NONEQUILIBRIUM THERMODYNAMIC THEORY OF TRANSPORT IN MEMBRANES

Thesis for the Degree of Ph. D. MICHIGAN STATE UNIVERSITY JING-SHYONG CHEN 1971



This is to certify that the

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ABSTRACT

NONEQUILIBRIUM THERMODYNAMIC THEORY OF TRANSPORT IN MEMBRANES

By

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The steady-state transport theory that accounts for the osmotic flow of fluids through biological membranes is obtained, subject to certain simplifying assumptions which may be removed in subsequent work. The principles of hydrodynamics and nonequilibrium thermodynamics are used to describe the simultaneous transport of mass and electric current and the osmotic flow rate in a fluid system undergoing osmosis. In order to understand better the osmotic flow phenomena in biological systems, the following particular subjects are thoroughly investigated: (1) the distribution of ions in charged membranes, including the effect of molar volumes of ions, (2) the solution of Poisson's equation modified by inclusion of the dependence of the dielectric constant of the salt solution on the salt concentration and the electric field, and (3) the distribution of pressure

including the effects of ionic concentrations and electric field. Their contributions to biological systems are discussed. Moreover, the range of applicability of such classical monuments as the Boltzmann equation and the linearized Debye-Hückel theory is examined.

After these fundamental problems are dealt with, the transport theory is obtained subject to membrane surface charge density of $\sigma \approx 10^{-3} \text{ C/m}^2$ (C = Coulomb: m = meter), which is apparently reasonable biologically. A capillary model is used for the membrane separating two aqueous salt solutions of different concentration at the same temperature. The theory is valid for total ionic concentrations between about 0.004 molar and 2 molar, a range which includes systems of biological interest and more concentrated systems. We assume that there is no hydrostatic pressure difference across the membrane. The steady-state solutions of the differential equations derived are obtained for the case of a symmetrical, binary electrolyte, yielding the average osmotic flow rate as a function of initial concentrations. The result of the theoretical section is then used to explain, at least qualitatively, the osmotic flow phenomena observed experimentally. In particular, the theoretical equations predict both the shape of the experimental curves of flow rate versus concentration and the direction of flow through charged membranes.

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NONEQUILIBRIUM THERMODYNAMIC THEORY OF

TRANSPORT IN MEMBRANES

Ву

Jing-Shyong Chen

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

To My Parents

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CHAPTER I

INTRODUCTION

A. Membranes and Membrane Phenomena

Transport phenomena across membranes, charged or uncharged, are encountered in many areas of life and physical sciences. For instance, chemists and chemical engineers would like to understand the mechanisms of membrane transport so that they would be able to fabricate membranes of any desired property or properties. Biologists, on the other hand, are interested in understanding the behavior of complex cell membranes in terms of established physicochemical principles.

A membrane, in simple terms, is a phase, internally heterogeneous or homogeneous, which acts as a barrier to flow of some of the molecules and ions present in the liquid and/or gases in contact with it. Most membranes, except the obvious ones such as oil membranes, are to be considered heterogeneous. Membranes may also be classified natural or artificial. All biological membranes are natural membranes.

Functionally, a membrane must be more or less active in the selective transport of some ions when used as a barrier to separate two solutions or phases, unless it is too fragile or too porous. Most artificial and natural membranes have been found to carry ionogenic groups either fixed to the three dimensional membrane matrix, as seen in a well-characterized ion exchange membrane, or adsorbed, as found in some colloidal systems (Kobatake, 1959). Ionogenic groups and pores (space occupied by water) in a membrane attribute certain functionality to the membrane. Thus a membrane may be considered permselective and/or semipermeable depending on its functionality. The phenomenological transport property that controls the former is the transport number or transference number, whereas the latter is determined by the so-called reflection coefficient (ratio of the actual hydrostatic pressure required to give zero net volume flow to that which is required if the membrane were truly semipermeable) introduced by Staverman (1951; 1952).

In the absence of external strains and external magnetic and gravitational forces, the driving forces that may produce a flow or flux of molecular or ionic species through a membrane separating two solutions are (1) gradient of concentration, (2) gradient of pressure, (3) gradient of temperature, (4) gradient of electric

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potential, and (5) chemical reactions. These forces may operate in various combinations and may generate a number of transport phenomena. To understand membrane phenomena, it is necessary to propose or design various transport systems or model systems consisting of membranes with particular and predetermined specific properties.

B. Motivation

The transport of solutes and water through living systems has been the subject of rather extensive study since the 19th century. In spite of many experiments, the fundamental mechanisms involved in the transport phenomena exhibited by various living systems have remained relatively obscure. There are many reasons for our failure to advance more rapidly, but a number of the problems encountered in the study of living systems arise from the complex nature of living cells when considered from the point of view of a membrane system. Thus, transport phenomena in various cell membranes are vital to many biological systems.

Among many theoretically-oriented investigators, Kobatake <u>et al</u>. (1964) were the first to initiate a study based on the principles of nonequilibrium, continuum thermodynamics. They were quite successful in attempting to explain the experimental findings (Grim, 1957) with

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regard to the osmotic flow of fluids through biological membranes. Since then, various other continuum theories (<u>cf</u>. Toyoshima, 1967; Fujita and Kobatake, 1968; Gross and Osterle, 1968) have been developed. Moreover, nonequilibrium thermodynamics is often used to study the discontinuous fluid-membrane systems. The difference in the approaches between the continuous and the discontinuous fluid-membrane systems will be discussed in more detail in the next chapter.

Most of the previous theories, although adequate in many cases, are, in general, limited in the following respects:

 Use of transport equations that are restricted only to dilute aqueous salt solutions (for detailed analysis, see, for example, Chapman, 1967).

Certain transport parameters are treated as constants.

3. The effect of pressure-induced current on the overall transport phenomena is neglected, implying that the pressure is considered independent of salt concentrations and electric field.

4. The dielectric constant of pure water is used in Poisson's equation, implying that the salt solution is very dilute and the electric field at the membrane surface is negligibly small. 5. The Debye-Hückel theory is used arbitrarily and inconsistently; in particular, it is usually assumed (Kobatake and Fujita, 1964) simultaneously that the Debye length κ^{-1} is very small and that the ionic strength is very small.

6. The classical Boltzmann distribution of ions is used with no attempt at justification.

The main purpose of this work is to obtain a phenomenological transport theory for osmotic flow in biological systems that is not subject to the above restrictions and that, hopefully, will resolve some of the discrepancies appearing in the literature (<u>cf</u>. Kobatake and Fujita, 1964). In addition, we hope to use the theory to explain experimental observations of osmotic flow phenomena. In general, it is hoped that our theory can be used to describe better and to understand further the membrane systems and the mechanisms of transport processes encountered in living cells.

C. The Thesis

In the following chapters, the steady-state transport theory that accounts for the osmotic flow of fluids through biological membranes is obtained. We make use of the principles of hydrodynamics and nonequilibrium thermodynamics in describing the simultaneous transport of mass

and electric current and the osmotic flow rate in a fluid system undergoing osmosis. In order to understand better the osmotic flow phenomena in biological systems, we investigate (1) the distribution of ions in charged membranes including the effect of molar volumes of ions, (2) the solution of Poisson's equation modified by inclusion of the dependence of the dielectric constant of the salt solution on the salt concentration and the electric field, and (3) the distribution of pressure including the effects of ionic concentrations and electric field. Their contributions to biological systems are discussed. Moreover, the range of applicability of such classical monuments as the Boltzmann equation and the linearized Debye-Hückel theory is examined.

The theory is obtained subject to membrane surface charge density of $\sigma \approx 10^{-3}$ C/m² (C = Coulomb; m = meter) which has been reported (Fair and Osterle, 1971) to be sensible biologically. A capillary model is used for the membrane separating two aqueous salt solutions of different concentration at the same temperature. The theory is valid for total ionic concentrations between about 0.004 molar and 2 molar, a range which includes systems of biological interest (Woodbury <u>et al</u>., 1970) and more concentrated systems. We assume that there is no hydrostatic pressure difference across the membrane.

The steady-state solutions of the differential equations derived are obtained for the case of a symmetrical electrolyte, yielding the average osmotic flow rate as a function of initial concentrations. The result of the theoretical section is then used to explain the osmotic flow phenomena observed experimentally.

CHAPTER II

THE TRANSPORT EQUATIONS

A. Introduction

In this chapter the differential equations which describe macroscopic transport phenomena are presented. Specialized equations used in the study of osmotic flow of fluids through charged membranes are deduced, together with appropriate boundary conditions. We consider only continuous, isotropic fluids in which no chemical reactions occur and which are subject to certain driving forces but not to a magnetic field. For more detailed analysis of the equations used in the study of various transport phenomena, refer, for example, to works by Horne (1966), Kirkwood and Crawford (1952), de Groot and Mazur (1962), Fitts (1962), Katchalsky and Curran (1967), and Haase (1969). The more fundamental, rational-mechanical approach of Truesdell (1969), Bartelt and Horne (1970), and others is not required here.

Katchalsky and Curran, and Haase, have also considered membranes. A general description of transport phenomena in membranes and an extensive list of

references may be found in the recent book by Lakshminarayanaiah (1969). However, nonequilibrium thermodynamics is frequently applied to the discontinuous fluid-membrane system which is particularly convenient for experimental analysis but is not readily subjected to a theoretical treatment. The system is not regarded as a continuum, and the state variables are not continuous functions of space and time. Here the phenomenological or transport coefficients are functions of the fluid and of the membrane. This approach is a "black box" approach in that no questions are asked about the interior of the membrane.

Alternatively, if we are able to describe the details of the inside of the membrane, the fluid-membrane system could be regarded as a continuum and the state variables as continuous functions of space and time. In this approach events in a small volume element are examined and the macroscopic properties derived by averaging over the entire volume of the system being studied. Consequently, it will be necessary to construct a dynamic model and then correlate the model with the macroscopic phenomenological description obtained experimentally. The averaging process will require the choice of a proper reference frame for the flows. Kobatake and coworkers (1964) and Osterle and coworkers (1968,1970) and Manning (1968) have also used the continuous approach.

B. Chemical Potential

The driving forces needed to produce a flux or flow of molecular and/or ionic species are the gradients of the chemical potential of all species in the system (e.g., Haase, 1969). In the absence of a magnetic field, the total chemical potential μ_{α} of Component α may be written (Horne, 1966)

$$\mu_{\alpha} = \mu_{\alpha}^{O} (T,p) + RT \ln a_{\alpha} + M_{\alpha}\Gamma + z_{\alpha}F\psi \qquad (2.1)$$

where \boldsymbol{a}_{α} is the activity of Component $\boldsymbol{\alpha}$,

$$\mathbf{a}_{\alpha} = \mathbf{x}_{\alpha} \mathbf{f}_{\alpha}, \qquad (2.2)$$

T is absolute temperature, p is pressure, R is the gas constant, M_{α} is molecular weight of α , Γ is the gravitational potential, z_{α} is the ionic charge per mole of α , F is Faraday's constant, and ψ is the electrostatic potential, and where μ_{α}^{O} and the activity coefficient 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 o),

$$\mu_{\alpha}^{O} = \lim \left[\mu_{\alpha} - RT \ln x_{\alpha} - M_{\alpha}\Gamma - z_{\alpha}F\psi \right]$$
(2.3)
$$x_{O}^{\rightarrow 1}$$

whence

$$\lim_{\alpha \to 1} f_{\alpha} = 1.$$
(2.4)

We are primarily concerned with the gradient of the chemical potential. Using the chain rule for differentiation of μ_{α} (T,p,x_β, Γ , ψ) we have, in general notation,

$$\nabla \mu_{\alpha} = \mu_{\alpha T} \nabla T + \mu_{\alpha p} \nabla p + \sum_{\beta=0}^{\nu-2} \mu_{\alpha\beta} \nabla \mathbf{x}_{\beta} + \mu_{\alpha\Gamma} \nabla \Gamma + \mu_{\alpha\psi} \nabla \psi \quad (2.5)$$

where

$$\begin{split} \mu_{\alpha T} &= (\partial \mu_{\alpha} / \partial T)_{p, \mathbf{x}_{\alpha}, \Gamma, \psi} = -\overline{s}_{\alpha} \text{ (partial molar entropy)} \\ \mu_{\alpha p} &= (\partial \mu_{\alpha} / \partial p)_{T, \mathbf{x}_{\alpha}, \Gamma, \psi} = \overline{v}_{\alpha} \text{ (partial molar volume)} \\ \mu_{\alpha \beta} &= (\partial \mu_{\alpha} / \partial \mathbf{x}_{\beta})_{T, p, \Gamma, \psi} = RT (\partial \ln \mathbf{x}_{\alpha} f_{\alpha} / \partial \mathbf{x}_{\beta})_{T, p, \Gamma, \psi} \\ \mu_{\alpha \Gamma} &= (\partial \mu_{\alpha} / \partial \Gamma)_{T, p, \mathbf{x}_{\alpha}, \psi} = M_{\alpha} \\ \mu_{\alpha \psi} &= (\partial \mu_{\alpha} / \partial \psi)_{T, p, \mathbf{x}_{\alpha}, \Gamma} = z_{\alpha} F \end{aligned}$$

$$(2.6)$$

Thus,

$$\nabla \mu_{\alpha} = -\overline{\mathbf{s}}_{\alpha} \nabla \mathbf{T} + \overline{\mathbf{v}}_{\alpha} \nabla \mathbf{p} + \sum_{\beta=0}^{\nu-2} \mu_{\alpha\beta} \nabla \mathbf{x}_{\beta} + \mathbf{M}_{\alpha} \nabla \Gamma + \mathbf{z}_{\alpha} F \nabla \psi. \quad (2.7)$$

The Gibbs-Duhem equation including the external forces is (Horne, 1966)

$$\begin{array}{ccc} \nu - \mathbf{l} \\ \Sigma \\ \alpha = \mathbf{0} \end{array} \quad \mathbf{x}_{\alpha} \quad \nabla \mu_{\alpha} = -\overline{\mathbf{s}} \quad \nabla \mathbf{T} + \overline{\mathbf{v}} \quad \nabla \mathbf{p} + \overline{\mathbf{M}} \nabla \Gamma + \overline{\mathbf{z}} F \nabla \psi , \qquad (2.8) \end{array}$$

where

$$\overline{\mathbf{s}} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \overline{\mathbf{s}}_{\alpha}, \ \overline{\mathbf{v}} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \overline{\mathbf{v}}_{\alpha},$$
$$\overline{\mathbf{M}} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \mathbf{M}_{\alpha}, \ \overline{\mathbf{z}} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \mathbf{z}_{\alpha}, \ \mathbf{0} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \boldsymbol{\mu}_{\alpha\beta}.$$
(2.9)

For the case we shall treat, wherein the gravitational potential is negligible and the temperature is uniform, (2.8) becomes, upon division by \overline{v} ,

where the molarity is defined by

$$c_{\alpha} = n_{\alpha} / V = x_{\alpha} / \overline{V}$$
(2.11)

and where

$$\overline{\mathbf{Z}} = \sum_{\alpha=0}^{\nu-1} \mathbf{c}_{\alpha} \mathbf{z}_{\alpha} = (\rho/\overline{\mathbf{M}}) \overline{\mathbf{z}} .$$
(2.12)

Note that \overline{z} and \overline{z} vanish for electroneutrality.

3 ł, . For most of our purposes, (2.7) is not the most useful form for the chemical potential gradient. Instead, taking the gradient of (2.1) directly, we have

$$\nabla \mu_{\alpha} = \nabla \mu_{\alpha}^{O} (\mathbf{T}, \mathbf{p}) + \mathbf{R} \nabla \mathbf{T} \ln \mathbf{a}_{\alpha} + \mathbf{M}_{\alpha} \nabla \Gamma + \mathbf{z}_{\alpha} F \nabla \psi , \quad (2.13)$$

which becomes, for the case of negligible gravitational potential and uniform temperature,

$$\nabla \mu_{\alpha} = \overline{\mathbf{v}}_{\alpha}^{\mathbf{O}} \quad \nabla \mathbf{p} + \mathbf{R} \mathbf{T} \nabla \boldsymbol{l} \mathbf{n} \quad \mathbf{a}_{\alpha} + \mathbf{z}_{\alpha} F \nabla \boldsymbol{\psi} , \qquad (2.14)$$

where

$$(\partial \mu_{\alpha}^{O} / \partial p)_{T,\Gamma,\psi} = \overline{v}_{\alpha}^{O} = \lim_{\alpha} \overline{v}_{\alpha}, \qquad (2.15)$$

 $x_{O} \neq 1$

and where

$$RT\nabla \ln a_{\alpha} = \sum_{\beta=0}^{\nu-2} \mu_{\alpha\beta} \nabla x_{\beta} + RT (\partial \ln f_{\alpha}/\partial p)_{T,p,x_{\alpha}} \nabla p (2.16)$$

Note that

$$\overline{\mathbf{v}}_{\alpha} = \overline{\mathbf{v}}_{\alpha}^{\mathbf{O}} + RT \left(\frac{\partial \ln f_{\alpha}}{\partial p} \right)_{T,p,x_{\alpha}}$$
 (2.17)

C. Hydrodynamic Equations

Equation of Continuity of Mass

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

$$(d\rho/dt) + \rho \nabla \cdot \vec{u} = 0$$
, (2.18)

$$\rho (dw_{\alpha}/dt) + \nabla \cdot \dot{j}_{\alpha} = 0 , \qquad (2.19)$$

where ρ is density, t is time, \vec{u} is the center of mass, or barycentric velocity, and w_{α} and \vec{j}_{α} are mass fraction and diffusion flux of Component α , respectively. The barycentric velocity \vec{u} is defined by

$$\dot{\mathbf{u}} = \sum_{\alpha=0}^{\nu-1} \mathbf{w}_{\alpha} \dot{\mathbf{u}}_{\alpha}, \qquad (2.20)$$

where \vec{u}_{α} is the velocity of Component α relative to a **laboratory frame** of reference. The diffusion flux \vec{j}_{α} is defined by

$$\dot{j}_{\alpha} = \rho_{\alpha} (\dot{u}_{\alpha} - \dot{u}), \alpha = 0, \dots, \nu - 1$$
 (2.21)

Note that $\rho_{\alpha} = w_{\alpha}\rho$. The diffusion fluxes, however, are not all independent,

$$\sum_{\alpha=0}^{\nu-1} j_{\alpha} = 0 . \qquad (2.22)$$

Substantial time derivatives d/dt are relative to local time derivative $\partial/\partial t$ by

$$(d/dt) = (\partial/\partial t) + \vec{u} \cdot \nabla$$
 (2.23)

The operator " ∇ " is defined by

•

$$\nabla = \vec{1} (\partial/\partial x) + \vec{j} (\partial/\partial y) + \vec{k} (\partial/\partial z) , \qquad (2.24)$$

where \vec{i} , \vec{j} , and \vec{k} are the unit vectors of a three dimensional Cartesian coordinate system. For more detailed analysis in the use of various coordinate systems, see, for example, Irving and Mullineux (1959).

Navier-Stokes Equation

The Navier-Stokes equation which relates the velocity of barycentric frame of reference of fluids to the external forces is (Horne, 1966)

$$\rho (d\vec{u}/dt) + \nabla [(\frac{2}{3}\eta - \eta')(\nabla \cdot \vec{u})] - 2\nabla \cdot \eta \operatorname{sym} \nabla \vec{u}$$
$$= \rho \vec{X} - \nabla p , \qquad (2.25)$$

where $sym\nabla \vec{u}$ is the symmetrical part of the tensor $\nabla \vec{u}$, and where η is the coefficient of shear viscosity and η' is the coefficient of bulk viscosity, both taken as nonconstant. In writing (2.25) we have used the equation of motion,

$$\rho (d\vec{u}/dt) - \nabla \cdot \vec{\sigma} = \rho \vec{X}$$
 (2.26)

where $\dot{\vec{\sigma}}$ is the stress tensor, given approximately by the Newtonian linear phenomenological relation

$$\vec{\sigma} = - [p + (\frac{2}{3}\eta - \eta') (\nabla \cdot \vec{u})]^{\frac{2}{1}} + 2\eta \text{sym} \nabla \vec{u} , \qquad (2.27)$$

and where $\rho \mathbf{X}$, the net external force, is

$$\rho \vec{\mathbf{X}} = -\rho \nabla \Gamma - \mathbf{Z} F \nabla \psi \quad . \tag{2.28}$$

Introducing (2.23) into (2.25) and rearranging, we obtain

$$\rho (\partial \vec{u} / \partial t) = \rho \vec{X} - \nabla p + \eta \nabla^2 \vec{u} + (\frac{1}{3} \eta + \eta') \nabla (\nabla \cdot \vec{u})$$
$$- \rho \vec{u} \nabla \cdot \vec{u} , \qquad (2.29)$$

where we take η and η' to be constants.

If the system considered is at steady state, (2.29) becomes, by setting $\partial/\partial t = 0$ and rearranging,

$$\nabla \mathbf{p} - \rho \vec{\mathbf{x}} = \eta \nabla^2 \vec{\mathbf{u}} + (\frac{1}{3} \eta + \eta') \nabla (\nabla \cdot \vec{\mathbf{u}}) - \rho \vec{\mathbf{u}} \nabla \cdot \vec{\mathbf{u}} . \qquad (2.30)$$

However, most fluids except very dense ones are essentially incompressible. For an incompressible fluid, the density ρ is constant in time and position. Thus according to (2.18),

 $\nabla \cdot \vec{u} = 0 \quad . \tag{2.31}$

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

$$\nabla \mathbf{p} - \rho \dot{\mathbf{x}} = \eta \nabla^2 \dot{\mathbf{u}} . \qquad (2.32)$$
Energy Transport Equation

The general equation of continuity of total energy is

$$(\partial \rho \overline{E}_{T} / \partial t) + \nabla \cdot \vec{J}_{E_{T}} = 0$$
, (2.33)

where $\vec{J}_{E_{T}}$ is the total energy and where \overline{E}_{T} is the total specific energy,

$$\overline{E}_{T} = \overline{E} + \frac{1}{2} u^{2} . \qquad (2.34)$$

where \overline{E} is the specific internal energy and $u^2/2$ is the local kinetic energy of the center of mass. Note also that

$$u^2 = \vec{u} \cdot \vec{u}$$
(2.35)

Although it may be preferable (see Bartelt and Horne, 1970; Gyarmati, 1970; and Ingle, 1971) to obtain the kinetic energy by summing over the kinetic energies of the components, the difference between the two definitions is negligible for the present purpose (see Horne, 1966).

