTINUE
      RETURN
      END
```

PROGRAM BULCON

```
C     THIS PROGRAM CALCULATES THE AXIAL BULK CONCENTRATION DISTRIBUTION
      PROGRAM BULCON (INPUT,OUTPUT,TAPE55=INPUT,TAPE65=OUTPUT,PUNCH)
      DIMENSION B(10),BT(13),Z(6),CON(6),CH(6),SH(6)
      EXTERNAL C
      READ (55,70) L
      AL=L
      XR=0.1*(AL-1.)
      PRINT 71
      DO 68 M=1,11
      AM=M
      ZR=0.5*(AM-1.)
      READ (55,74) (B(J),J=1,10)
      READ (55,75) (BT(J),J=1,13)
      DO 50 J=1,6
      AJ=J
      IF (J .LE. 4) Z(J)=0.001+0.001*(AJ-1.)*3.
      IF (J .GT. 4) Z(J)=0.01+0.01*(AJ-4.)*3.
      CON(J)=0.
      DO 40 K=1,10
   40 CON(J)=CON(J)+(B(K)*EXP(-BT(K)*BT(K)*Z(J))*GAUSS(BT(K),XR,C))
      CON(J)=2.*CON(J)
      CH(J)=0.
      DO 48 K=1,10
   48 CH(J)=CH(J)+(B(K)*EXP(-BT(K)*BT(K)*Z(J))*CC(BT(K),XR,1.))
      CH(J)=2.*CH(J)
C     CALCULATE THE LOCAL SHERWOOD NUMBER
      SH(J)=-CH(J)/CON(J)
      WRITE (65,72) XR,ZR,J,Z(J),CON(J),SH(J)
   50 CONTINUE
      PUNCH 73,(CON(J),SH(J),J=1,6)
   68 CONTINUE
   70 FORMAT (I1)
   71 FORMAT (1H1)
   72 FORMAT (/,*     XR    =  *,F8.3,*    ZR    =   *,F8.3,*   Z(*,I2,*)
     1=  *,F7.3,*    CON    =  *,E16.9,*    SH    =    *,E16.9)
   73 FORMAT (4E16.9)
   74 FORMAT (5E16.9)
   75 FORMAT (5E16.9)
      END


C     EIGENFUNCTION FOR THE TUBULAR MEMBRANE PROBLEM
      FUNCTION CC(W,X,Y)
C     W CORRESPONDS TO B(N), X CORRESPONDS TO K AND Y CORRESPONDS TO R.
      S=1.
      T=0.5-((X*X*W*W*W+W)/4.)
      TP=T+1.$TPI=TP$TI=T
      B=W*Y*Y$BI=B$XX=EXP(-0.5*B)
      CI=1.+T*B
      CT=1.+TP*B
      DO 13 I=1,100
      AI=I$T=T*(AI+TI)$TP=TP*(AI+TPI)
```

```
      B=B*BI$S=S*(AI+1.)
      CII=T*B/(S*S)
      CTI=TP*B/(S*S)
      CI=CII+CI
      CT=CTI+CT
      IF (CTI .EQ. 0. .AND. CII .EQ. 0.) GO TO 99
   13 CONTINUE
   99 CC=(CT*2.*TI-((2.*TI)+W)*CI)*XX
      RETURN
      END


C     EIGENFUNCTION FOR THE TUBULAR MEMBRANE PROBLEM
C     EXP(-0.5*B(N)*R*R)*M(A,1,B(N)*R*R)
C     W CORRESPONDS TO B(N), X CORRESPONDS TO K AND Y CORRESPONDS TO R.
      FUNCTION C(W,X,Y)
      S=1.
      T=0.5-((X*X*W*W*W+W)/4.)
      TI=T
      B=W*Y
      BI=B
      XX=(EXP(-0.5*B))*(1.-Y)
      CI=1.+T*B
      DO 13 I=1,100
      AI=I
      T=T*(AI+TI)
      B=B*BI
      S=S*(AI+1.)
      CII=T*B/(S*S)
      CI=CII+CI
      IF (CII .EQ. 0.) GO TO 99
   13 CONTINUE
   99 C=CI*XX
      RETURN
      END