The energy transport equation can be expressed as

$$\rho (d\overline{E}/dt) + \nabla \cdot \dot{j}_{E} = \vec{\sigma} : \nabla \vec{u} - \rho \vec{u} \cdot \vec{X}$$
(2.36)

where \dot{j}_E is the internal energy flux not due to bulk flow

$$\vec{j}_{E} = \vec{j}_{E_{T}} - \rho \vec{u} \vec{E} + \vec{u} \cdot \vec{\vec{\sigma}} - (\vec{I} + \rho \vec{u} z F) \psi \qquad (2.37)$$

where the electric current \vec{I} is the sum of the partial currents \vec{I}_{α}

$$\vec{\mathbf{I}} = \sum_{\alpha=0}^{\nu-1} \vec{\mathbf{i}}_{\alpha} = \sum_{\alpha=0}^{\nu-1} \rho_{\alpha} \vec{\mathbf{u}}_{\alpha} (\mathbf{z}_{\alpha}/\mathbf{M}_{\alpha}) F , \qquad (2.38)$$

and where

$$\rho \mathbf{z} = \rho \sum_{\alpha=0}^{\nu-1} (\mathbf{w}_{\alpha} / \mathbf{M}_{\alpha}) \mathbf{z}_{\alpha} = \overline{\mathbf{z}}$$
(2.39)

D. Principles of Nonequilibrium Thermodynamics

The above treatment of nonequilibrium system is as far as we can proceed from hydrodynamics alone. In order to proceed in the discussion of the general theory of irreversible processes, we could describe the elegant, rational, fundamental approach of Truesdell (1969), Müller (1968), Bartelt (1968), Bartelt and Horne (1970), Gyarmati (1970), and Ingle (1971). Alternatively, we could present the conventional, heuristic approach as exemplified by de Groot and Mazur (1962), Fitts (1962), and Haase (1969). For simplicity, we choose the latter course, and we emphasize that the more fundamental approach apparently gives the same results for the simple systems investigated here (Bartelt and Horne, 1970). We need to introduce two fundamental assumptions regarding 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 \vec{j}_{α} are linear, homogeneous functions of the forces \vec{Y}_{α} . That is,

$$\vec{j}_{\alpha} = \sum_{\alpha'=0}^{\nu-1} \mathbf{L}_{\alpha\alpha'}, \quad \vec{Y}_{\alpha'}$$
(2.40)

The forces are "driving forces" for the fluxes. The phenomenological coefficients $L_{\alpha\alpha}$, are independent of the forces. The diagonal coefficients $L_{\alpha\alpha}$ relate conjugate fluxes and forces, while the off-diagonal elements $L_{\alpha\alpha}$, $(\alpha \neq \alpha')$ give rise to cross phenomena which are produced due to interference when two transport processes take place simultaneously. As in the case of postulate I, postulate II is apparently valid when the system is close to equilibrium. Thus, both postulates apply to systems with small space and time gradients of the local thermodynamic variables. Based on both postulates, we now treat the linear phenomenological theory for nonequilibrium systems.

The Gibbsian equation for $d\overline{E}$ is

$$d\vec{E} = Td\vec{S} - pd\vec{V} + \sum_{\alpha=0}^{\nu-1} dw_{\alpha} + d\Gamma + zFd\psi , \qquad (2.41)$$

Applying the chain rule for differentiation of \overline{E} (T,p,w_{α}, Γ , ψ), we obtain by the principle of local state and various thermodynamic formulas,

$$d\overline{E}/dt = (\overline{C}_{p} - p\overline{V}\beta) (dT/dt) - (T\overline{V}\beta - p\overline{V}\beta') (dp/dt) + \sum_{\alpha=0}^{\nu-2} (\overline{E}_{\alpha} - \overline{E}_{\nu-1}) (dw_{\alpha}/dt) + \frac{d\Gamma}{dt} + z_{F} \frac{d\psi}{dt}$$
(2.42)

where \overline{C}_{p} is specific heat capacity at constant pressure (and external fields), β is thermal expansivity,

$$\beta \equiv \overline{\nabla}^{-1} (\partial \overline{\nabla} / \partial T)_{p, w_{\alpha}, \Gamma, \psi}$$
(2.43)

 β ' is isothermal compressibility,

$$\beta' \equiv - \overline{\nabla}^{-1} \left(\frac{\partial \overline{\nabla}}{\partial p} \right)_{\mathrm{T}, \mathbf{w}_{\alpha}, \Gamma, \psi}$$
(2.44)

and $\overline{\mathbf{E}}_{\alpha}$ is partial specific internal energy,

$$\overline{\mathbf{E}}_{\alpha} = (\partial \overline{\mathbf{E}} / \partial \mathbf{m}_{\alpha})_{\mathbf{T},\mathbf{p},\mathbf{m}_{\beta},\Gamma,\psi}$$
(2.45)

Note also that

$$\overline{E} = \sum_{\alpha=0}^{\nu-1} w_{\alpha} \overline{E}_{\alpha} . \qquad (2.46)$$

Application of the chain rule for differentiation to the equation of state $\rho = \rho$ (T,p,w_{α}) gives a similar relation,

$$d\rho/dt = -\rho\beta (dT/dt) + \rho\beta' (dp/dt)$$
$$-\rho^{2} \sum_{\alpha=0}^{\nu-2} (\overline{\nu}_{\alpha} - \overline{\nu}_{\nu-1}) (dw_{\alpha}/dt) \qquad (2.47)$$

Substitution of (2.18), (2.19), (2.23), (2.42), and (2.47) into (2.36) yields, after rearrangement,

$$\rho \overline{C}_{p} (dT/dt) - T\beta (dp/dt) = \phi_{1} - \nabla \cdot \vec{q} - \sum_{\alpha=0}^{\nu-2} \vec{j}_{\alpha} \cdot (\vec{H}_{\alpha}' - \vec{H}_{\nu-1}'), \quad (2.48)$$

where $\boldsymbol{\varphi}_1$ is the entropy source term for bulk flow,

$$\phi_1 = (\vec{\sigma} + \vec{pI}) : \nabla \vec{u} , \qquad (2.49)$$

 $\dot{\vec{q}}$ is the heat flux

$$\vec{q} = \vec{j}_E - \sum_{\alpha=0}^{\nu-1} j_\alpha \vec{H}_\alpha$$
, (2.50)

 $\overline{\mathtt{H}}_{\alpha}$ is partial specific enthalpy, and

$$\overline{H}_{\alpha}^{\prime} = \overline{H}_{\alpha} + \Gamma + \frac{Z_{\alpha}}{M_{\alpha}} F \psi ,$$

$$\overline{H}_{\alpha}^{\prime} - \overline{H}_{\nu-1}^{\prime} = \overline{H}_{\alpha} - \overline{H}_{\nu-1} + (\frac{Z_{\alpha}}{M_{\alpha}} - \frac{Z_{\nu-1}}{M_{\nu-1}}) F \psi . \quad (2.51)$$

It has been shown (Fitts, 1962; Kirkwood and Crawford, 1952; de Groot and Mazur, 1962; Haase, 1969) that the driving forces conjugate to \vec{q} and \vec{j}_{α} are $\nabla \ln T$ and $\nabla_{T} \overline{\mu}_{\alpha}$,

where

$$\overline{\mu}_{\alpha} = \mu_{\alpha} / M_{\alpha}$$

$$\nabla_{T} \overline{\mu}_{\alpha} = \nabla \overline{\mu}_{\alpha} + \overline{S}_{\alpha} \nabla T, \ \alpha = 0, \dots, -1 \qquad (2.52)$$

By postulate II, the linear phenomenological fluxes are

$$-\vec{q} = \Omega_{TT} \nabla \ln T + \sum_{\alpha=0}^{\nu-1} \Omega_{\alpha T} \nabla_{T} \overline{\mu}_{\alpha}$$
$$-\vec{j}_{\alpha} = \Omega_{\alpha T} \nabla \ln T + \sum_{\beta=0}^{\nu-1} \Omega_{\alpha\beta} \nabla_{T} \overline{\mu}_{\beta}, \quad \alpha=0, \dots, \nu-1 \quad (2.53)$$

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

$$\begin{array}{c} \nu - 1 \\ \Sigma \\ \alpha = 0 \end{array} \stackrel{\alpha \beta}{=} 0, \ \beta = 0, \ldots, \nu - 1$$
 (2.54)

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

$$\sum_{\beta=0}^{\nu-1} \alpha_{\beta} = 0, \ \alpha = 0, \dots, \nu-1$$

$$(2.55)$$



Thus, for the v independent fluxes $\dot{j}_T = \dot{q}, \dot{j}_0, \dot{j}_1, \dots, \dot{j}_{\nu-2}$, the linear phenomenological equations are

$$-\dot{\mathbf{j}}_{\alpha} = \Omega_{\alpha \mathbf{T}} \quad \nabla \ln \mathbf{T} + \sum_{\beta=0}^{\nu-2} \Omega_{\alpha\beta} \quad \nabla_{\mathbf{T}} (\overline{\mu}_{\beta} - \overline{\mu}_{\nu-1}) ,$$
$$\alpha = \mathbf{T}, 0, 1, \dots, \nu-2 . \qquad (2.56)$$

For most purposes, it is more convenient to use (2.53), which is permissible because of (2.55). If the fluxes and forces of (2.56) satisfy Onsager's (1931) condition, which seems very likely but cannot be shown theoretically (Coleman and Truesdell, 1960; Andrews, 1967), then the matrix of Onsager coefficients is symmetric; i.e., $\Omega_{\alpha\beta} = \Omega_{\beta\alpha}$ for $\alpha,\beta = T$, 0, 1,..., ν -2. However, since one of the goals of experimental studies of transport phenomena is the verification of Onsager's Reciprocal Relations (Miller, 1960), we do not use them.

Substitution of (2.7), and (2.52) into (2.53) yields

$$-\mathbf{j}_{\alpha} = \Omega_{\alpha \mathbf{T}} \nabla \ell \mathbf{n} \mathbf{T} + \sum_{\beta=0}^{\nu-1} \Omega_{\alpha\beta} (\overline{\mathbf{v}}_{\beta}/\mathbf{M}_{\beta}) \nabla \mathbf{p} + \sum_{\beta=0}^{\nu-1} \Omega_{\alpha\beta} \sum_{\gamma=0}^{\nu-2} (\mu_{\beta\gamma}/\mathbf{M}_{\beta}) \nabla \mathbf{x}_{\gamma}$$

+
$$\sum_{\beta=0}^{\nu-1} \alpha_{\alpha\beta} (z_{\beta}/M_{\beta}) F\nabla \psi, \alpha=T, 0, 1, \dots, \nu-1$$
 (2.57)

General discussion about the physical implication of various phenomenological coefficients can be found elsewhere (Fitts, 1962; de Groot and Mazur, 1962; Haase, 1969; Horne, 1966).

E. The Differential Equations Describing the Osmotic Flow of Fluids Through a Charged Membrane

The System and the Simplifying Assumptions

We are mainly concerned with the derivation of the steady-state phenomenological theory for the transport of fluids undergoing osmosis through biological membranes. As has been mentioned in Chapter I, the transport system for the study is composed of a charged, continuous membrane separating two electrolyte solutions of different concentration at the same temperature.

Before we can start to write the equations for our transport system, we must take full account of the fundamental problems which are pertinent to our present investigation. As has been recognized for years, a normally grown living thing is, from thermodynamic point of view, an open system in a stationary state (the flows of all the species are constant in time), inside of which irreversible processes occur continuously and slowly (Haase, 1969). If, moreover, the fluxes and the gradients are small, we may use the principles of nonequilibrium thermodynamics such as those which enable us to use equilibrium properties (postulate I) and linear phenomenological relations for the fluxes (postulate II).

Moreover, for the system in question we consider (a) an isothermal, incompressible fluid; (b) a capillary model for the membrane in which uniform cylindrical capillaries penetrate across the membrane with flows of all components in the direction of the capillary or axial axis; (c) absence of chemical reactions; (d) absence of external magnetic, gravitational, and centrifugal fields; (e) constant viscosities; and (f) slow motion, i.e., a quasi-steady-state in which local time derivatives are zero. These requirements can be realized experimentally, and do not, in principle, introduce error. It is advantageous to introduce them into the phenomenological theory, the net effect being a simplification of the differential equations.

We do not, however, make use of the previous assumptions such as (i) constant diffusion coefficients and ionic mobility in the flow equations; (ii) constant dielectric constant of water in Poisson's equation; (iii) radial-independent pressure; (iv) the classical Boltzmann distribution of ions; and (v) the linearized Debye-Hückel theory for "all" cases. Moreover, (vi), the assumption that $\kappa_a >> 1$, where κ is the reciprocal of the effective

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thickness of electric double layer (Debye length) and a is the radius of the capillary, is found here to be not always necessary. In the next several chapters we shall discuss these assumptions in more detail. Our main purpose is to derive, subject only to a minimum number of assumptions, the steady-state phenomenological theory that describes for the transport of fluids across biological membranes.

The Differential Equations and the Appropriate Boundary Conditions

We now can set up the differential equations necessary for describing the transport system in question. Making use of the principles of hydrodynamics and nonequilibrium thermodynamics and subject to the conditions considered above, the relevant transport equations, relative to the local center of mass are

$$-\mathbf{j}_{\alpha} = \sum_{\beta=0}^{\nu-1} \alpha_{\alpha\beta} (\overline{v}_{\beta}/M_{\beta}) \nabla \mathbf{p} + \sum_{\beta=0}^{\nu-1} \alpha_{\alpha\beta} \sum_{\gamma=0}^{\nu-2} (\mu_{\beta\gamma}/M_{\beta}) \nabla \mathbf{x}_{\gamma}$$

+
$$\sum_{\beta=0}^{\nu-1} \alpha_{\beta} (z_{\beta}/M_{\beta}) F \nabla \psi, \alpha = T, 0, 1, \dots, \nu-1$$
 (2.58)

$$\rho \vec{u} \cdot \nabla w_{\alpha} + \nabla \cdot \vec{j}_{\alpha} = 0$$
 (2.59)

$$-\mathbf{T}\beta \mathbf{\vec{u}} \cdot \nabla \mathbf{p} = \phi_{1} - \nabla \cdot \mathbf{\vec{q}} - \sum_{\alpha=0}^{\nu-2} \mathbf{\vec{j}}_{\alpha} \cdot \nabla (\mathbf{\vec{H}}_{\alpha}' - \mathbf{\vec{H}}_{\nu-1}') . \qquad (2.60)$$

$$\nabla \mathbf{p} + \mathbf{\overline{Z}}_F \nabla \psi = \eta \nabla^2 \dot{\mathbf{u}} . \qquad (2.61)$$

Only (2.58) and (2.61) are considered in what follows; the other equations deal with effects too small to be observed in membrane transport in ordinary electrolyte solutions.

The partial electric current relative to the local center of mass is

 $\vec{i}_{\alpha} = (z_{\alpha}/M_{\alpha}) \vec{j}_{\alpha}$, (2.62)

and the total current is given by (2.38).

Poisson's equation, which relates the electrostatic potential ψ to the excess charge ρzF is

$$\nabla \cdot \mathbf{D} \nabla \psi = -4\pi \rho z F = -4\pi \overline{Z} F , \qquad (2.63)$$

where D is the dielectric tensor of the electrolyte solution, taken as nonconstant, and z and \overline{Z} are given by (2.41) and (2.12). The units of ψ are volts throughout this work. At this point our description of the system under consideration is, in principle, complete.

In problems of electric conduction, however, it is useful to relate the diffusion fluxes and electric currents of all the species to the velocity of the solvent and thus to adopt the Hittorf reference system (Haase, 1969). The solvent-fixed (SF) frame (i.e., $(\frac{1}{J}_0)_0 \equiv 0$) is extremely convenient and transference numbers are usually referred to it (Miller, 1966). The reference velocity is now denoted by the velocity of solvent molecules, \dot{u}_0 . Moreover, since the solutions are relatively dilute, it is useful to use molarity c_{α} instead of mole fraction x_{α} to describe composition.

Before we can write explicitly the transport equations for the SF reference frame, it is essential to require considerable knowledge about conversion from a reference velocity \vec{w}_a to a second velocity \vec{w}_b . For simplicity, we follow the treatment of Haase (1969).

We consider, in the general case, the transition from one diffusion current density

$$\vec{a}_{\alpha} = c_{\alpha} (\vec{u}_{\alpha} - \vec{\omega}_{a})$$
 (2.64)

to a second diffusion current density

$$\mathbf{\dot{b}}_{\alpha} = \mathbf{c}_{\alpha} \quad (\mathbf{\dot{u}}_{\alpha} - \mathbf{\dot{\omega}}_{b}) \quad . \tag{2.65}$$

For fluid systems, the reference velocity $\vec{\omega}_a$ and $\vec{\omega}_b$ are so chosen that the relations

$$\vec{\hat{\omega}}_{a} = \sum_{\alpha=0}^{\nu-1} (w_{\alpha})_{a} \vec{\hat{u}}_{\alpha}$$
(2.66)

$$\sum_{\alpha=0}^{\nu-1} (\mathbf{w}_{\alpha})_{a} = 1$$
(2.67)

$$\dot{\tilde{\omega}}_{b} = \sum_{\alpha=0}^{\nu-1} (\tilde{w}_{\alpha})_{b} \dot{\tilde{u}}_{\alpha}$$
(2.68)

$$\sum_{\alpha=0}^{\nu-1} (w_{\alpha})_{b} = 1$$
(2.69)

hold. The $(w_{\alpha})_{a}$ and $(w_{\alpha})_{b}$ are the normalized weights, i.e., "weight factors" for averaging the velocities subject to the normalization (2.67) and (2.69). For the barycentric velocity, defined in (2.20), the "weight factors" are the mass fractions. It can easily be shown from (2.66), (2.67), and (2.64) that

$$\sum_{\alpha=0}^{\nu-1} [(w_{\alpha})_{\alpha}/c_{\alpha}]_{\alpha} \stackrel{\dagger}{}_{\alpha} = 0 , \qquad (2.70)$$

and from (2.68), (2.69), and (2.65) that

$$\sum_{\alpha=0}^{\nu-1} [(\mathbf{w}_{\alpha})_{b}/c_{\alpha}]_{b}^{\dagger} = 0 . \qquad (2.71)$$

Combination of (2.64) - (2.71) yields the conversion relation between two frames of reference:

$$\mathbf{b}^{\dagger}_{\alpha} = \mathbf{a}^{\dagger}_{\alpha} - \mathbf{c}_{\alpha} \sum_{\beta=0}^{\nu-1} \left[(\mathbf{w}_{\beta})_{\mathbf{b}} / \mathbf{c}_{\beta} \right] \mathbf{a}^{\dagger}_{\beta} \cdot (2.72)$$

We are, however, primarily concerned with the conversion from the barycentric system to Hittorf's reference system. Let

$$a^{\dagger}_{\alpha} = j_{\alpha} / M_{\alpha'} \quad b^{\dagger}_{\alpha} = (j_{\alpha})_{0}$$
(2.73)

Note that in Hittorf's frame of reference,

$$(w_0)_0 = 1, (w_\alpha)_0 = 0, \alpha = 1, 2, \dots, \nu - 1,$$
 (2.74)

so that (2.69) is immediately satisfied, i.e., $\sum_{\alpha=0}^{\nu-1} (w_{\alpha})_{\alpha} = 1$, and

$$(\mathbf{j}_{0})_{0} \equiv 0$$
 (2.75)

Hence we obtain from (2.74) and (2.72)

$$(\dot{j}_{\alpha})_{o} = \dot{j}_{\alpha}/M_{\alpha} - c_{\alpha} \dot{j}_{o}/c_{o} M_{o}, \qquad (2.76)$$

yielding the conversion from the barycentric system to Hittorf's reference system. By definition of \dot{J}_0 , the two reference velocities are related by

$$\vec{u} = \vec{u}_0 - (1/\rho_0)\vec{j}_0$$
 (2.77)

Consequently, if SF reference frame is chosen for the system, the diffusion flux and electric current of species α can now be expressed, relative to SF reference frame, as

$$-(\overset{\dagger}{\mathbf{j}}_{\alpha})_{\mathbf{O}} = \overset{\nu-1}{\underset{\beta=1}{\Sigma}} \overset{\mathbf{O}}{\underset{\alpha\beta}{\alpha}} \overset{\mathbf{v}}{\mathbf{v}}_{\beta}^{\mathbf{O}} \nabla \mathbf{p} + \overset{\nu-1}{\underset{\beta=1}{\Sigma}} \overset{\mathbf{O}}{\underset{\alpha\beta}{\alpha}} \overset{\mathbf{RT}\nabla \ln \mathbf{a}_{\beta}}{\underset{\beta=1}{\Sigma}} + \overset{\nu-1}{\underset{\alpha\beta}{\Sigma}} \overset{\mathbf{O}}{\underset{\alpha\beta}{\alpha}} z_{\beta}^{F\nabla\psi}, \alpha = 1, 2, \dots, \nu-1 \qquad (2.78)$$

$$(\vec{i}_{\alpha})_{o} = z_{\alpha}F (\vec{j}_{\alpha})_{o}$$
(2.79)

where $\Omega_{\alpha\beta}^{0}$ are the phenomenological coefficients in SF reference frame. The Navier-Stokes equation in SF reference frame then becomes, according to (2.77),

$$\nabla \mathbf{p} + \overline{\mathbf{Z}}F\nabla \psi = \eta \nabla^2 \, \vec{\mathbf{u}}_0 - \eta \nabla^2 \, \frac{1}{\rho_0} \, \vec{\mathbf{j}}_0 \tag{2.80}$$

We assume, for the Navier-Stokes equation only, that the difference between \vec{u} and \vec{u}_0 is negligible and, therefore, that

$$\nabla \mathbf{p} + \overline{\mathbf{z}} F \nabla \psi = \eta \nabla^2 \vec{u}_0$$
 (2.81)

The appropriate boundary conditions for the problem

$$c_{\alpha 0} = c_{\alpha 0}$$
 (0) at $x = 0$, and $c_{\alpha 0} = c_{\alpha 0}$ (l) at $x = l$
 $p_0 (x = l) - p_0 (x = 0) = 0$

 $\Phi = \Phi$ (0) at x = 0, and $\Phi = \Phi$ (l) at x = l, (2.82)

where $c_{\alpha 0}$ (0) and $c_{\alpha 0}$ (ℓ) are initial molar concentrations of Component α at the boundaries, p_0 ($x = \ell$) and p_0 (x = 0) are initial hydrostatic pressures at the boundaries, Φ is partial electric potential along the axial axis, and Φ (0) and Φ (ℓ) are initial values of Φ at the boundaires. The appropriate boundary conditions to ψ and u_0 are

$$d\psi/dr = \partial u_0/\partial r = 0$$

are

$$d\psi/dr = 4\pi\sigma/D_{a}$$
, and $u_{o} = 0$ at $r = a$, (2.83)

where σ is the surface charge density fixed on the membrane, D_a is the dielectric constant of the solution at the wall, and u_o is the velocity of solvent molecules or the SF reference velocity along the axial axis.

The experimental transport parameters, for some binary electrolyte solutions, which are necessary for the study have been obtained based on the SF frame of reference and can be found elsewhere (Miller, 1966).

CHAPTER III

EQUILIBRIUM DISTRIBUTION OF IONS

IN AN ELECTRIC FIELD

A. Introduction

Before we can obtain the solution of the steadystate phenomenological theory which describes osmotic flow phenomena in biological systems, it is necessary to acquire considerably more knowledge of the local distribution of ions, charge density, electrostatic potential, and pressure in nonequilibrium system. This information is essential in describing transport phenomena in membranes and thus must be resolved and discussed beforehand. In the present chapter we derive an equation for the local distribution of ions in an electric field and then obtain the excess charge density in the system considered. The principal enabling step is the assumption that the system is in chemical equilibrium radially, i.e., that the chemical potential of each species is uniform radially.

The fundamental problem in a study of a membrane system or any electrochemical system in which the charges are unequally distributed (i.e., $\overline{z} \neq 0$) in the volume or

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on the surface is the knowledge of the macroscopic distribution of ions at each point of the system since the presence of a net charge produces a macroscopic electric field which tends to displace charged species. From knowledge of this distribution it will be possible to calculate several electrochemical properties and thus to describe accurately the behavior of electrolyte solutions in electric fields.

However, as has been known for years, there are great difficulties in calculating the distribution of ions in the field, due partially to the lack of a coherent theoretical formulation, and partially to the mathematical difficulty in solving the problem. For these reasons one often uses the classical Boltzmann distribution equation without adequate justification (<u>cf</u>. Kobatake and Fujita, 1964; Fujita and Kobatake, 1968; Gross and Osterle, 1968). Thus, it is assumed for each species α that

$$\mathbf{x}_{\alpha} = \overline{\mathbf{x}}_{\alpha} \exp(-z_{\alpha}F\psi/RT) = \mathbf{x}_{\alpha}^{B}$$
, (3.1)

where $\overline{\mathbf{x}}_{\alpha}$ is the mole fraction of α in the absence of an electric field and where, for subsequent use, we denote the Boltzmann equation mole fraction by $\mathbf{x}_{\alpha}^{\mathrm{B}}$.

Many assumptions have been made in conjunction with (3.1); the usual ones are: (a) existence of point charges, which implies that molar volumes of ions are

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zero; (b) absence of polarizable components; (c) absence of activity coefficients; (d) uniformity of pressure, which implies among other things that the pressureinduced gradient of the electrochemical potential of a charged species is negligibly small. Despite the fact that various authors have attempted to correct the Boltzmann equation, often empirically, some by introducing a finite volume (Sparnaay, 1958), some by introducing polarization, and others by introducing pressure, none of the theories is complete. Moreover, many of these authors treat the parts of the double layer very close to the interface as special media, very different from the parts remote from the interface. Further, the microscopic nature of these parts of the layer give rise to difficulties in their description in terms of macroscopic guantities such as polarization or pressure. The most complete theory for the distribution of ions in an electric field so far has been that of Sanfeld (1968) derived by means of the local thermodynamic method (Prigogine, 1953; Mazur, 1953; Defay, 1954). Unfortunately, the theory is limited only to equilibrium systems and is valid only for very dilute solutions and gas mixtures.

Our purpose now is to calculate this distribution in the general case and to apply our result for calculation of the excess charge density in the system. We consider continuous, anisotropic fluids in which no chemical reactions occur and which are subject only to the external electric field. Unlike many other investigators, we make full use of the equations of chemical thermodynamics, including particularly all pressure terms. At present, we only treat systems (particularly, biological systems) in which the surface charge density fixed on the surface or on the membrane phase is such that the effects of polarization are small enough to be neglected. This requirement can always be realized experimentally without introducing error, but it could be modified in subsequent extensions of our theory.

B. Derivation of Modified Boltzmann Equation

Consider a charged, continuous phase (i.e., a membrane, a barrier, or a cylinder) which is static or through which there are steady-state flows of matter. We assume an isothermal electrolyte solution containing solutes which are dissociated in a neutral solvent, absence of chemical reactions and external fields except electric field, and a capillary model for the phase considered in which uniform cylindrical capillaries penetrate across the phase. Our results also apply to any single, non-capillary cylinder.

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When the only external force is electrical, the gradient of the molar electrochemical potential μ_{α} of Component α in the absence of polarization may be described, according to (2.14) by

$$\nabla \mu_{\alpha} = \overline{\mathbf{v}}_{\alpha}^{\mathbf{O}} \nabla \mathbf{p} + \mathbf{R} \mathbf{T} \nabla \mathbf{l} \mathbf{n} \mathbf{x}_{\alpha} \mathbf{f}_{\alpha} + \mathbf{z}_{\alpha} F \nabla \psi, \alpha = 0, 1, \dots, \nu - 1 \quad (3.2)$$

where $\overline{v}^{o}_{\alpha}$ is defined by (2.15). The gradient of μ_{α} in the radial direction is, by (3.2),

$$\partial \mu_{\alpha} / \partial r = \overline{v}_{\alpha}^{O} (\partial p / \partial r) + RT (\partial \ln x_{\alpha} f_{\alpha} / \partial r)$$

+ $z_{\alpha} F (\partial \psi / \partial r)$. (3.3)

We assume that the chemical potential of each species is uniform radially,

$$\partial \mu_{\alpha} / \partial r = 0, \ \alpha = 0, 1, \dots, \nu - 1$$
 (3.4)

That is to say, all the radial fluxes are zero everywhere in the system; chemical equilibrium obtains radially. Note, however, that the gradient of μ_{α} along the capillary Or cylindrical axis does not necessarily vanish,

$$\partial \mu_{\alpha} / \partial \mathbf{x} \neq 0$$
 (3.5)

Thus (3.4) by no means requires that the system is in a state of total thermodynamic chemical equilibrium (i.e., $abla \mu_{\alpha} \equiv 0$). Combination of (3.3) and (3.4) yields

$$\overline{\mathbf{v}}_{\alpha}^{\mathbf{O}}$$
 ($\partial \mathbf{p}/\partial \mathbf{r}$) + RT ($\partial \ln \mathbf{x}_{\alpha} \mathbf{f}_{\alpha}/\partial \mathbf{r}$) + $\mathbf{z}_{\alpha} F$ ($\partial \psi/\partial \mathbf{r}$) = 0. (3.6)

The Gibbs-Duhem equation (2.8) yields, for the radial direction and subject to (3.4),

$$\partial \mathbf{p} / \partial \mathbf{r} = - \overline{Z} F \left(\partial \psi / \partial \mathbf{r} \right)$$
 (3.7)

Substitution of (3.7) into (3.6) yields, for each species,

$$(1/\overline{v}_{\alpha}^{O})$$
 $(\partial \ln x_{\alpha} f_{\alpha}/\partial r) + (z_{\alpha}/\overline{v}_{\alpha}^{O}) (\partial \Psi/\partial r) = \overline{Z} (\partial \Psi/\partial r) , (3.8)$

where

$$\Psi = F \Psi / RT \quad . \tag{3.9}$$

In all other treatments of electrolyte solutions in electric fields, electroneutrality is assumed and the right hand side of (3.8) is set equal to zero. The solution of (3.8) for electroneutrality is, clearly, (3.1), the classical Boltzmann equation, as long as f_{α} is constant. We choose to retain the right hand side of (3.8), and thus to allow, consistently, for non-electroneutrality, at least near the walls. Although we could formally take account of nonconstancy of f_{α} and $\overline{v}_{\alpha}^{O}$ by, say, the perturbation scheme of Horne and Anderson (1970), we choose, for the first attempt, to regard f_{α} and $\overline{v}_{\alpha}^{O}$ as constants. The latter assumption is certainly reasonable since $\overline{v}_{\alpha}^{O}$ varies Only with pressure and since the isothermal compressibility is de má a 1951.

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as defined in (2.44), is of order 10^{-5} atm⁻¹ for water and aqueous solutions. Constancy of f_{α} is a stronger assumption <u>a priori</u>, since it is valid only to the extent that the composition distribution is not great. We shall find that this is indeed the case and that, therefore, the assumption of constant f_{α} is warranted.

With these assumptions, (3.8) becomes, in detail,

$$(1/\overline{v}_{0}^{O}) \quad (\partial \ln x_{0}/\partial r) = (1/\overline{v}_{1}^{O}) \quad (\partial \ln x_{1}/\partial r) + (z_{1}/\overline{v}_{1}^{O}) \quad (\partial \Psi/\partial r)$$
$$= (1/\overline{v}_{2}^{O}) \quad (\partial \ln x_{2}/\partial r) + (z_{2}/\overline{v}_{2}^{O}) \quad (\partial \Psi/\partial r)$$
$$= \dots$$
$$= (1/\overline{v}_{\nu-1}^{O}) \quad (\partial \ln x_{\nu-1}/\partial r) + (z_{\nu-1}/\overline{v}_{\nu-1}^{O}) \quad (\partial \Psi/\partial r)$$
$$= \overline{Z} \quad (\partial \Psi/\partial r) \quad , \qquad (3.10)$$

or,

$$(1/\overline{v_{o}^{o}}) \quad (\partial \ln x_{o}/\partial r) = (1/\overline{v_{\alpha}^{o}}) \quad (\partial \ln x_{\alpha}/\partial r) + (z_{\alpha}/\overline{v_{\alpha}^{o}}) \quad (\partial \Psi/\partial r)$$
$$= \overline{Z} \quad (\partial \Psi/\partial r) \quad \alpha = 1, \dots, \nu - 1 \qquad (3.11)$$

The first v-1 of (3.11) are solved immediately,

$$\mathbf{x}_{\alpha} = \overline{\mathbf{x}}_{\alpha} \left(\mathbf{x}_{0}/\overline{\mathbf{x}}_{0}\right)^{g_{\alpha 0}} \exp\left(-\mathbf{z}_{\alpha}\Psi\right)$$
$$= \left(\mathbf{x}_{0}/\overline{\mathbf{x}}_{0}\right)^{g_{\alpha 0}} \mathbf{x}_{\alpha}^{\mathrm{B}}, \alpha = 0, 1, \dots, \nu - 1 \qquad (3.12)$$

where \overline{x}_{α} is the value of x_{α} for no electric field, where x_{α}^{B} is defined by (3.1), and where

$$g_{\alpha o} = \overline{v}_{\alpha}^{o} / \overline{v}_{o}^{o} , \qquad (3.13)$$

The next task is to evaluate $(\mathbf{x}_{0}/\overline{\mathbf{x}}_{0})^{g_{\alpha 0}}$. Note that the ordinary Boltzmann equation, (3.1), is valid only for $\mathbf{x}_{0} = \overline{\mathbf{x}}_{0}$ (or, trivially, for $g_{\alpha 0} = 0$).

In order to evaluate \mathbf{x}_{o} , we use the facts that

$$\sum_{\alpha=1}^{\nu-1} \overline{\mathbf{x}}_{\alpha} = 1 - \overline{\mathbf{x}}_{0}, \quad \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} = 1 - \mathbf{x}_{0}^{B}, \quad \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha} = 1 - \mathbf{x}_{0}, \quad (3.14)$$

whence, from (3.12),

$$1 - \mathbf{x}_{0} = \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{0}/\overline{\mathbf{x}}_{0})^{g_{\alpha 0}} \mathbf{x}_{\alpha}^{\mathrm{B}} . \qquad (3.15)$$

Let

$$\mathbf{x}_{o} = \overline{\mathbf{x}}_{o} \quad (1-\xi) \quad , \tag{3.16}$$

and then

$$1 - \overline{\mathbf{x}}_{0} + \overline{\mathbf{x}}_{0}\xi = \sum_{\alpha=1}^{\nu-1} (1-\xi)^{g_{\alpha 0}} \mathbf{x}_{\alpha}^{B} . \qquad (3.17)$$

By the binomial theorem,

$$1 - \overline{x}_{0} + \overline{x}_{0} \xi = \sum_{\alpha=1}^{\nu-1} x_{\alpha}^{B} [1 - g_{\alpha 0} \xi + \frac{1}{2} g_{\alpha 0} (g_{\alpha 0} - 1) \xi^{2} - \frac{1}{6} g_{\alpha 0} (g_{\alpha 0} - 1) (g_{\alpha 0} - 2) \xi^{3} + \dots$$
$$= 1 - x_{0}^{B} - \xi \sum_{\alpha=1}^{\nu-1} x_{\alpha}^{B} g_{\alpha 0} + \frac{1}{2} \xi^{2} \sum_{\alpha=1}^{\nu-1} x_{\alpha}^{B} g_{\alpha 0} (g_{\alpha 0} - 1) - \frac{1}{6} \xi^{3} \sum_{\alpha=1}^{\nu-1} x_{\alpha}^{B} g_{\alpha 0} (g_{\alpha 0} - 1) (g_{\alpha 0} - 2) + \dots, (3.18)$$

or,

$$\overline{\mathbf{x}}_{\mathbf{0}}\xi = (\overline{\mathbf{x}}_{\mathbf{0}} - \mathbf{x}_{\mathbf{0}}^{\mathbf{B}}) - \xi \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{\mathbf{B}} \mathbf{g}_{\alpha 0} + \frac{1}{2} \xi^{2} \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{\mathbf{B}} \mathbf{g}_{\alpha 0} (\mathbf{g}_{\alpha 0} - 1)$$
$$- \frac{1}{6} \xi^{3} \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{\mathbf{B}} \mathbf{g}_{\alpha 0} (\mathbf{g}_{\alpha 0} - 1) (\mathbf{g}_{\alpha 0} - 2) + \dots (3.19)$$

Rather than use the ordinary reversion of series formula (Abrahamowitz and Stegun, 1964) to solve (3.19) for ξ , we observe that the difference $(\overline{\mathbf{x}}_{O}-\mathbf{x}_{O}^{B})$ is presumably very small and so is the value of any particular \mathbf{x}_{α}^{B} . This means that the second term on the right hand side of (3.19) is of second order in smallness since it is the product of $\xi \stackrel{\alpha}{=} (\overline{\mathbf{x}}_{O}-\mathbf{x}_{O}^{B})$ and $\Sigma \mathbf{x}_{\alpha}^{B} \mathbf{g}_{\alpha O}$ ($\mathbf{g}_{\alpha O}$ is of order unity or greater, in general). In order to keep consistent account of the order of smallness, we multiply both ($\overline{\mathbf{x}}_{O}-\mathbf{x}_{O}^{B}$) and \mathbf{x}_{α}^{B} by the bookkeeping parameter λ , and we write ξ as a perturbation-type power series in λ (see Horne and Anderson, 1970).

$$\hat{\xi} = \lambda \xi_1 + \lambda^2 \xi_2 + \lambda^3 \xi_3 + \dots$$
 (3.20)

where $\hat{\xi} = \xi$ when $\lambda = 1$. (3.19) becomes, then,

$$\overline{\mathbf{x}}_{0} (\lambda \xi_{1} + \lambda^{2} \xi_{2} + \lambda^{3} \xi_{3} + \dots) = \lambda (\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{B})$$

$$- \lambda (\lambda \xi_{1} + \lambda^{2} \xi_{2}) \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{g}_{\alpha 0}$$

$$+ \frac{1}{2} \lambda (\lambda^{2} \xi_{1}^{2}) \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{g}_{\alpha 0} (\mathbf{g}_{\alpha 0} - 1) + \dots (3.21)$$

Equating powers of λ , we find

$$\xi_1 = (\bar{x}_0 - x_0^B) / \bar{x}_0$$
 (3.22)

$$\xi_2 = -\xi_1 \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{\mathrm{B}}/\overline{\mathbf{x}}_{\mathrm{o}}) \mathbf{g}_{\alpha \mathrm{o}}$$
(3.23)

$$\xi_{3} = -\xi_{2} \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \mathbf{g}_{\alpha o}$$
$$+ \frac{1}{6} \xi_{1}^{2} \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \mathbf{g}_{\alpha o} (\mathbf{g}_{\alpha o}^{-1})$$
(3.24)

$$\xi_{4} = -\xi_{3} \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \mathbf{g}_{\alpha o} + \xi_{1} \xi_{2} \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \mathbf{g}_{\alpha o} (\mathbf{g}_{\alpha o}^{-1})$$

$$-\frac{1}{6} \xi_{1}^{3} \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \mathbf{g}_{\alpha o} (\mathbf{g}_{\alpha o}^{-1}) (\mathbf{g}_{\alpha o}^{-2}), (3.25)$$

and so forth.

The modified Boltzmann equation is, then,

$$\mathbf{x}_{\alpha} = \overline{\mathbf{x}}_{\alpha} \left[\exp \left(-\mathbf{z}_{\alpha} \Psi \right) \right] \left(1 - \xi \right)^{g_{\alpha O}} , \qquad (3.26)$$

with $g_{\alpha o} = \overline{v}_{\alpha}^{o} / \overline{v}_{o}^{o}$ and

$$\xi = \xi_1 + \xi_2 + \xi_3 + \xi_4 + \dots, \qquad (3.27)$$

the ξ_i being given by (3.22)-(3.25)

It would be most awkward, however, to have to deal with all the terms of (3.27) in all cases. As we shall see in Chapter IV, indeed only the first and the second terms in (3.27) are important. Then it is quite sufficient to take

$$\xi = \left[\left(\overline{\mathbf{x}}_{o} - \mathbf{x}_{o}^{B} \right) / \overline{\mathbf{x}}_{o} \right] \left[1 - \sum_{\alpha=1}^{\nu-1} \left(\mathbf{x}_{\alpha}^{B} / \overline{\mathbf{x}}_{o} \right) \mathbf{g}_{\alpha o} \right] , \qquad (3.28)$$

$$\mathbf{x}_{\alpha} = \overline{\mathbf{x}}_{\alpha} \left[\exp \left(-\mathbf{z}_{\alpha} \Psi \right) \right] \left\{ 1 - \mathbf{g}_{\alpha o} \left[\left(\overline{\mathbf{x}}_{o} - \mathbf{x}_{o}^{B} \right) / \overline{\mathbf{x}}_{o} \right] \right]$$

$$- \frac{1}{2} \mathbf{g}_{\alpha o} \left(\mathbf{g}_{\alpha o} - 1 \right) \left[\left(\overline{\mathbf{x}}_{o} - \mathbf{x}_{o}^{B} \right) / \overline{\mathbf{x}}_{o} \right]^{2}$$

$$+ \mathbf{g}_{\alpha o} \left[\left(\overline{\mathbf{x}}_{o} - \mathbf{x}_{o}^{B} \right) / \overline{\mathbf{x}}_{o} \right] \sum_{\beta=1}^{\nu-1} \left(\mathbf{x}_{\beta}^{B} / \overline{\mathbf{x}}_{o} \right) \mathbf{g}_{\beta o} \right\} ,$$

$$\alpha = 0, 1, 2, \dots, \nu - 1 . \qquad (3.29)$$

Since
$$\overline{z} = \sum_{\alpha=1}^{\nu-1} x_{\alpha} z_{\alpha}$$
, we have, from (3.29) and

(3.1),

$$\overline{\mathbf{z}} = \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{z}_{\alpha} - \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{z}_{\alpha} \mathbf{g}_{\alpha 0} \left[(\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{B}) / \overline{\mathbf{x}}_{0} \right]$$

$$- \frac{1}{2} \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{z}_{\alpha} \mathbf{g}_{\alpha 0} (\mathbf{g}_{\alpha 0} - 1) \left[(\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{B}) / \overline{\mathbf{x}}_{0} \right]^{2}$$

$$+ \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{B} \mathbf{z}_{\alpha} \mathbf{g}_{\alpha 0} \left[(\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{B}) / \overline{\mathbf{x}}_{0} \right] \sum_{\beta=1}^{\nu-1} (\mathbf{x}_{\beta}^{B} / \overline{\mathbf{x}}_{0}) \mathbf{g}_{\beta 0}$$

$$+ \dots \qquad (3.30)$$

Further,

$$\overline{\mathbf{v}} = \sum_{\alpha=0}^{\nu-1} \mathbf{x}_{\alpha} \ \overline{\mathbf{v}}_{\alpha}^{\mathbf{o}} = \mathbf{x}_{0} \overline{\mathbf{v}}_{0}^{\mathbf{o}} + \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha} \ \overline{\mathbf{v}}_{\alpha}^{\mathbf{o}}$$

$$= \overline{\mathbf{x}}_{0} \overline{\mathbf{v}}_{0}^{\mathbf{o}} (1-\xi) + \sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{\mathbf{B}} \ \overline{\mathbf{v}}_{\alpha}^{\mathbf{o}} (1-g_{\alpha 0} \ \xi) + \dots$$

$$= \overline{\mathbf{x}}_{0} \overline{\mathbf{v}}_{0}^{\mathbf{o}} \{1 - [(\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{\mathbf{B}})/\overline{\mathbf{x}}_{0}] + \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{\mathbf{B}}/\overline{\mathbf{x}}_{0}) \ g_{\alpha 0}$$

$$- [(\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{\mathbf{B}})/\overline{\mathbf{x}}_{0}] \sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{\mathbf{B}}/\overline{\mathbf{x}}_{0}) \ g_{\alpha 0} \ (g_{\alpha 0} - 1) + \dots \} (3.31)$$

Finally,

$$\overline{\mathbf{Z}} = (\overline{\mathbf{x}}/\overline{\mathbf{v}}) = (\overline{\mathbf{x}}_{0}\overline{\mathbf{v}}_{0}^{0})^{-1} \begin{cases} \overset{\vee}{\Sigma} & \mathbf{x}_{\alpha}^{B} & \mathbf{z}_{\alpha} \\ \overset{\vee}{\alpha=1} & \mathbf{x}_{\alpha}^{0} & \mathbf{z}_{\alpha} \end{cases}$$
$$- (\overline{\mathbf{x}}_{0}^{-}-\mathbf{x}_{0}^{B}) \overset{\vee}{\overset{\Sigma}{\alpha=1}} & (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{0}) & \mathbf{z}_{\alpha} (\mathbf{g}_{\alpha 0}^{-1})$$
$$- (\overset{\vee}{\overset{\vee}{\Sigma}} & \mathbf{x}_{\alpha}^{B} & \mathbf{z}_{\alpha}) & [\overset{\vee}{\overset{\vee}{\Sigma}} & (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{0}) & \mathbf{g}_{\alpha 0}^{-1}] + \dots \quad (3.32)$$

where we have used $(1 + x)^{-1} = 1 - x + \frac{1}{2}x^{2} + ...$

D. Uni-univalent Case

If all cationic species have charge $z_{\alpha} = +1$ and all anionic species have charge $z_{\alpha} = -1$ (the typical case of biological interest), then the general formulas found in the last two sections take on simpler forms. By electroneutrality of the starting materials,

$$\sum_{\alpha} \overline{\mathbf{x}}_{\alpha} = \sum_{\alpha} \overline{\mathbf{x}}_{\alpha}$$
(3.33)

and by (3.14),

$$\sum_{\alpha \in \alpha} \overline{x}_{\alpha} = \frac{1}{2} (1 - \overline{x}_{0}) = \sum_{\alpha \in \alpha} \overline{x}_{\alpha}$$
(3.34)
cations

Then,

$$1 - \mathbf{x}_{o}^{B} = \sum_{\alpha=1}^{\Sigma} \overline{\mathbf{x}}_{\alpha} \exp(-\mathbf{z}_{\alpha}\Psi)$$

$$= \sum_{\text{cations}} \overline{\mathbf{x}}_{\alpha} e^{-\Psi} + \sum_{\text{anions}} \overline{\mathbf{x}}_{\alpha} e^{\Psi}$$

$$= \frac{1}{2} (1 - \overline{\mathbf{x}}_{o}) (e^{-\Psi} + e^{\Psi})$$

$$= (1 - \overline{\mathbf{x}}_{o}) \cosh \Psi , \qquad (3.35)$$

and

$$\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{\mathrm{B}} = (1 - \overline{\mathbf{x}}_{0}) \quad (\cosh \Psi - 1) \tag{3.36}$$

Further, for the uni-univalent case,

$$\sum_{\alpha=1}^{\nu-1} \mathbf{x}_{\alpha}^{\mathbf{B}} \mathbf{z}_{\alpha} = \sum_{\text{cations}} \overline{\mathbf{x}}_{\alpha} e^{-\Psi} - \sum_{\text{anions}} \overline{\mathbf{x}}_{\alpha} e^{\Psi}$$
$$= \frac{1}{2} (1 - \overline{\mathbf{x}}_{0}) (e^{-\Psi} - e^{\Psi})$$
$$= - (1 - \overline{\mathbf{x}}_{0}) \sinh \Psi . \qquad (3.37)$$

From (3.36), (3.37), and (3.32) we finally obtain

$$\overline{Z} = - \left\{ (1 - \overline{x}_{0}) / \overline{x}_{0} \overline{v}_{0}^{O} \right\} \left\{ \sinh \Psi + \left[(1 - \overline{x}_{0}) / \overline{x}_{0} \right] \sinh \Psi \left(\cosh \Psi - 1 \right) \right.$$

$$+ \left(1 / \overline{x}_{0} \overline{v}_{0}^{O} \right) \left[(\cosh \Psi - 1) \left(v_{+} e^{-\Psi} - v_{-} e^{\Psi} \right) \right.$$

$$- \sinh \Psi \left(v_{+} e^{-\Psi} + v_{-} e^{\Psi} \right) \right] \right\}, \qquad (3.38)$$

where we have used

$$\mathbf{v}_{+} = \sum_{\text{cations}} \overline{\mathbf{x}}_{\alpha} \overline{\mathbf{v}}_{\alpha}^{\mathbf{O}}$$
$$\mathbf{v}_{-} = \sum_{\text{anions}} \overline{\mathbf{x}}_{\alpha} \overline{\mathbf{v}}_{\alpha}^{\mathbf{O}}$$

E. Discussion

For the first time we have a thermodynamic theory for the distribution of ions in an electric field, which takes account of the effect of pressure resulting from the gradient of electrical potential or nonzero local distribution of charge density, and which simultaneously takes account of the effect of molar volumes of ions. The results can be used either to justify the applicability of classical Boltzmann equation or as they stand when the Boltzmann equation is not applicable. The equations can be used further to predict the effect of molar volumes of ions on various electrochemical properties and thus are better in describing the system. Alternatively, further theoretical and experimental development can now be improved and interpreted more accurately on the basis of the equations. In general, use of the equations requires knowledge of molar volumes of ions and the surface potential or the fixed surface charge density, which we shall determine in Chapter IV. Further improvement may

be made in the equations by taking account of the effects of variable activity coefficients, polarization, and, in extreme cases, pressure dependence of partial molar volume.