      FUNCTION GAUSS(W,X,C)
      EXTERNAL C
C     THE FUNCTION GAUSS USES THE 15-POINT GAUSS-LEGENDRE QUADRATURE
C     FORMULA TO COMPUTE THE INTEGRAL OF C(W,X,Y)*RDR BETWEEN INTEGRA-
C     TION LIMITS 0 AND 1. THE ROOTS OF SEVEN LEGENDRE POLYNOMIALS AND
C     THE WEIGHT FACTORS FOR THE CORRESPONDING QUADRATURES ARE STORED
C     IN THE ZZ AND WEIGHT ARRAYS RESPECTIVELY.
      DIMENSION ZZ(8),WEIGHT(8)
      DATA ZZ/0.          ,0.2011940939,0.3941513470,0.5709721726,
     10.7244177313,0.8482065834,0.9372733924,0.9879925180/
      DATA WEIGHT/0.2025782419,0.1984314853,0.1861610001,0.1662692058,
     10.1395706779,0.1071592204,0.0703660474,0.0307532419/
C     SET UP INITIAL PARAMETERS
      D=0.5
C     ACCUMULATE THE SUM IN THE 15-POINT FORMULA
      SUM=0.0
      DO 5 J=1,8
      IF (ZZ(J) .EQ. 0.0) SUM=SUM+WEIGHT(J)*C(W,X,D)
    5 IF (ZZ(J) .NE. 0.0) SUM=SUM+WEIGHT(J)*(C(W,X,D*ZZ(J)+D)+C(W,X,-ZZ(
     1J)*D+D))
C     MAKE INTERVAL CORRECTION AND RETURN
      GAUSS=D*SUM
      RETURN
      END
```

PROGRAM OCM

```
      PROGRAM OCM (INPUT,OUTPUT,TAPE55=INPUT,TAPE65=OUTPUT,PUNCH)
C     THIS PROGRAM USES THE OVERDETERMINED COLLOCATION METHOD TO FIND
C     THE LINEAR COMBINATION COEFFICIENTS OF AN EIGENVALUE PROBLEM WITH
C     NON-ORTHOGONAL EIGENFUNCTIONS, SUCH THAT THE SOLUTIONS SATIFY THE
C     BOUNDARY CONDITIONS IN THE LEAST SQUARE SENSE
      DIMENSION A(21,13),E(21,13),BT(13),SUM(21)
      DO 34 J=1,6
      AJ=J
      XR=0.1*(AJ-1.)
      PRINT 32
      DO 33 M=1,11
      AM=M
      ZR=0.5*(AM-1.)
C     CALCULATE THE EIGENFUNCTION MATRIX
      READ (55,30) (BT(I),I=1,13)
      DO 8 K=1,21
      AK=K
      R=0.05*(AK-1.)
      DO 8 L=1,13
      E(K,L)=C(BT(L),XR,R)
    8 CONTINUE
C     CONSTRUCT THE ORIGINAL EIGEN FN. MATRIX FOR DIFFERENT DISCRETE
C     INTERVALS
      JTER=10
      N=JTER+1
C     START TO MINIMIZE THE MEAN SQUARE ERROR AND TO OBTAIN THE
C     NORMAL EQUATIONS
      DO 16 L=1,JTER
      A(L,N)=0.
C     USE SIMPSON≠S RULE TO EVALUATE THE INTEGRAL
      DO 6 I=1,21
      AI=I$HI=I/2$HAI=AI/2.$R=0.05*(AI-1.)
      IF (HI .EQ. HAI) A(L,N)=(2.*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,
     1L))+A(L,N)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 5
      IF (HI .NE. HAI) A(L,N)=(R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L))
     1+A(L,N)
      GO TO 6
    5 A(L,N)=(0.5*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L))+A(L,N)
    6 CONTINUE
      DO 15 K=L,JTER
      A(L,K)=0.
C     USE SIMPSON≠S RULE
      DO 18 I=1,21
      AI=I$HI=I/2$HAI=AI/2.$R=0.05*(AI-1.)
      IF (L .NE. K) GO TO 4
      IF (HI .EQ. HAI) A(L,K)=2.*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L
     1)*E(I,L)+A(L,K)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 3
      IF (HI .NE. HAI) A(L,K)=R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L)*E
     1(I,L)+A(L,K)
      GO TO 18
    3 A(L,K)=0.5*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L)*E(I,L)+A(L,K)
      GO TO 18
    4 IF (HI .EQ. HAI) A(L,K)=-2.*XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,
     1K)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 1
      IF (HI .NE. HAI) A(L,K)=-XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,K)
      GO TO 18
    1 A(L,K)=-0.5*XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,K)
   18 CONTINUE
      IF (L .NE. K) A(K,L)=A(L,K)*BT(L)*BT(L)/(BT(K)*BT(K))
   15 CONTINUE
   16 CONTINUE
C     BEGIN ELIMINATION PROCEDURE
      DETER=1.
      DO 23 I=1,JTER
C     UPDATE THE DETERMINANT
      DETER=DETER*A(I,I)
C     CHECK FOR PIVOT ELEMENT TOO SM/LL
      IF (ABS(A(I,I)) .GT. 1.0E-15) GO TO 14
```

PROGRAM OCM