CHAPTER IV

RADIAL DISTRIBUTION OF ELECTROSTATIC POTENTIAL IN A MODERATELY CHARGED CYLINDER

A. Introduction

As has been shown in Chapter III, knowledge of the distribution of electrostatic potential in an electrochemical system is essential to the understanding of physical and chemical properties of the electrolytic or polyelectrolytic solution in question. Poisson's equation relates the electrostatic potential to the fixed surface charge dnesity. In the past few years, solutions of Poisson's equation have been obtained numerically (Kotin, 1962; Gross and Osterle, 1968; Fair and Osterle, 1971) and analytically (Alexandrowicz, 1963; Philip, 1970) based on certain geometrical and mathematical models. Although the results are satisfactory in many respects, all previous investigators have used the classical Boltzmann equation, (3.1), without justifying its use, and all but one have used the dielectric constant of pure water rather than the actual dielectric "constant" of the mixture.

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It has been reported (Hasted, 1948; Booth, 1951) earlier that the dielectric constant of a salt solution in an electric field decreases monotonically with increasing salt concentration and/or the electric field strength. Recently, Devillez <u>et al</u>. (1967) have reported a numerical method of integration of Poisson's equation in which the concentration dependence of the dielectric constant is included. However, no report has yet been made with regard to the solution of such a modified equation by analytical techniques.

In this chapter our purpose is to specify the influence of the nature of the electrochemical systems (particularly, biological systems) and the salt concentrations of aqueous strong uni-univalent electrolytes on potential. We combine the macroscopic ion distribution equation derived in Chapter III with Poisson's equation and solve the resulting equation subject to the requirement that $|\Psi| =$ $(F|\psi|/RT) \leq 0.245$. The range of salt concentrations used is 0.004 to 2 mole/ ℓ . We solve the differential equation in cylindrical coordinates since we have employed a capillary model for the problem, and we consider the concentration dependence of the dielectric constant in Poisson's equation.

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B. Poisson's Equation

Poisson's equation is, in the general case,

$$\nabla \cdot \mathbf{D} \nabla \psi = - 4\pi \overline{\mathbf{Z}} F , \qquad (4.1)$$

where D is the dielectric tensor of the salt solution in question, ψ is the electrostatic potential in volts, F is Faraday's constant, and \overline{Z} is charge per unit volume as defined in (2.12). We consider in this chapter only the radial direction and thus solve Poisson's equation for a circle. Assuming azimuthal symmetry, Poisson's equation is, in radial coordinates,

$$\frac{1}{r}\frac{d}{dr} r D \frac{d\psi}{dr} = -4\pi \overline{Z}F . \qquad (4.2)$$

The boundary conditions are

$$(d\psi/dr)_{r=0} = 0$$
, $(d\psi/dr)_{r=a} = 4\pi\sigma/D_a = \sigma/\varepsilon_a$, (4.3)

where a is the radius, σ is the charge on the walls, in C m⁻² (C = coulomb; m = meter), D_a is the dielectric constant at the wall, and ε_a is the electric permittivity at the wall.

In Chapter III, we obtained an explicit formula (3.32) for \overline{z} as a function of composition. Composition is, in turn, related to electrostatic potential ψ by (3.29). Substitution of (3.32) and (3.1) into (4.2) yields a right-hand-side in which the only variable is ψ . The result is formidably complicated, however, and, being an infinite series of various terms of the type exp $(-z_{\alpha} \Psi)$, could no doubt not be solved. Instead, we use previous results (e.g., Fair and Osterle, 1971) to estimate various terms with the goal of restricting the conditions sufficiently that a tractable equation results.

These estimates will also be used in dealing with the composition and field strength dependence of the dielectric constant. According to Sanfeld (1968), who has summarized the results of all previous workers, the concentration and field strength dependence of the dielectric constant is quite well represented for binary uni-univalent mixtures by

$$D = D_{0} + \delta_{+} c_{+} + \delta_{-} c_{-} + hE^{2} , \qquad (4.4)$$

for concentrations c_+ and c_- less than about 3 molar and for field strengths less than about 0.5×10^8 volts per meter in magnitude. Some values of δ_+ and δ_- are tabulated in Table 4.1. According to Sanfeld, h is found empirically to be about $-3 \times 10^{-16} \text{ m}^2 \text{v}^{-2}$. D is plotted versus |E| in Fig. 4.1. For large concentrations the dielectric "constant" decreases inversely with concentrations (Pottel, 1964), and (4.4) cannot be used. We assume that (4.4) can be extended to accommodate any number of ionic species, and we define

ions	$\overline{v}_{\alpha}^{o}$, cm ³ /mole	$10^{-3} \delta_{\alpha}$, cm ³ /mole
Li ⁺	-0.9	-11
Na ⁺	-1.4	- 8
к+	8.8	- 8
н+	0	-17
ОН	-5.4	-13
F	-2.2	- 5
c1 ⁻	18	-3
I_	36.5	-7

Table 4.1--Values of δ_{α} and $\overline{v}_{\alpha}^{O}$ of some uni-univalent electrolytes at 25°C (Sanfeld, 1968).

$$\delta_{+} c_{+} = \sum_{\text{cations}} \delta_{\alpha} c_{\alpha}$$

$$\delta_{-} c_{-} = \sum_{\text{anions}} \delta_{\alpha} c_{\alpha} . \qquad (4.5)$$

C. Simplifying Approximations

The principal goal of this section is to render (4.2) tractable. In particular, we examine: (i) the formula, (3.32), for \overline{Z} , in order to simplify it for use in (4.2); (ii) the formula, (3.29), for c_{α} , in order to simplify it for use in (4.4), and thence in (4.2); (iii) the wall boundary condition for $(d\psi/dr)$, (4.3), in order



to estimate |E| and its effect on D as in (4.4); (iv) (F ψ /RT) = Ψ itself, in order to determine under what circumstances it is permissible to replace sinh Ψ by Ψ .

To these ends, we utilize the classical Chapman-Gouy relation (see its derivation in Appendix A), valid only for special circumstances,

$$|\sigma| = 2 (2c\epsilon RT)^{1/2} \sinh (|\Psi_a|/2) ,$$
 (4.6)

only for purposes of estimation. Subsequently we find an improved version of (4.6), but our estimates here are not importantly changed. In (4.6), a uni-univalent solution of large concentration c is assumed. Note that we fully expect $|\Psi|$ at the wall to be larger than $|\Psi|$ in the solution, as found numerically by Fair and Osterle (1971), and we shall therefore estimate the maximum value of $|\Psi_{\rm a}|$ from (4.6).

Let us begin by investigating item (iv) in the above list; i.e., we require

$$\sinh \Psi = \Psi$$
 (4.7)

Since of course

sinh
$$x = x + \frac{1}{3!} x^3 + \frac{1}{5!} x^5 + \dots,$$
 (4.8)

we require, in (4.7), that

$$1 >> \frac{1}{3!} \Psi^2 + \frac{1}{5!} \Psi^4 + \dots$$
 (4.9)

For better than 1% accuracy, we therefore require

$$0.01 >> \frac{1}{3!} \Psi^2 + \frac{1}{5!} \Psi^4 + \dots, \qquad (4.10)$$

which yields

$$|\Psi| < 0.245$$
 (4.11)

So, for $|\Psi_a| < 0.245$ (in fact, for $|\Psi_a| < 0.49$), the Chapman Gouy equation becomes

$$|\sigma| = (2c\epsilon RT)^{1/2} |\Psi_a|$$
, (4.12)

and (4.11) yields the following restriction on $|\sigma|/\sqrt{c}$,

$$(|\sigma|/\sqrt{c}) < 0.245 (2\varepsilon RT)^{1/2}$$
 (4.13)

For T = 298°K, R = 8.314 J mole⁻¹ K⁻¹, and $\varepsilon = 7 \times 10^{-10}$ C V⁻¹ m⁻¹,

$$(2\varepsilon RT)^{1/2} = 1.86 \times 10^{-3} C \text{ mole}^{-1/2} m^{-1/2}$$
 (4.14)

Therefore, for sinh $|\Psi_a|$ to equal $|\Psi_a|$ to better than 1% accuracy, it is necessary for

$$(|\sigma|/\sqrt{c}) < 0.45 \times 10^{-3} \text{ C mole}^{-1/2} \text{ m}^{-1/2}$$
 (4.15)

Concentrations of important metal ions in biological systems (Woodbury <u>et al</u>., 1970) lie in the range of 0.004 < c < 0.4, in units of moles per liter, while ion concentrations are often outside this range in other systems of

interest. We take c < 2 mole liter⁻¹ = 2 × 10⁻³ mole cm⁻³ = 2×10^3 mole m⁻³ since the validity of the simple linear correction to the dielectric constant, (4.4), would be questionable for higher concentrations. Then in order for both (4.15) and (4.16) to hold, $|\sigma|$ may be as large as 20×10^{-3} C m⁻². On the other hand, for c = 0.004 mole liter⁻¹ = 4 × 10⁻⁶ mole cm⁻³ = 4 mole m⁻³, $|\sigma|$ must not be larger than 0.9×10^{-3} C m⁻². Typically, charge densities are of the order of 10^{-3} C m⁻² (Fair and Osterle, 1971). However, for $|\sigma| \ge 10^{-3}$ C m⁻², we require c \ge 4×10^{-3} M. Otherwise, for fixed $|\sigma| \ge 10^{-3}$ C m⁻², smaller concentrations lead to values of $|\Psi|$ too large for (4.7) to hold. For such small concentrations (which do not appear to be of biological interest in any case), there exists no analytical solution of Poisson's equation. Fair and Osterle (1971) have obtained numerical solutions for $c \approx 10^{-5}$ M and $|\sigma| \approx 10^{-3}$ C m⁻². We hereafter restrict consideration to

$$0.004 M \le c \le 2 M$$
 (4.16)

and $|\sigma| \approx 10^{-3} \text{ Cm}^{-2}$, the actual upper bound on $|\sigma|$ being that given by (4.15) for the actual composition in question.

Working backwards, we now accomplish item (iii) by using (4.3),

$$|\mathbf{E}| \approx (d\Psi/d\mathbf{r})_{\mathbf{a}} = |\sigma|/\varepsilon_{\mathbf{a}}$$
(4.17)

For $|\sigma| \leq 20 \times 10^{-3} \text{ Cm}^{-2}$ and $\varepsilon_a \approx 7 \times 10^{-10} \text{ CV}^{-1} \text{ m}^{-1}$, $|E| \leq 3 \times 10^7 \text{ Vm}^{-1}$, so that $|h|E|^2| \leq 3 \times 10^{-16} \times 9 \times 10^{14}$ = 0.27, which is less than 1% of the dielectric constant D_o of water. Since this is the maximum correction to D, we confidently neglect the contribution of $|E|^2$ to the dielectric constant and write

$$D = D_{0} + \delta_{+} c_{+} + \delta_{-} c_{-}$$
(4.18)

By Table 4.1, the maximum contribution of the concentration terms to the dielectric constant would be for $c_+ = c_- =$ 2 M = 2 × 10⁻³ mole cm⁻³; for, say, 2 M LiI, D = 78.3 -22 - 14 = 42.3, a 46% reduction. The concentration correction term contributes less than 1% for total salt concentrations less than about 0.05 M, depending on the particular ions involved.

The next task is estimation of x_{α} and c_{α} . For total salt molarity ≤ 2 M, \overline{c}_{α} is at most 2 M and

$$\overline{\mathbf{x}}_{\alpha} = \overline{\mathbf{c}}_{\alpha} \ \overline{\mathbf{v}}_{\alpha}^{\mathsf{O}} \approx \overline{\mathbf{c}}_{\alpha} \ \overline{\mathbf{v}}_{\mathsf{O}}^{\mathsf{O}} = 18 \ \mathrm{cm}^{3} \ \mathrm{mole}^{-1} \ \overline{\mathbf{c}}_{\alpha} ,$$
$$\overline{\mathbf{c}}_{\alpha} \lesssim 0.002 \ \mathrm{mole} \ \mathrm{cm}^{-3}, \ \overline{\mathbf{x}}_{\alpha} \lesssim 0.036, \ \overline{\mathbf{x}}_{\mathsf{O}} \gtrsim 0.928 \quad (4.19)$$

For uni-univalent salts, by (3.35),

$$x_{o}^{B} = 1 - (1 - \bar{x}_{o}) \cosh \Psi$$
, (4.20)

and for $(1-\bar{x}_0) \leq 0.072$, $|\Psi| \leq 0.245$,

$$\mathbf{x}_{0}^{B} \ge 1 - 0.072 \times 1.03 = 0.926,$$

 $\overline{\mathbf{x}}_{0} - \mathbf{x}_{0}^{B} = (1 - \overline{\mathbf{x}}_{0}) \pmod{4 \cdot 21} \lesssim 0.00216$ (4.21)

Thus, correction terms proportional to $(x_0 - x_0^B)$ in (3.22) - (3.25) are entirely negligible compared to unity.

Correction terms due to volume terms, however, are not always negligible. For, say, 2 M KCl, by Table 4.1,

$$\sum_{\alpha=1}^{\nu-1} (\mathbf{x}_{\alpha}^{B}/\overline{\mathbf{x}}_{o}) \quad (\overline{\nu}^{O}/\overline{\nu}_{o}^{O})$$

$$= (0.036/0.928) e^{-\Psi} (8.8/18) + (0.036/0.928) e^{\Psi} (18/18)$$

$$\approx 0.063 .$$

$$(4.22)$$

Thus, for better than 1% accuracy, our equations from Chapter III become, with

$$\mathbf{v}^{\star} = \sum_{\beta=1}^{\nu-1} (\overline{\mathbf{x}}_{\beta}/\overline{\mathbf{x}}_{o}) [\exp(-\mathbf{z}_{\beta}\Psi)] (\overline{\mathbf{v}}_{\beta}^{o}/\overline{\mathbf{v}}_{o}^{o}) , \qquad (4.23)$$

the following:

$$\mathbf{x}_{\alpha} = \overline{\mathbf{x}}_{\alpha} \exp((-\mathbf{z}_{\alpha}\Psi)) \tag{4.24}$$

$$(1/\overline{v}) = (1-\overline{v}^*)/\overline{x}_0 \ \overline{v}_0^0$$
(4.25)

$$c_{\alpha} = (\mathbf{x}_{\alpha}^{\mathrm{B}} / \overline{\mathbf{x}}_{0} \overline{\mathbf{v}}_{0}^{\mathrm{O}}) \quad (1 - \overline{\mathbf{v}}^{*}) = \overline{c}_{\alpha} \exp((-z_{\alpha} \Psi)) \quad (4.26)$$

$$\overline{\mathbf{Z}} = (1/\overline{\mathbf{x}}_{0}\overline{\mathbf{v}}_{0}^{0}) \quad (\sum_{\alpha=1}^{\nu-1}\overline{\mathbf{x}}_{\alpha} \ \mathbf{z}_{\alpha} \ \exp((-\mathbf{z}_{\alpha}\Psi)) \quad (1-\overline{\mathbf{v}}^{*})$$
$$= \sum_{\alpha=1}^{\nu-1}\overline{\mathbf{c}}_{\alpha} \ \mathbf{z}_{\alpha} \ \exp((-\mathbf{z}_{\alpha}\Psi) \quad (4.27)$$

In obtaining (4.25) - (4.27), we neglect the difference between v^* and \overline{v}^* compared with unity since

$$\overline{\mathbf{v}}^{\star} = \sum_{\beta=1}^{\nu-1} (\overline{\mathbf{x}}_{\beta} / \overline{\mathbf{x}}_{o}) \quad (\overline{\mathbf{v}}_{\beta}^{o} / \overline{\mathbf{v}}_{o}^{o})$$
$$= \mathbf{v}^{\star} + \sum_{\beta=1}^{\nu-1} (\overline{\mathbf{x}}_{\beta} / \overline{\mathbf{x}}_{o}) \quad (1 - \exp((-z_{\beta} \Psi))) (\overline{\mathbf{v}}_{\beta}^{o} / \overline{\mathbf{v}}_{o}^{o}) \quad (4.28)$$

and, for small $|\Psi|$ and a uni-univalent mixture,

$$\overline{\mathbf{v}}^{*} - \mathbf{v}^{*} \approx \left(\sum_{\text{cations}} (\overline{\mathbf{x}}_{\beta} / \overline{\mathbf{x}}_{o}) (\overline{\mathbf{v}}_{\beta}^{o} / \overline{\mathbf{v}}_{o}^{o}) - \sum_{\text{cations}} (\overline{\mathbf{x}}_{\beta} / \overline{\mathbf{x}}_{o}) (\overline{\mathbf{v}}_{\beta}^{o} / \overline{\mathbf{v}}_{o}^{o}) \right)$$

$$(4.29)$$

For 2 M KCl, e.g., with $|\Psi| = 0.245$,

$$\overline{\mathbf{v}}^* - \mathbf{v}^* \approx 0.02 \times 0.245 = 0.005$$
 (4.30)

Thus, for the prescribed conditions the equations of Chapter III reduce to the simple Boltzmann equations.

If we further specialize to the uni-univalent case, we have

$$\overline{Z} = \sum_{\substack{\alpha \\ \text{cations}}} \overline{c}_{\alpha} e^{-\Psi} - \sum_{\substack{\alpha \\ \text{anions}}} \overline{c}_{\alpha} e^{\Psi}$$
$$= -2c \sinh \Psi = -2c \Psi , \qquad (4.31)$$

where we have used (4.7) and where

$$c = \sum_{\alpha \in \alpha} \overline{c}_{\alpha} = \sum_{\alpha \in \alpha} \overline{c}_{\alpha}$$
(4.32)

Moreover, the equation for the dielectric constant is

$$D = D_{0} + \sum_{\alpha} \delta_{\alpha} \overline{c}_{\alpha} e^{-\Psi} + \sum_{\alpha} \delta_{\alpha} \overline{c}_{\alpha} e^{\Psi} \quad (4.33)$$
cations anions

and Poisson's equation is

$$\frac{1}{r} \frac{d}{dr} r \left(\frac{D}{D_o}\right) \frac{d\Psi}{dr} = (8\pi cF^2/D_oRT) \Psi = \kappa^2 \Psi , \qquad (4.34)$$

where

$$\kappa = F (8\pi c/D_{O}RT)^{1/2}$$
 (4.35)

is usually called the reciprocal of the Debye length. The boundary conditions on (4.34) are

$$(d\Psi/dr)_{r=0} = 0$$
, $(d\Psi/dr)_{r=a} = (4\pi\sigma F/RTD_a)$, (4.36)

where

$$D_{a} = D_{o} + \sum_{\alpha cations} \delta_{\alpha} \overline{c}_{\alpha} e^{-\Psi_{a}} + \sum_{\alpha cations} \delta_{\alpha} \overline{c}_{\alpha} e^{\Psi_{a}}$$
(4.37)

D. Perturbation Scheme

The concentration dependence of the dielectric constant must be taken into account since it strongly affects the dielectric constant. However, it complicates the Poisson equation, (4.34), so much that it still cannot be solved directly. In order to take account of this last complication, we solve (4.34) by a perturbation scheme defined by

$$\hat{\mathbf{D}} = \mathbf{D}_{\mathbf{O}} + \varepsilon \left(\delta_{+} \mathbf{c}_{+} + \delta_{-} \mathbf{c}_{-} \right)$$
(4.38)

and

$$\hat{\Psi} = \Psi_{0} + \varepsilon \Psi_{1} + \varepsilon^{2} \Psi_{2} + O(\varepsilon^{3}) , \qquad (4.39)$$

When $\varepsilon = 1$, $\hat{D} = D$ and $\hat{\Psi} = \Psi$. The parameter ε is simply a bookkeeping device which allows us to keep track of the inclusion of the concentration dependence of D. In order to obtain an explicit perturbation expression for c_{\perp} and c_{\perp} , we note that

$$e^{\pm \Psi} = 1 \pm \Psi_{0} \pm \varepsilon \Psi_{1} + O (\varepsilon^{2})$$
$$+ \frac{1}{2} \Psi_{0}^{2} + \varepsilon \Psi_{0} \Psi_{1} + \dots \qquad (4.40)$$

and (4.33), (4.38), (4.40) yield

$$\hat{D} = D_{o} + \varepsilon \{\sum_{\text{cations}} \delta_{\alpha} \ \overline{c}_{\alpha} [1 - \Psi_{o} + \frac{1}{2} \ \Psi_{o}^{2} - \varepsilon \Psi_{1} \ (1 - \Psi_{o}) + \dots] \}$$

$$+ \sum_{\text{anions}} \delta_{\alpha} \ \overline{c}_{\alpha} \ [1 + \Psi_{o} + \frac{1}{2} \ \Psi_{o}^{2} + \varepsilon \Psi_{1} \ (1 + \Psi_{o}) + \dots] \}$$

$$= D_{o} + \varepsilon \{ (\sum_{\text{cations}} \delta_{\alpha} \ \overline{c}_{\alpha} + \sum_{\text{anions}} \delta_{\alpha} \ \overline{c}_{\alpha}) \ (1 + \frac{1}{2} \ \Psi_{o}^{2})$$

$$- (\sum_{\text{cations}} \delta_{\alpha} \ \overline{c}_{\alpha} - \sum_{\text{anions}} \delta_{\alpha} \ \overline{c}_{\alpha}) \ \Psi_{o} \}$$

$$+ O \ (\varepsilon^{2})$$

$$= D_{o} + \varepsilon D_{1} + O \ (\varepsilon^{2}) , \qquad (4.41)$$

where

$$D_{1} = \begin{pmatrix} \Sigma & \delta_{\alpha} \ \overline{c}_{\alpha} + \Sigma & \delta_{\alpha} \ \overline{c}_{\alpha} \end{pmatrix} \cosh \Psi_{0}$$

$$- \begin{pmatrix} \Sigma & \delta_{\alpha} \ \overline{c}_{\alpha} - \Sigma & \delta_{\alpha} \ \overline{c}_{\alpha} \end{pmatrix} \sinh \Psi_{0}$$

$$= D^{+} \cosh \Psi_{0} - D^{-} \sinh \Psi_{0} \qquad (4.42)$$

yields

$$(1/r) d/dr \{r (1 + \varepsilon D_1/D_0 + O (\varepsilon^2)) (d\Psi_0/dr + \varepsilon d\Psi_1/dr + O (\varepsilon^2))\}$$
$$= \kappa^2 (\Psi_0 + \varepsilon \Psi_1 + O (\varepsilon^2)) , \qquad (4.43)$$

with boundary conditions, from (4.36), (4.39), and (4.41),

$$(d\Psi_{o}/dr)_{r=0} + (d\Psi_{1}/dr)_{r=0} + 0 (\epsilon^{2}) = 0 , \qquad (4.44)$$
$$(d\Psi_{o}/dr)_{r=a} + \epsilon (d\Psi_{1}/dr)_{r=a} + 0 (\epsilon^{2})$$
$$= (4\pi\sigma F/RT) (D_{o} + \epsilon D_{1} (a) + 0 (\epsilon^{2}))^{-1} \qquad (4.45)$$

The zeroth order differential equation is, from (4.43),

$$(1/r)$$
 $(dr (d\Psi_0/dr)/dr) = \kappa^2 \Psi_0$ (4.46)

with boundary conditions

$$(d\Psi_{o}/dr)_{r=0} = 0$$
, $(d\Psi_{o}/dr)_{r=a} = 4\pi\sigma F/D_{o}RT$ (4.47)

The first order differential equation is, from (4.43),

$$(1/r) (dr (d\Psi_{1}/dr)/dr) = - (1/r) (dr (D_{1}/D_{0}) (d\Psi_{0}/dr)/dr) + \kappa^{2} \Psi_{1} , \quad (4.48)$$

and the boundary conditions are

$$(d\Psi_1/dr)_{r=0} = 0$$
, $(d\Psi_1/dr)_{r=a} = -4\pi\sigma FD_1(a)/D_0^2 RT$ (4.49)

Clearly, higher order equations could be obtained if desired.

E. Solutions of the Differential Equations

Substitution of Variables

First, make the substitution

$$\xi = \kappa \mathbf{r} \quad . \tag{4.50}$$

Then

$$r = \xi \kappa^{-1}$$
, $d/dr = \kappa (d/d\xi)$, (4.51)

and

$$\xi_{a} = \kappa a \tag{4.52}$$

The zeroth order equations are then

$$(1/\xi) (d\xi (d\Psi_0/d\xi)/d\xi) = \Psi_0$$
 (4.53)

or

$$d^{2}\Psi_{0}/d\xi^{2} + (1/\xi) (d\Psi_{0}/d\xi) - \Psi_{0} = 0 , \qquad (4.54)$$

$$(d\Psi_{o}/d\xi)_{\xi=0} = 0, \ (d\Psi_{o}/d\xi)_{\xi=\xi_{a}} = 4\pi\sigma F/\kappa D_{o}RT$$
 (4.55)

The first order equations are

$$d^{2}\Psi_{1}/d\xi^{2} + (1/\xi) (d\Psi_{1}/d\xi) - \Psi_{1} = q_{1}(\xi) , \qquad (4.56)$$
$$q_{1}(\xi) = -(1/\xi) (d\xi(D_{1}/D_{0}) (d\Psi_{0}/d\xi)/d\xi)$$
$$= -(D_{1}/D_{0}) [d^{2}\Psi_{0}/d\xi^{2} + (1/\xi) (d\Psi_{0}/d\xi)]$$

$$- (d\Psi_{0}/d\xi) (d(D_{1}/D_{0})/d\xi) ,$$

= - (D_{1}/D_{0}) Ψ_{0} - (d\Psi_{0}/d\xi) (d(D_{1}/D_{0})/d\xi) , (4.57)

with

$$(d\Psi_1/d\xi)_{\xi=0} = 0$$
, $(d\Psi_1/d\xi)_{\xi=\xi_a} = -4\pi\sigma FD_1(a)/D_0^2\kappa RT$ (4.58)

Zeroth Order Solution

Multiplication of (4.54) by ξ^2 yields

$$\xi^{2} \Psi_{O}^{"} + \xi \Psi_{O}^{'} - \xi^{2} \Psi_{O} = 0 , \qquad (4.59)$$

which is easily recognized as the modified Bessel Equation of order zero, whose general solution is (Irving and Mullineux, 1959)

$$\Psi_{0} = A I_{0} (\xi) + B K_{0} (\xi) , \qquad (4.60)$$

where I and K are the modified Bessel functions of order zero of, respectively, the first and second kinds.

In order to utilize the boundary conditions, we differentiate (4.60) with respect to ξ ,

 $\Psi'_{O} = A I_{1} (\xi) - B K_{1} (\xi) , \qquad (4.61)$

where we have used the recurrence relations

$$I'_{0} = I_{1}, K'_{0} = K_{1}$$
 (4.62)

As $\xi \neq 0$, $I_1(\xi) \neq 0$ but $K_1 \neq \infty$ (Abramowitz and Stegun, 1964). Consequently, since $\Psi'_0(0) = 0$, we must have B = 0 and therefore

$$\Psi'_{0} = A I_{1} (\xi)$$
 (4.63)

By the second of (4.55),

$$\mathbf{A} = 4\pi\sigma F/\kappa D_{O} RT \mathbf{I}_{1} (\kappa a) , \qquad (4.64)$$

and the zeroth order solution is

$$\Psi_{o} = A I_{o} (\xi) = (4\pi\sigma F/\kappa D_{o}RT I_{1} (\kappa a)) I_{o} (\kappa r)$$
$$= (\sigma/\sqrt{2\varepsilon_{o}CRT}) [I_{o} (\kappa r)/I_{1} (\kappa a)], \qquad (4.65)$$

where $\varepsilon_0 = D_0/4\pi$. The values of Ψ_0 at two locations are of particular interest:

$$\Psi_{o} (\mathbf{r}=0) = \Psi_{o} (0) = \sigma / \sqrt{2\varepsilon_{o} cRT} \mathbf{I}_{1} (\kappa a) , \qquad (4.66)$$

$$\Psi_{o} (\mathbf{r}=a) = \Psi_{o} (a) = \sigma / \sqrt{2\varepsilon_{o} cRT} [\mathbf{I}_{o} (\kappa a) / \mathbf{I}_{1} (\kappa a)]$$

$$= \mathbf{I}_{o} (\kappa a) \Psi_{o} (0) \qquad (4.67)$$

Two things are especially noteworthy: (i) Ψ_0 (0) $\neq 0$; (ii) the Chapman-Gouy equation, (4.12), is valid only for $[I_0 (\kappa a)/I_1 (\kappa a)] \rightarrow 1$, which never occurs, but is a fairly good approximation for $\kappa a >> 1$. Recalling that the motivation for the requirement (4.15) was that we wished to use (4.7), we may easily modify (4.15) in light of our results here. Formally, all we need is

$$(|\sigma|/\sqrt{c} \le 0.45 \times 10^{-3}/[I_{o}(\kappa a)/I_{1}(\kappa a)] \ C \ m^{-1/2} \ mole^{-1/2} \ (4.68)$$

where the denominator is tabulated in Table 4.2. For example, for $\kappa a = 0.5$, it is necessary that $(|\sigma|/\sqrt{c}) \leq 0.11 \times 10^{-3} \text{ Cm}^{1/2} \text{ mole}^{-1/2}$; for c = 2 M, the requirement becomes $|\sigma| \leq 5 \text{ Cm}^{-2}$; and so forth.

First Order Solution
By (4.42) and (4.7), as supported by (4.68),
$$D_1 = D^+ - D^- \Psi_0$$
 (4.69)

Then by (4.57),

$$q_{1}(\xi) = -D_{0}^{-1} \{ [D^{+} \Psi_{0} - D^{-} \Psi_{0}^{2}] - D^{-} \Psi_{0}^{2} \}$$

$$= - (AD^{+}D_{0}) I_{0}(\xi)$$

$$+ (A^{2}D^{-}/D_{0}) \{ [I_{0}(\xi)]^{2} + [I_{1}(\xi)]^{2} \}$$
(4.70)

Now the left-hand-side of (4.56) is the same as the left-hand-side of (4.54), and we therefore know that One solution of (4.56), if (4.56) were homogeneous, is

$$u_1 = I_0 (\xi) \tag{4.71}$$

ка	I ₀ (ка)/I ₁ (ка)	1/I ₁ (ĸa)
0.1	20.02	19.970
0.2	10.05	9.950
0.5	4.12	3.880
0.8	2.70	2.310
1.0	2.24	1.770
1.5	1.68	1.020
1.8	1.51	0.759
2.0	1.43	0.629
3.0	1.23	0.253
4.0	1.16	0.102
5.0	1.12	0.041
10.0	1.05	3.3×10^{-4}

Table 4.2--Some calculated values of I_0/I_1 and $1/I_1$.

Moreover, $K_{O}(\xi)$ cannot be a solution because both $K_{O}(0)$ and $K'_{O}(0)$ are infinite. To obtain the general solution of (4.56), we write

$$\Psi_{1} = \mathbf{v} \ (\xi) \ \mathbf{u}_{1} \ (\xi) \tag{4.72}$$

The boundary conditions are on the derivative,

 $\Psi'_{1} = \mathbf{v}' \mathbf{u}_{1} + \mathbf{v} \mathbf{u}'_{1} , \qquad (4.73)$

Since
$$I'_{O}(\xi) = I_{1}(\xi)$$
 and since $I_{1}(0) = 0$ and $I_{O}(0) = 1$,
(4.73), (4.71), (4.64), and (4.58) yield
v'(0) = 0 (4.74)
v'(\ka) $I_{O}(\ka) + v(\ka) I_{1}(\ka)$
 $= -4\pi\sigma FD_{1}(a)/D_{O}^{2} \kar$
 $= -[D_{1}(a)/D_{O}] \lambda I_{1}(\ka)$ (4.75)

Now introduce (4.72) into (4.56). There follows

$$v'u_1 + 2v'u_1' + \xi^{-1}v'u_1 + v (u_1'' + \xi^{-1}u_1' - u_1) = q_1$$
 (4.76)

But since u_1 is the homogeneous solution of (4.56), the expression in parentheses vanishes and the differential equation determining v becomes

$$v''u_1 + 2v'u_1' + \xi^{-1}v'u_1 = q_1$$
 (4.77)

or

$$(\mathbf{v'})' + (2\mathbf{u}_1'/\mathbf{u}_1 + \xi^{-1}) \mathbf{v'} = q_1/\mathbf{u}_1$$
 (4.78)

This equation is of first order in v', with an integrating factor of the form

$$\exp \{ \{ (2u_1'/u_1 + \xi^{-1}) \ d\xi \} = \xi u_1^2 .$$
(4.79)

The solution of (4.78) is therefore

$$\xi u_{1}^{2} v' = \int \xi u_{1} q_{1} d\xi + B_{1}$$
 (4.80)

By (4.74), the constant is simply

$$B_{1} = - ((\xi u_{1}q_{1}d\xi)_{\xi=0}), \qquad (4.81)$$

and hence,

$$\mathbf{v'} = (\xi u_1^2)^{-1} \int_0^{\xi} u_1 q_1 d\xi$$

= $(\xi u_1^2)^{-1} u_2$, (4.82)

where

$$u_2 = \int_0^{\xi} \xi u_1 q_1 d\xi \qquad (4.83)$$

Integration of (4.82) yields, formally,

$$\mathbf{v} = \int_{0}^{\xi} (\xi u_{1}^{2})^{-1} u_{2} d\xi + B_{2}$$
(4.84)

By (4.75), (4.71), (4.82), and (4.84),

$$B_{2} = -D_{1} (a) A/D_{0} (a) - (f(\xi u_{1}^{2})^{-1} u_{2} d\xi)_{\kappa a}$$
$$-u_{2} (\kappa a) /\kappa a I_{0} (\kappa a) I_{1} (\kappa a) \qquad (4.85)$$

The only remaining task, in this section, is evaluation of u_2 and its integral, (4.84), in order to complete the derivation of Ψ_1 . Substituting (4.70) and (4.71) into (4.83), there follows

$$u_{2} = - (AD^{+}/D_{o}) \int_{0}^{\xi} \xi I_{o}^{2} d\xi + (A^{2}D^{-}/D_{o}) [\int_{0}^{\xi} \xi I_{o}^{3} d\xi + \int_{0}^{\xi} \xi I_{o} I_{1}^{2} d\xi]$$
(4.86)

It can easily be shown (Appendix B), by integration by parts, that

$$\int_{0}^{\xi} \xi \mathbf{I}_{0} \mathbf{I}_{1}^{2} d\xi = \mathbf{I}_{0}^{2} \mathbf{I}_{1}^{2} - \int_{0}^{\xi} \xi \mathbf{I}_{0}^{3} d\xi^{2}$$
(4.87)

$$\int_{0}^{\xi} \xi \mathbf{I}_{0}^{2} d\xi = \xi^{2} (\mathbf{I}_{0}^{2} - \mathbf{I}_{1}^{2})/2 .$$
 (4.88)

Then

•

$$u_{2} = (A/2D_{0}) \{D^{+}\xi^{2} (I_{1}^{2} - I_{0}^{2}) + D^{-} [\int_{0}^{\xi} \xi I_{0}^{3} d\xi + \xi I_{0}^{2} I_{1}]\}, (4.89)$$

$$v' = (\xi u_{1}^{2})^{-1} u_{2} = (A/2D_{0}) \{D^{+}\xi (\frac{I_{1}^{2}}{I_{0}^{2}}) - 1\}$$

$$+ D^{-} [I_{1} + (\xi I_{0}^{2})^{-1} \int_{0}^{\xi} \xi I_{0}^{3} d\xi] \qquad (4.90)$$

and

$$v = (A/2D_0) [D^+ (S_1 - \xi^2/2) + D^- (I_0 + S_2)] + B_2$$
(4.91)

with

$$s_1(\xi) = \int \xi (I_1/I_0)^2 d\xi$$
 (4.92)

$$s_{2}(\xi) = \int (\xi I_{0}^{2})^{-1} (\int_{0}^{\xi} \xi I_{0}^{3} d\xi) d\xi$$
 (4.93)

.

Moreover, by (4.85),

$$B_{2} = -\left(\frac{A}{2D_{0}}\right) \left\{2D_{1}(a) + D^{+}\left[S_{1}(\kappa a) - \frac{1}{2}(\kappa a)^{2}\right] + D^{-}\left[I_{0}(\kappa a) + S_{2}(\kappa a)\right] + D^{+}(\kappa a)\left[\frac{I_{1}(\kappa a)}{I_{0}(\kappa a)} - \frac{I_{0}(\kappa a)}{I_{1}(\kappa a)}\right] + D^{-}\left[I_{0}(\kappa a) + \frac{1}{\kappa a I_{0}(\kappa a) I_{1}(\kappa a)}\int_{0}^{\kappa a} \xi I_{0}^{3} d\xi\right] \right\} = -\left(\frac{A}{2D_{0}}\right) \left\{D^{+}\left[\kappa a \frac{I_{1}(\kappa a)}{I_{0}(\kappa a)} - \kappa a \frac{I_{0}(\kappa a)}{I_{1}(\kappa a)} + S_{1}(\kappa a)\right] - \frac{1}{2}(\kappa a)^{2} + 2\right] + D^{-}\left[2 I_{0}(\kappa a) + S_{2}(\kappa a)\right] + \frac{\int_{0}^{\kappa a} \xi I_{0}^{3} d\xi}{\kappa a I_{0}(\kappa a) I_{1}(\kappa a)} - 2 A I_{0}(\kappa a)\right] \right\}$$
(4.94)

where we have used, by (4.42), (4.7), and (4.65),

$$D_1 (a) = D^+ - A I_0 (\kappa a) D^-$$
 (4.95)

Finally, put

$$\Psi_{1} = \Psi_{0} \Phi_{1} , \qquad (4.96)$$

where

•

$$\Psi_{O} = A I_{O}$$
(4.97)

and

$$\Phi_{1} = (1/2D_{0}) \{D^{+}(S_{1} - \xi^{2}/2) + D^{-}(S_{2} + I_{0}) + B_{2}(2D_{0}/A)\}$$
(4.98)

Introducing (4.96) into (4.39) and setting $\varepsilon = 1$, we have

$$\Psi = \Psi_{0} (\xi) [1 + \Phi_{1} (\xi) + \dots]$$
(4.99)

Here we include only the first-order perturbation. If necessary, extra terms may be calculated and added to (4.99) depending on nature of the system.

F. Discussion

It is evident that (4.98) involves the evaluation of integrals of the form

$$\int_{n}^{\xi} \xi f(\xi) I_{n}(\xi) d\xi$$
 (4.100)

The evaluation of such integrals in closed form is possible for only a few functions f (ξ). Consequently, recourse to numerical computation is usually necessary (cf. Irving and Mullineux, 1959). Hence, in evaluating (4.100) we make use of the following equations (Abramowitz and Stegun, pp. 375-377).

$$I_{n} (\xi) = \begin{cases} \sum_{k=0}^{\infty} (\xi/2)^{2k+n}/k! \ (k+n)!, \ 0 \leq \xi < 2 \ (4.101) \\ \frac{e^{\xi}}{\sqrt{2\pi\xi}} \{1 - (4n^{2}-1)/8\xi + (4n^{2}-1)(4n^{2}-9)/2!(8\xi)^{2} \\ - (4n^{2}-1)(4n^{2}-9)(4n^{2}-25)/3!(8\xi)^{3} + \dots, (4.102) \\ \xi > 2 \end{cases}$$

In general, however, if the actual physico-chemical properties of the system are specified, the evaluation of such integrals can be made tractable without introducing significant error.

To clarify this, we consider, as an example, a charged membrane for which the fixed surface charge density $|\sigma|$ is 10^{-3} C/m² and the radius of the capillary a is at 4.2Å. Consequently, for the case $\xi_a < 2$, we can evaluate the integrals by representing the products of various modified Bessel functions as a power series in ξ with the aid of numerical computation of the various coefficients necessary for the validity of such representation (Watson, 1968).

It can easily be calculated from (4.35) that at the salt concentration of 1.5 mole/ ℓ , the value of $\xi_a = \kappa a$ is 1.69235 at 25°C and hence S_1 (ξ) and S_2 (ξ) can be represented in practice by

$$S_{1} = \sum_{k=0}^{5} a_{k} \xi^{2k+4} / (2k+4) + \varepsilon_{1k} \quad (\xi) \quad (4.103)$$

and

$$S_{2} = \sum_{k=0}^{5} b_{k} \xi^{2k+2} / (2k+2) + \varepsilon_{2k} (\xi) , \qquad (4.104)$$

in which it can be shown numerically that the contributions of ε_{1k} to S₁ and ε_{2k} to S₂ are immaterial. Note that extra

terms, if necessary, can be calculated and added to (4.103)and (4.104) depending on the nature of the system. The values of the coefficients a_k and b_k (k=0,...,5) are listed in Table 4.3.

k	$a_k \times 10^4$	$b_k \times 10^4$
0	2500.0	5000.0
1	-625.00	-625.00
2	143.23	234.38
3	-30.925	-55.882
4	6.4155	9.5554
5	-1.2942	-2.6589

Table 4.3--Values of a_k and b_k (k=0,...5).

Returning to (4.99), the surface potential $|\psi_a|$ at the wall can be calculated, yielding the following result

$$|\psi_{a}| = (RT/F) \Psi_{0}(\xi_{a}) [1 + \Phi_{1}(\xi_{a}) + ...]$$
 (4.105)

where Φ_1 (ξ_a) is the value of Φ_1 (ξ) at the wall. From the results obtained above, we notice that the solution represented by (4.99) is valid for the entire domain of integration, $0 \le r \le a$, since, in particular, no singularity exists at the center of the capillary (r=0). In order to clarify the analytical approximation obtained above, in this section we carry out a numerical analysis on Ψ . As an example, we calculate the values of Ψ and Ψ_0 for $|\sigma| = 10^{-3} \text{ C/m}^2$ and a = 4.2 Å for the case of $\xi_a = \kappa a < 2$. The salt concentration used in the calculation is 1.5 mole/ ℓ and the temperature is 25°C. Some values of Ψ , Ψ_0 and $\Psi - \Psi_0$ calculated are listed in Table 4.4. A comparison of the results of Ψ and Ψ_0 is shown in Fig. 4.2.

Table 4.4--Some calculated values of Ψ , Ψ , and $\overset{\Psi}{\circ}$ - $\overset{\Psi}{\circ}$. T = 298°K, $|\sigma| = 10^{-3}$ C m⁻², a^o= 4.2 A, and $\kappa a = 1.692$.

ξ	Ψ (ξ)	Ψ _ο (ξ)	Ψ – Ψ _Ο
0.000	0.00855	0.0117	-0.00317
0.051	0.00856	0.0117	-0.00317
0.355	0.00890	0.0121	-0.00320
0.592	0.00954	0.0128	-0.00323
0.728	0.01007	0.0133	-0.00326
0.998	0.01151	0.0148	-0.00332
1.472	0.01558	0.0190	-0.00341
1.675	0.01811	0.0215	-0.00340



According to our analysis, we notice that $\Psi - \Psi_{o}$ is nonpositive. This indicates that the inclusion of the concentration dependence of the dielectric constant in Poisson's equation actually results in the decrease of the overall potential function at any point in the system. However, the decrement $\Psi - \Psi_{o}$ is very small. As a result, we can anticipate that the solution represented by $\Psi_{o} + \Psi_{1}$, where Ψ_{1} is the first-order solution, should give an excellent approximation to Ψ . For larger values of κ_{a} , more complicated numerical analysis is required, but there is no conceptual difficulty. For smaller values of c, the contribution of the concentration dependence of D will of course be less, and Φ_{1} will be less important.

G. Conclusion

Including the radial dependence of the dielectric constant in Poisson's equation, we have obtained analytically, in the general case, an improved potential distribution equation for an uni-univalent electrolyte system, subject to (4.68) and for salt concentrations of ~ 10^{-3} to 2 mole/&. The equation can be used to study various biological systems. A practical potential distribution equation is also derived for the case of $\kappa a < 2$ where a = 4.2 Å. Consequently, the physico-chemical properties of aqueous uniunivalent electrolyte solutions in biological systems and other charged systems can now be interpreted more accurately. In the derivation of the equation, we have required sinh $\Psi = \Psi$. Recently, MacGillivray <u>et al</u>. (1966) have demonstrated that the solution of the Poisson-Boltzmann equation for a charged cylinder can be approximated by the solution of the Debye-Hückel equation even when the molarity of the electrolyte is low, i.e., when $\Psi >> 1$, provided the cylinder is "moderately charged," that is, when $2\pi |\sigma| F$ $a/D_0 RT < 1$. For the example mentioned in the preceding section, it can be shown that $2\pi |\sigma| F a/D_0 RT = 0.0118$ at $25^{\circ}C$. We have here obtained explicit conditions (4.68) on the ratio of $|\sigma|$ to \sqrt{c} and have thereby eliminated the need for restriction on κ itself. In fact, we have not used Debye-Hückel theory as such at all.