```
      PROGRAM OCM (INPUT,OUTPUT,TAPE55=INPUT,TAPE65=OUTPUT,PUNCH)
C     THIS PROGRAM USES THE OVERDETERMINED COLLOCATION METHOD TO FIND
C     THE LINEAR COMBINATION COEFFICIENTS OF AN EIGENVALUE PROBLEM WITH
C     NON-ORTHOGONAL EIGENFUNCTIONS. SUCH THAT THE SOLUTIONS SATIFY THE
C     BOUNDARY CONDITIONS IN THE LEAST SQUARE SENSE
      DIMENSION A(21,13),E(21,13),BT(13),SUM(21)
      DO 34 J=1,6
      AJ=J
      XR=0.1*(AJ-1.)
      PRINT 32
      DO 33 M=1,11
      AM=M
      ZR=0.5*(AM-1.)
C     CALCULATE THE EIGENFUNCTION MATRIX
      READ (55,30) (BT(I),I=1,13)
      DO 8 K=1,21
      AK=K
      R=0.05*(AK-1.)
      DO 8 L=1,13
      E(K,L)=C(BT(L),XR,R)
    8 CONTINUE
C     CONSTRUCT THE ORIGINAL EIGEN FN. MATRIX FOR DIFFERENT DISCRETE
C     INTERVALS
      JTER=10
      N=JTER+1
C     START TO MINIMIZE THE MEAN SQUARE ERROR AND TO OBTAIN THE
C     NORMAL EQUATIONS
      DO 16 L=1,JTER
      A(L,N)=0.
C     USE SIMPSON≠S RULE TO EVALUATE THE INTEGRAL
      DO 6 I=1,21
      AI=I$HI=I/2$HAI=AI/2.$R=0.05*(AI-1.)
      IF (HI .EQ. HAI) A(L,N)=(2.*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,
     1L))+A(L,N)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 5
      IF (HI .NE. HAI) A(L,N)=(R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L))
     1+A(L,N)
      GO TO 6
    5 A(L,N)=(0.5*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L))+A(L,N)
    6 CONTINUE
      DO 15 K=L,JTER
      A(L,K)=0.
C     USE SIMPSON≠S RULE
      DO 18 I=1,21
      AI=I$HI=I/2$HAI=AI/2.$R=0.05*(AI-1.)
      IF (L .NE. K) GO TO 4
      IF (HI .EQ. HAI) A(L,K)=2.*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L
     1)*E(I,L)+A(L,K)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 3
      IF (HI .NE. HAI) A(L,K)=R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L)*E
     1(I,L)+A(L,K)
      GO TO 18
    3 A(L,K)=0.5*R*(1.-(R*R)+1.*XR*XR*BT(L)*BT(L))*E(I,L)*E(I,L)+A(L,K)
      GO TO 18
    4 IF (HI .EQ. HAI) A(L,K)=-2.*XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,
     1K)
      IF (I .EQ. 1 .OR. I .EQ. 21) GO TO 1
      IF (HI .NE. HAI) A(L,K)=-XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,K)
      GO TO 18
    1 A(L,K)=-0.5*XR*XR*BT(K)*BT(K)*R*E(I,L)*E(I,K)+A(L,K)
   18 CONTINUE
      IF (L .NE. K) A(K,L)=A(L,K)*BT(L)*BT(L)/(BT(K)*BT(K))
   15 CONTINUE
   16 CONTINUE
C     BEGIN ELIMINATION PROCEDURE
      DETER=1.
      DO 23 I=1,JTER
C     UPDATE THE DETERMINANT
      DETER=DETER*A(I,I)
C     CHECK FOR PIVOT ELEMENT TOO SM/LL
      IF (ABS(A(I,I)) .GT. 1.0E-15) GO TO 14
```