CHAPTER V

THE STEADY-STATE DISTRIBUTION OF PRESSURE IN MODERATELY CHARGED SYSTEMS

A. Introduction

In the study of electrochemical systems, knowledge of the pressure distribution has been realized to be essential in the understanding of interfacial diffuse double layers and thin liquid films (Verwey, 1948; Derjaguin, 1966; Herwitz, 1964; Defay, 1963; Sanfeld, 1966). The difficulty in obtaining a simple equation for the pressure distribution is primarily due to the lack of a theoretical formulation for the problem. As a result, many authors have either neglected its existence or considered the pressure to be independent of electric field (cf. Kobatake and Fujita, 1964) without justification. As we shall see in the next chapter, the effect of the pressure is important and vital to the understanding of osmotic flow phenomena of fluids across a charged, continuous phase; i.e., a membrane. Previously, no explicit, practical pressure distribution equation has been obtained, and its various important applications have not been discussed.

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In this chapter, our primary purpose is to make use of the potential distribution equation derived in Chapter IV and to derive, in the general case, an explicit formula for the pressure distribution at any point in a moderately charged system where the conditions of Chapter IV are satisfied. We consider a nonequilibrium system at steady state, an isotropic fluid, and absence of electric polarization. A capillary model is adopted for the membrane. We are primarily concerned with the uni-univalent case.

One of the fundamental approaches in the study of flow phenomena in membranes, charged or uncharged, is the knowledge of macroscopic osmotic pressure in the system. The differential equation that governs the pressure of fluid at any point in the system is, in the general case, by (3.3),

$$dp = - (RT/\overline{v}_{0}^{0}) d \ln x_{0},$$
 (5.1)

where p is the pressure at any point in the system, x_0 is the mole fraction of water at any point in the system, \overline{v}_0^0 is the molar volume of pure water, R is gas constant, T is the uniform, absolute temperature, and $\ln f_0$ is assumed constant. From (5.1) we immediately obtain

$$p = - (RT/\overline{v}_{0}^{0}) \ln x_{0} + B$$
, (5.2)

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where B is the constant of integration. This equation can be used in a variety of ways. For example, the difference in pressure between any two points a and b in a system is the osmotic pressure π_{ba} :

$$\pi_{ba} = p (b) - p (a) = - (RT/\overline{v}_{o}^{O}) \ln [x_{o}(b)/x_{o}(a)] (5.3)$$

By using this equation and the results of Chapters III and IV, we could calculate π_{ba} between any two points in the membrane.

We are, however, primarily concerned with osmotic flow through the charged membrane. We hereby define π_{mo} as the steady-state value of the macroscopic osmotic pressure between the membrane phase m and the aqueous phase in compartment 0 (the other compartment will be called compartment L),

$$\pi_{\rm mo} = p \ (m) - p_{\rm o} \ (0) \ , \tag{5.4}$$

where p (m) is the <u>average</u> pressure in the capillary and p_0 (0) is the <u>average</u> pressure in compartment 0. Moreover, define π_{lo} as the steady-state value of the osmotic pressure across the charged membrane.

$$\pi_{lo} = p(l) - p(0), \qquad (5.5)$$

where p(l) and p(0) are the average pressures over the cross section of the capillary at, respectively, l and 0,

the positions of the interfaces of the membrane with, respectively, compartments L and O. From (5.2), (5.4), and (5.5), there follows

$$\pi_{\rm mo} = - \left({\rm RT}/\overline{v}_{\rm o}^{\rm O} \right) \, \ln \left[\overline{x}_{\rm om}/x_{\rm o} \left(0 \right) \right] \tag{5.6}$$

$$\pi_{lo} = - (RT/\overline{v}_{o}^{O}) \ln (\overline{x}_{ol}/\overline{x}_{oo}) , \qquad (5.7)$$

where \overline{x}_{om} is the steady-state value of the <u>average</u> water concentration in the capillary, x_o (0) is the average value of water concentration in compartment 0, and \overline{x}_{ol} and \overline{x}_{oo} are the steady-state values of the average water concentrations over the cross section of the capillary at, respectively, l and 0.

In order to obtain the relative distribution of water, i.e., $[\bar{x}_{om}/x_{o}(0)]$ or $(\bar{x}_{ol}/\bar{x}_{oo})$ at steady state, we could use directly the results of Chapters III and IV to obtain the desired averages. It is more illuminating, however, and somewhat simpler to focus attention on the pressure itself. Hence, our second goal in this chapter is to make use of the pressure distribution equation and to derive the practical equations for π_{mo} and π_{lo} as functions of the salt concentrations and the electric field for use in the study of transport phenomena of water in charged systems.

Consider a charged, continuous phase separating two aqueous electrolyte solutions of different concentration at the same temperature. We wish to derive, in the general case, the pressure distribution equation for the system.

By (3.7),
$$\partial p/\partial r = -\overline{Z}F (\partial \psi/\partial r)$$
. (5.8)

By (4.27) (the conditions which make it valid are therefore required here),

$$(\partial p/\partial r) = - (RT) \sum_{\alpha=1}^{\nu-1} \overline{c}_{\alpha} z_{\alpha} [exp(-z_{\alpha} \Psi)] (\partial \Psi/\partial r)$$
 (5.9)

This is easily integrated to yield

$$p = p_{0} + RT \sum_{\alpha=1}^{\nu-1} \overline{c}_{\alpha} [exp(-z_{\alpha}\Psi) - 1], \qquad (5.10)$$

where p is the value of p for zero electric field.

For a uni-univalent system, (5.10) becomes

$$p = p_0 + 2cRT (cosh\Psi - 1)$$
, (5.11)

where we have used (4.32). We have now obtained explicitly the pressure distribution equations which take account of the concentration dependence of the pressure. Since osmotic flow is our concern here, we are interested in the longitudinal, or axial, dependence of the pressure. Differentiation of (5.11) yields

$$(\partial p/\partial x) = (\partial p_0/\partial x) + 2RT (\cosh \Psi - 1) (\partial c/\partial x)$$

- $RT\overline{Z} (\partial \Psi/\partial x)$, (5.12)

where we have also used (4.31). If we now assume that the last term on the right-hand-side is negligible, we have

$$(\partial p/\partial x) = (\partial p_0/\partial x) + 2RT (\cosh \Psi - 1) (\partial c/\partial x)$$
 (5.13)

This assumption is reasonable on two counts: (i) we do not expect the potential difference across the membrane to be significant, and (ii) the <u>average</u> net charge in the solution inside the membrane must be small. In any case, we are interested here in illuminating the contribution of the concentration gradient to the pressure gradient, and we therefore use (5.13), wherein Ψ is taken to be the value of $F\Psi/RT$ for \overline{c} , the average salt concentration in the membrane.

B. The Macroscopic Osmotic Pressure Between the Membrane Phase and the Aqueous Phase in a Moderately Charged System

Making use of the pressure distribution equation derived above, in the following treatment we derive an explicit formula to represent the macroscopic osmotic pressure π_{mo} between the membrane phase m and the aqueous phase 0 for a moderately charged membrane, separating two uni-univalent electrolyte solutions.
We introduce (5.11) into the following equation

$$\overline{p}(r) = \int_{0}^{\ell} p dx / (\ell - 0) ,$$
 (5.14)

where \overline{p} (r) is the average axial pressure, and where l is the length of the capillary or the thickness of the membrane. Then, there results

$$\overline{p}(r) = \int_{0}^{\ell} p_{0} dx/(\ell-0) + 2RT \{\cosh \Psi - 1\} \int_{0}^{\ell} cdx/(\ell-0) (5.15)$$

where we again, and for the same reasons, take Ψ to be its average in the membrane.

Clearly, the evaluation of integrals in (5.15) requires knowledge of the explicit expressions of p_0 and c as functions of x. We assume, as a first approximation, that p_0 (x) and c (x) are linear functions of x. That is, we may write

$$p_{0} = (\Delta p_{0}/\ell) x + p_{0} (0)$$
 (5.16)

$$c = (\Delta c/l) x + c (0)$$
, (5.17)

where Δp_{o} and Δc are defined as

$$\Delta p_{0} = p_{0} (l) - p_{0} (0)$$
 (5.18)

$$\Delta c = c (l) - c (0)$$
 (5.19)

Combination of (5.16), (5.17) and (5.15) yields the explicit expression for the radial pressure in the system,

 \overline{p} (r) = {p₀ (l) + p₀ (0)}/2 + RT {coshΨ-1}{c(l)+c(0)} (5.20)

We rewrite (5.26) as

$$\overline{p}$$
 (r) - p_0 (0) = $\Delta p_0/2$ + RT {cosh Ψ -1}{c(l)+c(0)} (5.21)

The macroscopic osmotic pressure π_{mo} between the membrane phase m and the aqueous phase 0 can be deduced from (5.21), yielding the following equation

$$\pi_{mo} = \Delta p_{0}/2 + RT\{c (l) \\ + c(0) \} \begin{bmatrix} \int 2\pi r \{cosh\Psi - l\} dr / \int 2\pi r dr \end{bmatrix}, \quad (5.22) \\ 0 \qquad 0$$

where π_{mo} is defined by (5.4) in which p (m) is given as

$$p(m) = \int_{0}^{a} 2\pi r \overline{p}(r) dr / \int_{0}^{a} 2\pi r dr . \qquad (5.23)$$

In the absence of initial hydrostatic pressure difference, i.e., when $\Delta p_0 = 0$, then, (5.23) becomes

$$\pi_{mo} = RT \{c(l) + c(0)\} \int_{0}^{a} 2\pi r \{coshy - 1\} dr/\pi a^{2} . (5.24)$$

For experimental convenience, in general, the salt concentration at one side of the membrane is fixed while that at the other side of the membrane is varied. Thus, in practice we may rewrite (5.24) as

$$\pi_{\rm mo} = c(\ell) RT(1+q) \int_{0}^{a} 2r (\cosh \Psi - 1) dr/a^{2}$$
 (5.25)

where q is given as

$$q = c(0)/c(l)$$
, (5.26)

The value of q can then be varied during the experiment.

To evaluate the integral in (5.26), we make use of the conditions of Chapter IV. There follows, then,

$$\int_{0}^{a} 2r \left(\cosh \Psi - 1\right) dr \cong \int_{0}^{a} r \Psi^{2} dr \qquad (5.27)$$

where we have used

$$\cosh \Psi = 1 + \Psi^2/2 + \frac{1}{24} \Psi^4 + \dots \approx 1 + \frac{1}{2} \Psi^2$$
(5.28)

Introducing (4.50) and (4.52) into (5.27), we write

$$\int_{0}^{a} r\Psi^{2} dr = (1/\kappa^{2}) \int_{0}^{\xi} \xi\Psi^{2} d\xi , \qquad (5.29)$$

where κ is the reciprocal of Debye length defined by (4.35), and hence (5.25) becomes

$$\pi_{mo} \cong \{c (0) RT (1 + q) / \xi_a^2\} \int_0^{\xi_a} \xi \Psi^2 d\xi . \qquad (5.30)$$

Making use of the substitution: $\Psi = \Psi_0 + \Psi_1$, where Ψ_0 and Ψ_1 are defined by (4.65) and (4.96) respectively, we have

$$\int_{0}^{\xi_{a}} \xi \Psi^{2} d\xi = \int_{0}^{\xi_{a}} \xi \Psi^{2}_{0} d\xi + 2 \int_{0}^{\xi_{a}} \xi \Psi_{0} \Psi_{1} d\xi + \int_{0}^{\xi_{a}} \xi \Psi^{2}_{1} d\xi \cdot$$
(5.31)

For simplicity, denote

$$L_{1} = \int_{0}^{\xi_{a}} \xi \Psi_{0}^{2} d\xi$$
 (5.32)

$$L_{2} = \int_{0}^{\xi_{a}} \xi \Psi_{0} \Psi_{1} d\xi$$
(5.33)
$$L_{3} = \int_{0}^{\xi_{a}} \xi \Psi_{1}^{2} d\xi$$
(5.34)

$$L_{1} = A^{2} \xi_{a}^{2} \{I_{o}^{2}(\xi_{a}) - I_{1}^{2}(\xi_{a})\}/2 .$$
 (5.35)

However, from (4.96) and (4.98) we notice that there is great difficulty in evaluating (5.33) and (5.34) in closed forms, and hence the evaluation of such integrals requires knowledge of the physical situation. Hence, (5.30) becomes

$$\pi_{\rm mo} \cong \{ c \ (l) \ RT \ (l+q)/\xi_a^2 \} \ [A^2 \ \xi_a^2 \ \{ I_o^2 \ (\xi_a) - I_1^2 \ (\xi_a) \}/2 + 2L_2 + L_3] \ .$$
(5.36)

The equation can, moreover, be used to determine the relative distribution of water between the membrane phase m and the aqueous phase 0, since by (5.6),

$$\bar{\mathbf{x}}_{om}/\mathbf{x}_{o}$$
 (0) = exp (- $\pi_{mo} \bar{\mathbf{v}}_{o}^{O}/RT$) (5.37)

C. The Macroscopic Osmotic Pressure Across a Moderately Charged Membrane

In this section, we derive a formula to represent the macroscopic osmotic pressure π_{lo} across a moderately charged membrane. Returning to (5.13), we integrate the equation over the length of the capillary, i.e., $0 \le x \le l$. There results

 $\Delta \mathbf{p} (\mathbf{r}) = \Delta \mathbf{p}_0 + 2RT \{\cosh \Psi - 1\} \Delta \mathbf{c}$ (5.38)

where Δp_0 and Δc are defined by (5.18) and (5.19), respectively.

The macroscopic osmotic pressure across a charged membrane can, then, be deduced from (5.38), yielding

$$\pi_{lo} = \Delta p_{o} + 2RT\Delta c \int_{0}^{a} 2r \{\cosh \Psi - 1\} dr/a^{2}$$
 (5.39)

In the absence of initial hydrostatic pressure difference, i.e., when $\Delta p_0 = 0$, (5.39) becomes

$$\pi_{lo} = 2RT\Delta c \int_{0}^{a} 2r (\cosh \Psi - 1) dr/a^2$$
(5.40)

From (5.27), (5.29), (5.31), (5.35), and (5.26), there
follows

$$\pi_{lo} = 2 \{ c(l) \text{ RT } (l-q) / \xi_a^2 \} [A^2 \xi_a^2 \{ I_o (\xi)^2 - I_1 (\xi_a)^2 \} / 2 + 2L_2 + L_3].$$
 (5.41)

This equation can be also used to determine the relative distribution of water at the interfaces with the two aqueous phases, by (5.7):

$$\overline{\mathbf{x}}_{ol}/\overline{\mathbf{x}}_{oo} = \exp\left(-\pi_{lo}\overline{\mathbf{v}}_{o}^{O}/\mathrm{RT}\right)$$
(5.42)

D. Osmotic Flow of Water in a Charged Membrane

As has been known for years, knowledge of the macroscopic osmotic pressure is useful in the understanding of the mechanism of transport process of solutes and water across a charged membrane. In the following treatment we make use of (5.41) to study the osmotic flow phenomena of water across a charged membrane. As an example, we consider a charged membrane for which the fixed surface charge density is 10^{-3} C/m² and the radius of the capillary is 17.6 Å. The temperature is 25°C. The concentration of one solution is fixed at 2.0 M whereas the concentration of the salt solution varied is in the range of 0.02 to 2.0 M, where $\xi_a > 5$. Hence, the conditions of Chapter IV are valid throughout.

Subject to the external conditions considered above, we now compute the macroscopic osmotic pressure π_{lo} across the charged membrane against the concentration varied. It is apparent that at very large ξ_a the effect of the concentration dependence of the dielectric constant on potential becomes negligibly small and, hence, in computing π_{lo} , in general, we may neglect the contributions due to L_2 and L_3 in the equation. To clarify this, we perform numerical computation on π_{lo} and π'_{lo} , where π_{lo} and π'_{lo} are defined as

$$\pi_{lo} \cong 2 \{ c (l) RT (l-q) / \xi_a^2 \} [A^2 \xi_a^2 \{ I_o (\xi_a)^2 - I_1 (\xi_a)^2 \} / 2 + 2L_2 \}$$
(5.43)

and

$$\pi_{lo}^{\prime} = c \ (l) \ RT \ (l - q) \ A^{2} \ \{I_{o} \ (\xi_{a})^{2} - I_{l} \ (\xi_{a})^{2}\} \ (5.44)$$

Note also that π'_{lo} is the contribution due only to the zero-order solution in Ψ and that in writing (5.43) the contribution due to L_3 is excluded since it is easily realizable to be immaterial. Some calculated results of π_{lo} and π'_{lo} are listed in Table 5.1. It can be shown from the results that the effect of $\pi_{lo} - \pi'_{lo}$ on π'_{lo} is, in general, about 1% at very large ξ_a . Hence, at very large ξ_a , equations (5.36) and (5.41) tend to be

$$\pi_{mo} = c (l) RT (l + q) A^{2} \{I_{0} (\xi_{a})^{2} - I_{1} (\xi_{a})^{2}\}/2 (5.45)$$

$$\pi_{lo} = 2c (l) RT (l - q) A^2 \{ I_0 (\xi_a)^2 - I_1 (\xi_a)^2 \} (5.46)$$

without introducing significant error. These equations are useful in studying and interpreting osmotic flow of

c (0) $\times 10^{-3}$, mole/m ³	ĸa	$\pi_{lo}^{*} \times 10^{-3},$ J/m ³	$\pi_{lo} \times 10^{-3}, J/m^{3}$
0.02	5.819	0.291	0.2928
0 05	5.862	0.280	0.2818
0.80	6.851	0.105	0.1059
0.95	7.032	0.085	0.0854
1.55	7.714	0.027	0.0274
1.97	8.158	0.002	0.0015

Table 5.1--Some calculated values of π_{lo} and π'_{lo} at various salt concentrations. c (l) = 2.0 10^{-3} mole/m³. a = 17.6 A. $|\sigma| = 10^{-3}$ C/m². t = 25°C.

water across various loose or porous charged membranes, when there is no initial hydrostatic pressure difference across the membrane. Making use of (5.46), π_{lo} is plotted against the logarithm of the salt concentration varied in Fig. 5.1.

On the basis of our calculation, it is found that π_{lo} required decreases monotonically with increasing concentration varied, and that π_{lo} is positive when c (0)/c (l) < 1. Hence, our results are in good agreement with the experimentally observed phenomena that the flow of water moves toward the more dilute solution. This is contrary to the flow of solutes which tends to move toward the more



concentrated solution in charged membranes. The latter phenomena is referred to as "anomalous osmosis," which we shall disucss in more detail in the next chapter.

E. Conclusion and Discussion

Considering the field dependence of the pressure, i.e., $\partial p/\partial \psi \neq 0$, for the first time we have obtained, for a v-component system, and an uni-univalent electrolyte system, the macroscopic pressure distribution equations which simultaneously take account of the concentration dependence of the pressure. As a result, the macroscopic formula for the osmotic pressure $\pi_{l,o}$ across a moderately charged membrane has been obtained for an uni-univalent electrolyte system and, accordingly, the relative distribution of water in two aqueous phases has been calculated. We have also derived, for an uni-univalent electrolyte system, the macroscopic formula for the osmotic pressure π_{mo} between the membrane phase m and the aqueous phase 0 and hence calculated the relative distribution of water between the phases. These equations are useful in the treatment of osmotic flow phenomena of water in a porous, moderately charged membrane at steady state, subject to various salt concentrations and geometrical conditions of the membrane in question. Consequently, the fluidmembrane system dealing with an uni-univalent electrolyte

solution can now be described more adequately, and experiments in the study of transport phenomena of water across a porous, moderately charged membrane can now be interpreted more accurately.

CHAPTER VI

THE STEADY-STATE PHENOMENOLOGICAL THEORY OF OSMOSIS IN CHARGED SYSTEMS

A. Introduction

Osmotic flow phenomena of fluids across a charged continuous phase separating two aqueous solutions of different concentrations have been known for years to be important and vital in the understanding of various mechanisms of transport process encountered in many areas of physical and life sciences. It has been realized experimentally (Grim, 1957) that the flow in a charged continuous phase, in contrast to the normal experience obtained with uncharged phases or with nonelectrolyte solutions, occurs toward the more concentrated solution (anomalous positive osmosis), and its rate is roughly proportional to the concentration difference. Moreover, when the concentration of one solution is fixed and that of the other is varied, plots of the flow rate against the logarithm of the varied concentration often give an N-shaped curve.

Since the early findings of Dutrochet (1835), various transport theories have been developed (cf.

Kobatake and Fujita, 1964; Gross and Osterle, 1967; Toyoshima, 1967; Fujita and Kobatake, 1968), in order to interpret the mechanism of osmotic flow in a charged membrane. Although most of the theories are satisfactory in many respects, they are all inadequate in one way or another--e.g., the theory of Kobatake and coworkers contains many contradictory assumptions, while the theory of Osterle and coworkers is restricted to extremely dilute solutions. Moreover, the conditions of numerous experiments so far reported have usually not been well-defined.

As has been known for years, membranes--artificial or natural--vary so widely in structure and function that it is impossible to say that anything approaching a general membrane transport theory has been established. In this chapter, we make use of the principles of nonequilibrium thermodynamics and the equations of hydrodynamics without recourse to most of the restrictive simplifications required by previous workers, and we derive a steady-state phenomenological theory that accounts for the osmotic flow of fluids across a charged continuous phase. It is hoped that the theory can be used better to describe and understand transport phenomena in charged membrane systems.

In the following treatment, we consider the system which is composed of a moderately charged membrane for which the fixed surface charge density is about 10^{-3} C/m²

and which separates two aqueous uni-univalent electrolyte solutions of different concentrations at the same temperature without the presence of initial hydrostatic pressure difference. A capillary model is used for the membrane. We make use of the macroscopic distribution equations of ions, pressure, and electrostatic potential in the transport equations derived in the previous chapters. The resulting steady-state differential equations are then solved to yield the average osmotic flow rate as a function of initial salt concentrations. Finally, the theory is compared with experimental observations.

B. Transport Equations

As mentioned in Chapter II, the transport equations dealing with electrochemical systems are conveniently written with respect to the solvent-fixed (SF) frame of reference. In the following treatment we consider the fluid-membrane system in which the conditions of Chapter IV are all satisfied. Moreover, we hereafter confine the discussion to the system which separates two aqueous solutions containing the solvent molecules and a single uni-univalent electrolyte of the same kind. Positive ions and negative ions are denoted by 1 and 2, respectively. It is of course quite important for biological and other purposes to consider also solutions of many

components. In that context, our purpose in this chapter, and in this thesis, is to lay the foundation upon which a general theory can be built. Transport equations for multi-component systems are similar in form to those for a binary system, but they are so long and complicated that they could obscure our simple, central purpose.

The diffusional fluxes of species 1 and 2 in the direction of the capillary axis relative to the SF reference frame are, according to (2.78),

$$(\mathbf{j}_{1})_{o} = - \left(\Omega_{11}^{o} \overline{\mathbf{v}}_{1}^{o} + \Omega_{12}^{o} \overline{\mathbf{v}}_{2}^{o}\right) (\partial \mathbf{p} / \partial \mathbf{x}) - \Omega_{11}^{o} \operatorname{RT} (\partial \ln c_{1} / \partial \mathbf{x})$$

$$- \Omega_{12}^{o} \operatorname{RT} (\partial \ln c_{2} / \partial \mathbf{x}) - (\Omega_{11}^{o} z_{1} F + \Omega_{12}^{o} z_{2} F) (\partial \Phi / \partial \mathbf{x})$$

$$(\mathbf{j}_{2})_{o} = - \left(\Omega_{21}^{o} \overline{\mathbf{v}}_{1}^{o} + \Omega_{22}^{o} \overline{\mathbf{v}}_{2}^{o}\right) (\partial \mathbf{p} / \partial \mathbf{x}) - \Omega_{21}^{o} \operatorname{RT} (\partial \ln c_{1} / \partial \mathbf{x})$$

$$- \Omega_{22}^{o} \operatorname{RT} (\partial \ln c_{2} / \partial \mathbf{x}) - (\Omega_{21}^{o} z_{1} F + \Omega_{22}^{o} z_{2} F) (\partial \Phi / \partial \mathbf{x}) , \quad (6.1)$$

where we also make the important assumption that the total electrostatic potential ψ is separable into a part Φ which depends only on x and a part $\overline{\psi}$ which depends only on r:

$$\psi (\mathbf{x},\mathbf{r}) = \Phi (\mathbf{x}) + \overline{\psi} (\mathbf{r}) . \qquad (6.2)$$

The second term, $\overline{\psi}$ (r), on the right-hand-side of (6.2) is what we have considered exclusively in Chapters II--V. A deeper analysis may reveal that the separation of (6.2) is not adequate [e.g., it may well be that ψ (xr) = ϕ (x) + $\overline{\psi}$ (x,r)] to satisfy all the governing equations. It should certainly be an excellent approximation physically, however, since it is clearly experimentally possible to vary independently the trans-membrane potential difference $\Delta \Phi = \Phi$ (ℓ) - Φ (0) and the charge.

Also in (6.1), we have taken $\ln f_{n}$ to be constant, and c_{α} is the concentration of species α in mole m⁻³, z_{α} $(\alpha = 1,2)$ is the charge valency of species α per mole, R is the gas constant, T is the uniform temperature, F is the Faraday constant, and the $\Omega^{O}_{\alpha\beta}$ (α,β = 1,2) are the phenomenological coefficients in the SF reference frame. We see that for the problem at hand the solute ions are subject to three kinds of forces, namely, osmotic forces corresponding to concentration gradients, mechanical forces corresponding to pressure gradients and electrical forces corresponding to potential gradients. The solvent molecules, however, are subject to only osmotic forces and mechanical forces according to (5.13) in Chapter V. These "forces" are of course not independent--there are only two independent "forces," the chemical potential gradients of 1 and 2.

The partial electric current and the diffusion flux of the salt along the capillary axis relative to the SF reference frame are, by (2.78) and (2.79),

$$(\mathbf{i}_{s})_{o} = \sum_{\alpha=1}^{2} \mathbf{z}_{\alpha} F (\mathbf{j}_{\alpha})_{o}$$
(6.3)

$$(j_s)_o = \sum_{\alpha=1}^{2} (j_\alpha)_o$$
(6.4)

By (2.65), the electric current and the diffusion flux of the salt along the capillary axis both relative to the capillary wall are, then,

$$J = \sum_{\alpha=1}^{2} (j_{\alpha})_{0} + \sum_{\alpha=1}^{2} c_{\alpha} u_{0} = \sum_{\alpha=1}^{2} c_{\alpha} u_{\alpha}$$
(6.5)
$$I = \sum_{\alpha=1}^{2} z_{\alpha} F(j_{\alpha})_{0} + \sum_{\alpha=1}^{2} c_{\alpha} z_{\alpha} Fu_{0} = \sum_{\alpha=1}^{2} z_{\alpha} Fc_{\alpha} u_{\alpha}$$
(6.6)

where u_o is the axial component of the reference velocity in SF frame of reference which, under the assumptions which give (2.81), satisfies the axial component of the Navier-Stokes equation in the form

$$(\partial p/\partial x) + \overline{Z} F (d\Phi/dx) = \eta r^{-1} [(d/dr) r (du_0/dr)] , (6.7)$$

where we have used (6.2) and where we assume that u_0 is independent of x. In (6.7), n is the isothermal shear viscosity of the fluid, taken as a constant, and \overline{Z} is defined by (2.12).

Poisson's equation which relates the electrostatic potential to the excess surface charge density is, by (4.1) and (6.2),

$$\mathbf{r}^{-1} \left[\left(\frac{d}{d\mathbf{r}} \right) \left(\mathbf{r} \mathbf{D} \left(\frac{d\overline{\psi}}{d\mathbf{r}} \right) \right] = -4\pi \overline{\mathbf{Z}} F, \qquad (6.8)$$

where D is the dielectric tensor of the electrolyte solution, taken as nonconstant. This equation was solved in Chapter IV, under the conditions listed there. For uniunivalent electrolytes, we have, by (4.99),

$$\overline{\psi} = (RT/F) AI_{O}(\xi) [1 + \Phi_{1}(\xi)],$$
 (6.9)

where $\xi = \kappa r$, $A = 4\pi\sigma F/\kappa D_0 RTI_1$ (κa), $\kappa = (8\pi F^2 \overline{c}/D_0 RT)^{1/2}$, and Φ_1 , defined by (4.98), results from inclusion of the concentration dependence of the dielectric constant. We have also, by (5.13),

$$(\partial p/\partial x) = (dp_dx) + 2RT(\cosh \Psi - 1)(dc/dx) , \qquad (6.10)$$

where $\Psi = F\overline{\psi}/RT$, where p_0 (assumed a function of x only) is the pressure when $\overline{\psi} = 0$, and where c is assumed a function of x only--thus, c is effectively, the average over any cross section of the capillary. Finally, for any uni-univalent electrolyte, by (4.31),

 $\overline{Z} = -2c \sinh \Psi , \qquad (6.11)$

C. General Formula for u_0

In the following treatment, we combine all the differential equations, solve the resulting equations subject to the appropriate boundary conditions and derive a steady-state phenomenological theory of osmosis in a charged continuous phase for an uni-univalent electrolyte system. It has been realized experimentally (Sollner, 1945) that anomalous osmosis of fluid occur only if the continuous phase is in a charged state and is porous to some degree. It is evident that anomalous osmosis does not occur for semipermeable phases. Thus, we take a and ka very large compared to unity.

We have demonstrated in Chapter V through numerical computation that at very large $\xi_a = \kappa a$, (6.9) can, in practice, be represented by the zeroth-order solution of the form

$$\overline{\Psi} = (RT/F) AI_{O}(\xi)$$
(6.12)

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since, for large κa , A is very small.

Making use of (6.10) and (6.11), we rewrite (6.7)

$$nr^{-1} [(d/dr) (rdu_0/dr)] = F (x,r)$$
 (6.13)

where

as

$$F(x,r) = dp_0/dx + 2RT (cosh \Psi - 1) (dc/dx)$$

- 2cFsinh \Psi (d Φ/dx). (6.14)

We solve (6.13) subject to (2.83), yielding the expression,

$$\eta u_0 = \int_{r}^{a} r^{-1} \int_{r}^{r} F(x,r) r dr dr \qquad (6.15)$$

Introduction of (6.14) into (6.15)

$$u_{o} = + \{ (a^{2} - r^{2})/4\eta \} (dp_{o}/dx) + (RT/\eta) \int_{r}^{a} r^{-1} \int_{0}^{r} \psi^{2} r dr dr (dc/dx) - (2cF/\eta) \int_{r}^{a} r^{-1} \int_{0}^{r} \psi r dr dr (d\Phi/dx)$$
(6.16)

where we have used

$$\cosh \Psi = 1 + \Psi^2/2$$
, $\sinh \Psi = \Psi$ (6.17)

Substitution of (6.12) into (6.1) yields

$$u_{o} = + \{ (\xi_{a}^{2} - \xi^{2})/4\kappa^{2}\eta \} (dp_{o}/dx) + (A^{2}RT/2\kappa^{2}\eta) \int_{\xi}^{\xi_{a}} \xi (I_{o}^{2} - I_{1}^{2}) d\xi (dc/dx) - (2AcF/\kappa^{2}\eta) \{ I_{o}(\xi_{a}) - I_{o}(\xi) \} (d\phi/dx)$$
(6.18)

where we have made use of the substitutions

$$\xi = \kappa r$$

$$\xi_a = \kappa a \qquad (6.19)$$

and where we have used the recurrence formulas

$$d (\xi I_{1})/d\xi = \xi I_{0}, d I_{0}/d\xi = I_{1},$$

$$\int_{0}^{\xi} \xi I_{0}^{2} d\xi = \xi^{2} (I_{0}^{2} - I_{1}^{2})/2 \qquad (6.20)$$

D. Special Formula for u and its Consequences

Although the general formula (6.18) could be used for any experimental situation which fulfills the requirements previously listed in Chapter IV and in this chapter, the occurrence of the integral term on the right-hand-side would require numerical integration. In order to obtain formulas to which we may easily attach physical significance, we now specialize to the case in which the second term on the right-hand-side of (6.18) is negligible compared to the third term. The requirement we find, (6.22), is so easily met that we may claim with confidence that our "special" formulas are in fact those which apply to the great majority of experimental situations.

Rather than deal directly with (6.18), we find a stronger condition by requiring, in (6.14),

 $|2RT (cosh\Psi-1) (dc/dx)| \leq 0.01 |2cFsinh\Psi(d\Phi/dx)|$ (6.21)

By (6.17) and the definition of Ψ ($\equiv F\overline{\psi}/RT$), (6.21) becomes

$$|(d \ln c/dx)/(d\Phi/dx)| < 0.02 |\overline{\psi}|^{-1}$$
 (6.22)

In Chapter IV, we required $|\Psi| \leq 0.245$. For 298°K, $F/RT = 38.93 V^{-1}$ and we therefore have

$$|\overline{\psi}| \leq 0.0063 \, \mathrm{V}$$
,
 $|\overline{\psi}|^{-1} \geq 158.9 \, \mathrm{V}^{-1}$ (6.23)

So for the largest allowed value of $|\overline{\psi}|$, we get

$$|(d \ln c/dx)/(d\Phi/dx)| \leq 3.2$$
 (6.24)

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Ordinarily, $|\overline{\psi}|$ is much smaller than 0.0063 V because it decreases strongly with the square root of average composition and with increasing pore size. Noting that it is ln c which appears in the denominator of (6.22) and (6.24), it is clear that (6.22) will ordinarily be easily satisfied. Typical values of the trans-membrane potential $\Delta \Phi$ are 60 to 100 mV (Woodbury, <u>et al.</u>, 1970) and therefore (6.24) would be satisfied for $|\Delta \ln c| \leq 0.3$. For smaller, more typical value of $|\overline{\psi}|$, $|\Delta \ln c|$ may be even larger but still negligible.

We therefore reduce (6.18) to

$$u_{o} = \{ (\xi_{a}^{2} - \xi^{2}) / 4\kappa^{2} \eta \} (dp_{o} / dx) - (2AcF / \kappa^{2} \eta) \{ I_{o} (\xi_{a}) - I_{o} (\xi) \} (d\phi / dx)$$
(6.25)

Equation (6.25) is generally valid for loose membranes with very large pores. Moreover, it is mathematically more tractable.

The average values of the reference velocity, electric current density, and the diffusional flux of the electrolyte component over the cross-section of the capillary are

$$U_{0} = \int_{0}^{a} 2\pi r (u_{0}) dr / \int_{0}^{a} 2\pi r dr$$
 (6.26)

$$\overline{I} = \int_{0}^{a} 2\pi r (I) dr / \int_{0}^{a} 2\pi r dr$$
 (6.27)

$$\overline{J} = \int_{0}^{a} 2\pi r (J) dr / \int_{0}^{a} 2\pi r dr$$
(6.28)

Introducing (6.25) into (6.26), there follows

$$U_{o} = A_{ol} (dp_{o}/dx) + A_{o2} (d\Phi/dx)$$
 (6.29)

where the coefficients A_{01} and A_{02} are

$$A_{01} = \xi_{a}^{2} / 8\kappa^{2} \eta$$
 (6.30)

$$A_{o2} = - (4AcF/\xi_{a}^{2}\kappa^{2}\eta) \{\xi_{a}^{2} I_{o}(\xi_{a})/2-\xi_{a}I_{1}(\xi_{a})\}$$

where we have used (6.20). It is interesting to note that in the coefficient A_{02} of $(d\phi/dx)$, usually referred to as the electroosmotic coefficient, is a function of the salt concentration. Previous existing theories for the anomalous osmosis (Schlögl, 1955; Kedom, 1961; Kobatake, 1958) have not taken this fact into account. As we shall see later, this effect is essential for the observed phenomenological behavior of the osmotic flow in charged membranes.

We substitute (6.1) into (6.5) and (6.6) and hence have, for the general case,

$$J = -\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha 2}^{\circ} \overline{v}_{2}^{\circ} \right) \left(\frac{\partial p}{\partial x} \right) - \sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} + \Omega_{\alpha 2}^{\circ} \right)$$

$$RT \left(\frac{d \ln c_{\alpha 0}}{dx} \right) - \sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} z_{1} + \Omega_{\alpha 2}^{\circ} z_{2} \right) F \left(\frac{d \phi}{dx} \right)$$

$$+ \sum_{\alpha=1}^{2} c_{\alpha 0} \exp \left(-z_{\alpha} \Psi \right) u_{0} \qquad (6.31)$$

$$I = - \sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha 2}^{\circ} \overline{v}_{2}^{\circ} \right) z_{\alpha} F \left(\frac{\partial p}{\partial x} \right)$$

$$- \sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} + \Omega_{\alpha2}^{\circ}) z_{\alpha}^{F} RT (dlnc_{\alpha0}/dx)$$

$$- \sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} z_{1} + \Omega_{\alpha2}^{\circ} z_{2}) z_{\alpha}^{F^{2}} (d\Phi/dx)$$

$$+ \sum_{\alpha=1}^{2} c_{\alpha0} \exp (-z_{\alpha}\Psi) z_{\alpha}^{Fu}$$
(6.32)

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where we have made use of the substitution,

$$dlnc_{\alpha}/dx = dlnc_{\alpha 0}/dx , \qquad (6.33)$$

since (6.33) is assumed independent of radical coordinate.
For an uni-univalent electrolyte system, there result

$$J = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha2}^{\circ} \overline{v}_{2}^{\circ}) \quad (\partial p / \partial x)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} + \Omega_{\alpha2}^{\circ}) \operatorname{RT} (d \ln c / d x) - \sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} - \Omega_{\alpha2}^{\circ}) F (d \Phi / d x)$$

$$+ 2c \operatorname{cosh\Psi} u_{o} \qquad (6.34)$$

$$I = -\sum_{\alpha=1}^{2} (\Omega_{\alpha 1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha 2}^{\circ} \overline{v}_{2}^{\circ}) (-1)^{\alpha+1} F (\partial p / \partial x)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha 1}^{\circ} + \Omega_{\alpha 2}^{\circ}) (-1)^{\alpha+1} F RT (d \ln c / d x)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha 1}^{\circ} - \Omega_{\alpha 2}^{\circ}) (-1)^{\alpha+1} F^{2} (d \phi / d x)$$

$$- 2c F \sinh \Psi u_{0} \qquad (6.35)$$

The practical equation for the axial pressure gradient $(\partial p/\partial x)$ can be deduced from (6.10), yielding

$$\partial p/\partial x \simeq dp_0/dx + RT \Psi^2 (dc/dx)$$
 (6.36)

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where we have used (6.17). Hence, (6.34) and (6.35) become

$$J = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha2}^{\circ} \overline{v}_{2}^{\circ}) (dp_{0}/dx)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha2}^{\circ} \overline{v}_{2}^{\circ}) RT \Psi^{2} (dc/dx)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} + \Omega_{\alpha2}^{\circ}) RT (dlnc/dx) - \sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} - \Omega_{\alpha2}^{\circ}) (d\Phi/dx)$$

$$+ 2c (1 + \Psi^{2}/2) u_{0} \qquad (6.37)$$

$$I = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha2}^{\circ} \overline{v}_{2}^{\circ}) (-1)^{\alpha+1} F (dp_{0}/dx)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} \overline{v}_{1}^{\circ} + \Omega_{\alpha2}^{\circ} \overline{v}_{2}^{\circ}) (-1)^{\alpha+1} F RT \Psi^{2} (dc/dx)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} + \Omega_{\alpha2}^{\circ}) (-1)^{\alpha+1} F RT (dlnc/dx)$$

$$-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{\circ} - \Omega_{\alpha2}^{\circ}) (-1)^{\alpha+1} F^{2} (d\Phi/dx)$$

$$+ 2cF\Psi u_{0}, \qquad (6.38)$$

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where we have used (6.17).

Introduction of (6.37) and (6.38) into (6.27) and (6.28) and use of (6.12) and (6.19) yield

$$\overline{\mathbf{I}} = -\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} \overline{\mathbf{v}}_{1}^{\circ} + \Omega_{\alpha 2}^{\circ} \overline{\mathbf{v}}_{2}^{\circ}\right) (-1)^{\alpha+1} F \left(dp_{0}/dx\right)$$

$$-\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} \overline{\mathbf{v}}_{1}^{\circ} + \Omega_{\alpha 2}^{\circ} \overline{\mathbf{v}}_{2}^{\circ}\right) (-1)^{\alpha+1} \left\{\left(2A^{2}FRT/\xi_{a}^{2}\right)\right\}$$

$$\int_{0}^{\xi_{a}} \xi I_{0}^{2} d\xi \left(dc/dx\right)$$

$$-\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} + \Omega_{\alpha 2}^{\circ}\right) (-1)^{\alpha+1} F RT \left(d\ln c/dx\right)$$

$$-\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\circ} - \Omega_{\alpha 2}^{\circ}\right) (-1)^{\alpha+1} F^{2} \left(d\phi/dx\right)$$

$$+ \left(4AcF/\xi_{a}^{2}\right) \int_{0}^{\xi_{a}} \xi I_{0} u_{0} d\xi \qquad (6.39)$$

$$\overline{\mathbf{J}} = -\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\mathbf{O}} \overline{\mathbf{v}}_{1}^{\mathbf{O}} + \Omega_{\alpha 2} \overline{\mathbf{v}}_{2}^{\mathbf{O}}\right) \left(d\mathbf{p}_{0}/d\mathbf{x}\right)$$

$$-\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\mathbf{O}} \overline{\mathbf{v}}_{1}^{\mathbf{O}} + \Omega_{\alpha 2} \overline{\mathbf{v}}_{2}^{\mathbf{O}}\right) \left(2\mathbf{A}^{2}\mathbf{RT}/\xi_{a}^{2}\right) \int_{0}^{\xi} \mathbf{z}_{0}^{2} d\xi \left(d\mathbf{c}/d\mathbf{x}\right)$$

$$-\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\mathbf{O}} + \Omega_{\alpha 2}^{\mathbf{O}}\right) \mathbf{RT} \left(d\mathbf{lnc}/d\mathbf{x}\right) - \sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{\mathbf{O}} - \Omega_{\alpha 2}^{\mathbf{O}}\right) F \left(d\Phi/d\mathbf{x}\right)$$

$$+ \left(4\mathbf{c}/\xi_{a}^{2}\right) \int_{0}^{\xi} \mathbf{z}_{a}^{2} \left(1 + \mathbf{A}^{2}\mathbf{I}_{0}^{2}/2\right) \mathbf{u}_{0} d\xi . \qquad (6.40)$$

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The integrals in (6.39) are readily evaluated, yielding

$$\int_{0}^{\xi_{a}} \xi I_{o}^{2} d\xi = \xi_{a}^{2} \{ I_{o}(\xi_{a})^{2} - I_{1}(\xi_{a})^{2} \} / 2$$
 (6.41)

and

$$\int_{0}^{\xi_{a}} \xi I_{o} u_{o} d\xi = + (1/2\kappa^{2}\eta) \xi_{a}^{2} I_{2} (\xi_{a}) (dp_{o}/dx)$$

$$- (2AcF/\kappa^{2}\eta) [\xi_{a}I_{o} (\xi_{a})I_{1} (\xi_{a})$$

$$- \xi_{a}^{2} \{I_{o} (\xi_{a})^{2} - I_{1} (\xi_{a})^{2}\}/2] (d\Phi/dx) (6.42)$$

where we have used (6.20) and the recurrence formula

$$\int_{0}^{\xi_{a}} \xi^{3} I_{o}(\xi) d\xi = \xi_{a}^{3} I_{1}(\xi_{a}) - 2\xi_{a}^{2} I_{2}(\xi_{a})$$
(6.43)

Nevertheless, it is apparent that at very large ξ_a , the integral in (6.40)

$$\int_{0}^{\xi} \xi \{1 + A^{2} I_{0}(\xi)^{2}/2\} u_{0} d\xi$$
 (6.44)

tends to be

$$\xi_a$$

 $\int \xi_u d\xi$ (6.45)
0

because $A \rightarrow 0$ as $\kappa a \rightarrow \infty$. This can be evaluated easily in closed form, yielding the following result,

+
$$(\xi_{a}^{4}/16\kappa^{2}\eta)$$
 (dp_{o}/dx) - $(2AcF/\kappa^{2}\eta)$ $\{\xi_{a}^{2} I_{o}(\xi_{a})/2$
- $\xi_{a} I_{1}(\xi_{a})$ $(d\Phi/dx)$ (6.46)

Introduction of (6.41), (6.42) and (6.46) into (6.39) and (6.40) finally yields, in the general case,

$$\overline{I} = B_{01} (dp_0/dx) + B_{02} (d\Phi/dx) + B_{03} (dc/dx) + B_{04} (dlnc/dx)$$
(6.47)

and

$$\overline{J} = R_{01} (dp_0/dx) + R_{02} (d\Phi/dx) + R_{03} (dc/dx) + R_{04} (dlnc/dx) , \qquad (6.48)$$

where the coefficients B_{oi} and R_{oi} (i = 1,...4) are

$$B_{01} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha 1}^{0} \overline{v}_{1}^{0} + \Omega_{\alpha 2}^{0} \overline{v}_{2}^{0}) (-1)^{\alpha+1} F + (2AcF/\kappa^{2}\eta) I_{2}(\xi_{a})$$

$$B_{02} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha 1}^{0} - \Omega_{\alpha 2}^{0}) (-1)^{\alpha+1} F^{2}$$

$$- (8A^{2}c^{2}F^{2}/\xi_{a}^{2}\kappa^{2}\eta) [\xi_{a} I_{0} (\xi_{a}) I_{1} (\xi_{a})$$

$$- \xi_{a}^{2} [I_{0} (\xi_{a})^{2} - I_{1} (\xi_{a})^{2}]/2]$$

$$B_{o3} = -\sum_{\alpha=1}^{2} \left(\Omega_{\alpha 1}^{o} \overline{v}_{1}^{o} + \Omega_{\alpha 2}^{o} \overline{v}_{2}^{o} \right) (-1)^{\alpha+1} \left(A^{2} FRT \right) \left\{ I_{o} \left(\xi_{a} \right)^{2} - I_{1} \left(\xi_{a} \right)^{2} \right\}$$

$$B_{04} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0} + \Omega_{\alpha2}^{0}) (-1)^{\alpha+1} FRT$$
$$R_{01} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0} \overline{v}_{1}^{0} + \Omega_{\alpha2}^{0} \overline{v}_{2}^{0}) + \xi_{a}^{2} c/4\kappa^{2}\eta$$

$$R_{02} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0} - \Omega_{\alpha2}^{0}) - (8Ac^{2}F/\kappa^{2}\eta\xi_{a}^{2})\{\xi_{a}^{2}I_{0}(\xi_{a})/2 - \xi_{a}I_{1}(\xi_{a})\}$$

$$R_{03} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0}\overline{v}_{1}^{0} + \Omega_{\alpha2}^{0}\overline{v}_{2}^{0}) (A^{2}RT) \{I_{0}(\xi_{a})^{2} - I_{1}(\xi_{a})^{2}\}$$

$$R_{04} = -\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0} + \Omega_{\alpha2}^{0}) RT \qquad (6.49)$$

Although the (dc/dx) term and the (d ln c/dx) term could obviously be combined in (6.47) and (6.48), and elsewhere, no useful simplification is thereby obtained. Formally, the coefficient of (d ln c/dx) in (6.47) would be ($\overline{c} B_{03} + B_{04}$) and the coefficient of (d ln c/dx) in (6.48) would be ($\overline{c} R_{03} + R_{04}$), where \overline{c} is some average value of c.