```
      WRITE (65,29)
      GO TO 33
   14 IP1=I+1
      DO 21 L=IP1,N
   21 A(I,L)=A(I,L)/A(I,I)
      A(I,I)=1.
C     ELIMINATE K(TH) COLUMN ELEMENTS EXCEPT FOR PIVOT
      DO 23 K=1,JTER
      IF (K .EQ. I .OR. A(K,I) .EQ. 0.) GO TO 23
      DO 22 L=IP1,N
   22 A(K,L)=A(K,L)-A(K,I)*A(I,L)
      A(K,I)=0.
   23 CONTINUE
      WRITE (65,28) XR,ZR,DETER
      DO 24 I=1,JTER
      WRITE (65,27) I,BT(I),I,A(I,N)
   24 CONTINUE
      PUNCH 25,(A(I,N),I=1,JTER)
C     DETERMINE ROOT MEAN SQUARE ERROR
      TS=0.
      DO 12 L=1,21
      SUM(L)=-1.
      DO 10 I=1,JTER
   10 SUM(L)=A(I,N)*E(L,I)+SUM(L)
      SUMS=SUM(L)*SUM(L)
      TS=SUMS+TS
   12 CONTINUE
      RMS=SQRT(TS/21.)
      WRITE (65,31) RMS
C     FORMATS FOR INPUT AND OUTPUT STATEMENT
   25 FORMAT (5(E16.9))
   27 FORMAT (*    BT(*,I2,*)  =  *,E16.9,*    B(*,I2,*)  =  *,1PE15.8)
   28 FORMAT ( / ,*   XR      =  *,F5.3,/,*    ZR      =  *,F5.3,/,*   DETE
     1R  =  *,1PE15.8,//,*                            THE RESULTING COEFFICI
     2ENTS ARE*,/,*   WHERE BT(I) IS THE I≠TH EIGENVALUE, B(I) IS THE I≠
     3TH COEFFICIENT*,/)
   29 FORMAT (*   SMALL PIVOT, THE MATRIX MAY BE SINGULAR*)
   30 FORMAT (5E16.9)
   31 FORMAT (*   ROOT MEAN SQUARE ERROR RMS   =   *,1PE15.8)
   32 FORMAT (1H1)
   33 CONTINUE
   34 CONTINUE
      END


C     EIGENFUNCTION FOR THE CONVECTIVE DIFFUSION PROBLEM WITH AXIAL
C     DIFFUSION
C     EXP(-0.5*B(N)*R*R)*M(A,1,B(N)*R*R)
      FUNCTION C(W,X,Y)
C     W CORRESPONDS TO B(N), X CORRESPONDS TO K AND Y CORRESPOBDS TO R.
      S=1.
      T=0.5-((X*X*W*W*W+W)/4.)
      TI=T
      B=W*Y*Y
      BI=B
      XX=EXP(-0.5*B)
      CI=1.+T*B
      IF (B .EQ. 0.) GO TO 99
      DO 13 I=1,100
      AI=I
      T=T*(AI+TI)
      B=B*BI
      S=S*(AI+1.)
      CCI=(T*B/(S*S))
      CI=CCI+CI
      IF (CCI .EQ. 0.) GO TO 99
   13 CONTINUE
   99 C=CI*XX
      RETURN
      END
```