E. The Working Equation for Anomalous Osmosis

We have so far obtained explicitly, making use of some explicit, justifiable simplifying assumptions, the equations for the averages of reference velocity, electric current density and diffusional flux of the electrolyte component over the cross section of the capillary. From these equations we now derive a working equation which can be used to interpret the characteristic behavior of osmotic flow through a charged membrane. As mentioned before, we consider that initially there is no hydrostatic pressure difference between the two sides of the membrane, and assume that the system has attained a steady state. The steady-state assumption is justifiable since it is realizable in most biological systems and physicalchemical systems.

Returning to (6.29), (6.47) and (6.48), at steady state, from the conservations of mass and electric current density and from the incompressibility of the fluid there follow

$$d U_0/dx = 0, d\overline{I}/dx = 0, d\overline{J}/dx = 0.$$
 (6.50)

Furthermore, in the present system there is no applied electric field across the membrane and, hence, from (6.60) we have

$$U_{c} = \text{constant}, \overline{I} = 0, \overline{J} = \text{constant}.$$
 (6.51)

According to the assumptions made above the appropriate boundary conditions for the problem are, then,

$$c = c$$
 (0) at $x = 0$ and $c = c$ (1) at $x = 1$

 $p_{0}(x = l) = p_{0}(x = 0)$

$$\Phi = \Phi (0) \text{ at } \mathbf{x} = 0 \text{ and } \Phi = \Phi (l) \text{ at } \mathbf{x} = l$$
 (6.52)

Making use of the conditions given by (6.51) we now integrate (6.29), (6.47), and (6.48) over the length of the capillary, i.e., $0 \le x \le l$, subject to (6.52). However, by examination of (6.30) and (6.49) we immediately notice that the coefficients A_{02} , B_{01} , B_{02} , R_{01} and R_{02} are concentration-dependent. Hence, we may write

$$U_{o} = A_{o1} (\Delta p_{o}/\ell) + \int_{0}^{\ell} A_{o2} (d\Phi/dx) dx/\ell = \text{constant} (6.53)$$

$$\overline{I} = \int_{0}^{\ell} B_{o1} (dp_{o}/dx) dx/\ell + \int_{0}^{\ell} B_{o2} (d\Phi/dx) dx/\ell$$

$$+ B_{o3} (\Delta c/\ell) + B_{o4} (\Delta \ell n c/\ell) = 0 \qquad (6.54)$$

$$\overline{J} = \int_{0}^{\ell} R_{o1} (dp_{o}/dx) dx/\ell + \int_{0}^{\ell} R_{o2} (d\Phi/dx) dx/\ell$$

$$+ R_{o3} (\Delta c/\ell) + R_{o4} (\Delta \ell n c/\ell) = \text{constant} (6.55)$$

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where Δp_{o} , Δc , and Δlnc are defined as

$$\Delta p_{0} = p_{0} (x = l) - p_{0} (x = 0)$$

$$\Delta c = c (l) - c (0)$$

$$\Delta lnc = lnc (l) - lnc (0) = ln \{c (l)/c (0)\} (6.56)$$

Furthermore, we have required in Chapter V that

$$p_{O} = (\Delta p_{O}/\ell) \mathbf{x} + p_{O} (\mathbf{x} = 0)$$

$$\mathbf{c} = (\Delta c/\ell) \mathbf{x} + \mathbf{c} (0)$$

$$\Phi = (\Delta \Phi/\ell) \mathbf{x} + \Phi (0) , \qquad (6.57)$$

whence

$$dp_{0}/dx = \Delta p_{0}/\ell$$
$$dc/dx = \Delta c/\ell$$
$$d\phi/dx = \Delta \phi/\ell \qquad (6.58)$$

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With the aid of the above equations, the evaluation of the integrals in equations (6.53)-(6.55) then can easily be performed. The resulting expressions are

$$\int_{0}^{\ell} A_{o2} (d\Phi/dx) dx/\ell = - (2AF/\xi_{a}^{2}\kappa^{2}n) c (\ell) (1+q) \{\xi_{a}^{2}I_{o}(\xi_{a})/2$$

$$- \xi_{a} I_{1} (\xi_{a}) \} (\Delta\Phi/\ell) \qquad (6.59)$$

$$\int_{0}^{\ell} B_{o1} (dP_{o}/dx) dx/\ell = (\Delta P_{o}/\ell) [-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{o}\overline{v}_{1}^{o} + \Omega_{\alpha2}^{o}\overline{v}_{2}^{o}) (-1)^{\alpha+1}F$$

$$- (AF/\kappa^{2}n) I_{2} (\xi_{a})c(\ell) (1+q)] \qquad (6.60)$$

$$\int_{0}^{\ell} B_{o2} (d\Phi/dx) dx/\ell = (\Delta\Phi/\ell) [-\sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{o} - \Omega_{\alpha2}^{o}) (-1)^{\alpha+1}F^{2}$$

$$- (8A^{2}F^{2}/\xi_{a}^{2}\kappa^{2}n) \{\{c (\ell)\}^{2} (1 + q + q^{2})/3\}$$

$$[\xi_{a} I_{o} (\xi_{a}) I_{1} (\xi_{a}) - \xi_{a}^{2} \{I_{o} (\xi_{a})^{2} - I_{1} (\xi_{a})^{2}\}/2]\}] (6.61)$$

$$\int_{0}^{\ell} R_{01} (dp_{0}/dx) dx/\ell = (\Delta p_{0}/\ell) \left[- \sum_{\alpha=1}^{2} (\Omega_{\alpha}^{0} \overline{v}_{1}^{0} + \Omega_{\alpha2}^{0} \overline{v}_{2}^{0}) - (\xi_{a}^{2}/8\kappa^{2}\eta) c(\ell) (1+q) \right]$$
(6.62)
$$\int_{0}^{\ell} R_{02} (d\Phi/dx) dx/\ell = (\Delta\Phi/\ell) \left[- \sum_{\alpha=1}^{2} (\Omega_{\alpha1}^{0} - \Omega_{\alpha2}^{0}) F - (8AF/\kappa^{2}\xi_{a}^{2}\eta) \left\{ \left\{ c(\ell)^{2} (1+q+q^{2})/3 \right\} \right\}$$

$$\{\xi_{a}^{2} I_{o}(\xi_{a})/2 - \xi_{a} I_{1}(\xi_{a})\}\}$$
(6.63)

We introduce equations (6.59)-(6.63) into equations (6.53)-(6.55). From (6.52), there follow

$$U_{0} = \overline{A}_{02} (\Delta \Phi/\ell) = \text{constant}$$
(6.64)
$$\overline{I} = \overline{B}_{02} (\Delta \Phi/\ell) + B_{03} (\Delta c/\ell) + B_{04} (\Delta \ln c/\ell) = 0 (6.65)$$

$$\overline{J} = \overline{R}_{02} (\Delta \Phi/\ell) + R_{03} (\Delta c/\ell) + R_{04} (\Delta \ln c/\ell) = \text{constant} (6.66)$$

where \overline{A}_{02} , \overline{B}_{02} , and \overline{R}_{02} are given by

$$\begin{split} \overline{\mathbf{A}}_{o2} &= -(2\mathbf{A}F/\xi_{a}^{2}\kappa^{2}\eta) \{c(\ell)(1+q)\} [\xi_{a}^{2} \mathbf{I}_{o}(\xi_{a})/2-\xi_{a}\mathbf{I}_{1}(\xi_{a})] (6.67) \\ \overline{\mathbf{B}}_{o2} &= -\frac{2}{\alpha=1} (\Omega_{\alpha1}^{O} - \Omega_{\alpha2}^{O}) (-1)^{\alpha+1} F^{2} \\ &- (8\mathbf{A}^{2}F^{2}/\xi_{a}^{2}\kappa^{2}\eta) \{\{c(\ell)^{2} (1+q+q^{2})/3\} \\ &[\xi_{a} \mathbf{I}_{o} (\xi_{a}) \mathbf{I}_{1} (\xi_{a})-\xi_{a}^{2}\{\mathbf{I}_{o}(\xi_{a})^{2}-\mathbf{I}_{1}(\xi_{a})^{2}\}/2]\} (6.68) \\ \overline{\mathbf{R}}_{o2} &= -\frac{2}{\alpha=1} (\Omega_{\alpha1}^{O} - \Omega_{\alpha2}^{O}) F - (8\mathbf{A}F/\xi_{a}^{2}\kappa^{2}\eta) \{\{c(\ell)^{2} (1+q+q^{2})/3\} \\ &[\xi_{a}^{2} \mathbf{I}_{o} (\xi_{a})/2 - \xi_{a} \mathbf{I}_{1} (\xi_{a})]\} \end{split}$$

Our chief goal, however, is to obtain explicitly the expressions for U_0 and \overline{J} as functions of salt concentrations. Hence, we combine (6.64) through (6.66) appropriately and rearrange the resulting equations. There follow, then,

$$U_{o}^{\ell} = - (\overline{A}_{o2}^{B}_{o3}/\overline{B}_{o2}) \quad \Delta c - (\overline{A}_{o2}^{B}_{o4}/\overline{B}_{o2}) \quad \Delta lnc \quad (6.70)$$

and

$$\overline{J} \ \ell = \{R_{03} - (\overline{R}_{02}B_{03}/\overline{B}_{02})\} \ \Delta c$$
$$+ \{R_{04} - (\overline{R}_{02}B_{04}/\overline{B}_{02})\} \ \Delta \ell nc \qquad (6.71)$$

which give $\bigcup_{O} \ l$ and $\overline{J} \ l$ as functions of salt concentrations. As we shall see later, these equations can be used to study and interpret osmotic flow phenomena of fluids in loose, moderately charged membranes.

F. The Onsager Transport Coefficients

Before we can proceed further to investigate our results numerically, it is essential to acquire considerably more knowledge of the physical and chemical properties of the linear phenomenological coefficients, or Onsager Coefficients, $\Omega^{o}_{\alpha\beta}$. For simplicity, we follow the treatment of Miller (1966) since it is probably the best reference which deals with the determination of ionic transport coefficients $\Omega^{\circ}_{\alpha\beta}$, for isothermal vector transport process in binary electrolyte systems based on the SF reference frame.

Consider an isothermal system consisting of a neutral solvent, e.g., water, and a binary electrolyte which ionizes completely into the solution giving two ions. The independent flows for the system are those of the two ions since $(\vec{j}_0)_0 \equiv 0$ for the SF reference frame. Hence, the transport equations are

$$(\dot{j}_{1})_{0} = \Omega_{11}^{0} \, \dot{\vec{x}}_{1} + \Omega_{12}^{0} \, \dot{\vec{x}}_{2}$$
 (6.72)

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$$(\dot{j}_{2})_{0} = \Omega_{21}^{0} \dot{\vec{x}}_{1} + \Omega_{22}^{0} \dot{\vec{x}}_{2}$$
 (6.73)

where the \dot{x}_{α} ($\alpha = 1,2$) are the conjugate forces, as given explicitly in Chapter II. These equations completely describe the isothermal vector transport properties in a binary electrolyte solution provided the $\Omega_{\alpha\beta}^{0}$ are known as functions of the temperature T, the pressure p, and composition.

The $\Omega_{\alpha\beta}^{O}$ are the fundamental transport coefficients because they arise from a fundamental thermodynamic theory as outlined in Chapter II. Any isothermal transport process in a binary system is completely characterized by equations (6.72) and (6.73) together with a knowledge of the $\Omega_{\alpha\beta}^{O}$ as functions of c, T, p. Moreover, the same $\Omega_{\alpha\beta}^{O}$, apply when the phenomena is two or three dimensional, e.g., where an electric field is perpendicular to the diffusion direction. Consequently, even though the concentration dependence of the $\Omega_{\alpha\beta}^{O}$, is determined experimentally from the one-dimensional special cases, the resulting numbers can be applied to any process no matter how complex. The experimental Onsager transport coefficients for some uni-univalent electrolytes are listed in Table 6.1.

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G. Results and Discussion

In the following treatment we make use of equation (6.70) to study anomalous osmosis. We consider a porous, moderately charged membrane for which the fixed surface charge density $|\sigma|$ is 10^{-3} C/m² and capillary radius 150 Å, whence $\kappa a >> 1$ in the range of the salt concentrations used for this study. In particular, we assume a negatively charged membrane with $\sigma = -10^{-3}$ C/m², and choose the following experimental conditions: the salt used is NaCl, the temperature is 25°c, the isothermal shear viscosity of water, n at 25°C is 8.903 $\times 10^{-10}$ J sec cm⁻³, the electric permittivity of water, i.e., $D_0/4\pi$, at 25°C is 6.94 $\times 10^{-10}$ C V⁻¹ m⁻¹, and the partial molar volumes of Na⁺ and Cl⁻ ions at infinite dilution are -1.4 and 18 cm³ mole⁻¹, respectively (see also Table 4.1,
ē,	$10^{12} \times \Omega_{11}^{\circ} / \overline{c},$	$10^{12} \times \Omega_{12}^{0} / \overline{c},$	$10^{12} \times \Omega_{22}^{\circ}/\overline{c}$,
mole/l	mole cm ² /J sec	mole cm ² /J sec	mole cm ² /J sec
0.0000	5.381	0.000	8.201
0.0010	5.363	0.026	8.177
0.0005	5.341	0.058	8.146
0.0010	5.325	0.081	8.123
0.0050	5.263	0.170	8.036
0.0100	5.219	0.233	7.974
0.0500	5.065	0.440	7.742
0.1000	4.971	0.554	7.601
0.2000	4.851	0.682	7.435
0.5000	4.613	0.840	7.121
0.7000	4.484	0.882	6.950
1.0000	4.311	0.911	6.772
1.5000	4.053	0.923	6.370
2.0000	3.812	0.911	6.035
2.5000	3.581	0.884	5.708
3.0000	3.366	0.858	5.393

Table 6.1a--The Onsager transport coefficients for H_2^{0-NaCl} at 25°C.

\overline{c} , mole/k	$10^{12} \times \Omega_{11}^{\circ} / \overline{c}$,	$10^{12} \times \Omega_{12}^{\circ} / \overline{c},$	$10^{12} \times \Omega_{22}^{\circ}/\overline{c},$
	mole cm ⁻ /J sec	mole cm ² /J sec	mole cm ⁻ /J sec
0.0000	7.892	0.000	8.198
0.0001	7.872	0.026	8.176
0.0005	7.844	0.059	8.148
0.0010	7.826	0.086	8.129
0.0050	7.746	0.187	8.045
0.0100	7.694	0.256	7.991
0.0500	7.520	0.503	7.810
0.1000	7.430	0.647	7.715
0.2000	7.331	0.809	7.613
0.5000	7.193	1.038	7.478
0.7000	7.140	1.124	7.425
1.0000	7.077	1.214	7.365
1.5000	6.972	1.304	7.265
2.0000	6.866	1.362	7.160
2.5000	6.754	1.404	7.050
3.0000	6.634	1.440	6.929

Table 6.1b--The Onsager transport coefficients for H₂0-KCl at 25°C.

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. ,	$10^{12} \times \Omega_{11}^{\circ} / \overline{c},$	$10^{12} \times \Omega_{12}^{0} / \overline{c},$	$10^{12} \times \Omega_{22}^{\circ} / \overline{c}$,
mole/l	mole cm ² /J sec	mole cm ² /J sec 1	mole cm ² /J sec
0.0000	4.153	0.000	8.197
0.0001	4.137	0.021	8.166
0.0005	4.115	0.051	8.136
0.0010	4.103	0.073	8.112
0.0050	4.046	0.162	8.020
0.0100	4.011	0.223	7.956
0.0500	3.870	0.417	7.718
0.1000	3.774	0.513	7.547
0.2000	3.624	0.614	7.290
0.5000	3.316	0.700	6.827
0.7000	3.159	0.714	6.593
1.0000	2.942	0.699	6.286
1.5000	2.662	0.677	5.877
2.0000	2.406	0.622	5.475
2.5000	2.156	0.548	5.073
3.0000	1.954	0.500	4.718

Table 6.1c--The Onsager transport coefficients for H_2^{0-LiCl} at 25°C.

Chapter IV). The experimental Onsager transport coefficients for the NaCl-H₂0 system at 25°C are taken from Table 6.1. The ratio of the concentrations of two solutions is fixed. Plots of U_o (ℓ) calculated from (6.80) at q = 0.5 and 0.25 against the logarithm of the salt concentration varied are shown in Fig. 6.1. It can be seen from Fig. 6.1 that bell-shaped curves are obtained for both cases, and the maximum flow rate at q = 0.5 occurs approximately at the salt concentration of 0.06667 mole ℓ^{-1} while that at q = 0.25 occurs approximately at the salt concentration of 0.08 mole ℓ^{-1} .

Moreover, to see that our equation is also useful for positively charged membranes, we plot $U_0 \ \ell$ calculated from (6.70) at q = 0.5, taking $\sigma = + 10^{-3} \ C/m^2$ against the logarithm of the salt concentration varied. The result is shown in Fig. 6.2. It is found that the values of $U_0 \ \ell$ are all negative. This indicates that the direction of the osmotic flow of fluid is changed and the flow moves toward the more dilute solution (anomalous negative osmosis) as can be seen from Fig. 6.2.

As a result, it is apparent that the direction of the osmostic flow of fluid in charged membranes changes as the sign of σ changes. This fact has not been explained by previous theories (<u>cf</u>. Kobatake, 1964). The failure of previous theories to account for this fact





apparently arises from the use of restrictive simplifications in their treatment of the theories, which we have discussed before. These restrictions have been excluded in our theoretical development. Hence, we are confident that our equation is much more complete and better in describing various membrane systems. Consequently, the experiments in study of osmotic flow phenomena in charged membranes can now be interpreted more accurately, in principle. Unfortunately, so little experimental information is available regarding the actual values of membrane charge and pore size that we cannot make a full comparison with experiment. Perhaps our equation can be used to determine charge and pore size in conjunction with fully-characterized experiment. The shapes of our curves are qualitatively the same as those found experimentally (Kobatake and Fujita, 1964; Tasaka, Kondo and Nagasawa, 1969) and we certainly predict the proper direction of flow.

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In the theoretical development of this chapter, we have made use of the assumptions that $\kappa a >> 1$, and that the gradient of $\ln c$ is small enough compared to the trans-membrane potential that (6.22) is satisfied, and have adopted only the zeroth order solution for the potential. Although we have clearly made only a start at obtaining a complete theory of transport through

membranes, it is at last, a well-formulated, selfconsistent start. Hopefully, we have laid the foundation sufficiently firmly that future investigators, including ourselves, will not need to reexamine the foundation, but may instead build upon it.



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APPENDICES

APPENDIX A

A DERIVATION OF THE CHAPMAN-GOUY EQUATION FOR A CHARGED CYLINDER

Consider a charged cylinder containing an aqueous, binary, uni-univalent electrolyte solution. The Chapman-Gouy equation can be derived from the usual Poisson-Boltzmann equation in the form

$$(D_{o}/r) (dr (d\psi/dr)/dr) = -4\pi F (c_{+}^{B} - c_{-}^{B})$$
 (A.1)

where r is the radial coordinate, D_0 is the isothermal dielectric constant of water, ψ is the electrostatic potential, F is the Faraday constant, and where c_{α}^{B} ($\alpha = +, -$) is the Boltzmann equation molar concentration of species α ,

$$c_{\alpha}^{B} = \overline{c} \exp(-z_{\alpha}F\psi/RT)$$
, (A.2)

where \overline{c} is the average salt concentration, z_{α} is the valency of α , R is gas constant, and T is the absolute temperature. The boundary conditions are

$$d\psi/dr = 0$$
 at $r = 0$, and $d\psi/dr = 4\pi\sigma/D_0$ at $r = a$, (A.3)

where σ is the surface charge density fixed on the cylinder wall, and a is the radius of the cylinder.

We introduce (A.2) into (A.1) and make use of the following substitutions:

$$F\psi/RT = \Psi$$
 (A.4)

$$\mathbf{r} = \xi/\kappa \tag{A.5}$$

where κ^{-1} is the Debye length

$$\kappa = \sqrt{8\pi F^2 \overline{c} / D_0 RT}$$
(A.6)

There results, then,

$$(1/\xi) (d\xi(d\Psi/d\xi)/d\xi) = \sinh \Psi$$
, (A.7)

where we have made use of the transformation

$$\frac{e^{\Psi} - e^{-\Psi}}{2} = \sinh \Psi . \tag{A.8}$$

We rewrite (A.7) as

$$d^2 \Psi/d\xi^2 + (1/\xi) (d\Psi/d\xi) = \sinh \Psi$$
 (A.9)

Equation (A.9) reduces to

$$d^2 \Psi/d\xi^2 = \sinh \Psi , \qquad (A.10)$$

for $(1/\xi)$ $(d\Psi/d\xi) << d^2 \Psi/d\xi^2$, in particular, for $\kappa a >> 1$ and $(d\Psi/d\xi)_0 = 0$. It is also assumed in this derivation that Ψ vanishes at $\xi = 0$. The boundary conditions on Ψ then become,

$$d\Psi/d\xi = 0 \text{ and } \Psi = 0 \text{ at } \xi = 0 \tag{A.11}$$

$$d\Psi/d\xi = 4\pi\sigma F/D_{O}RT\kappa \text{ at } \xi = \xi_{a}, \qquad (A.12)$$

where ξ_a is the value of ξ at the wall, i.e., $\xi_a = \kappa a$, and where we have used (A.3) and (A.4).

We now solve (A.10) subject to (A.11) and (A.12). Making use of the transformation

$$d\Psi/d\xi = p , \qquad (A.13)$$

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whence

$$d^2 \Psi/d\xi^2 = p (dp/d\Psi)$$
, (A.14)

there follows, from (A.10),

$$p (dp/d\Psi) = \sinh \Psi . \tag{A.15}$$

The solution to (A.15) is immediately obtained, yielding

$$p^2/2 = \cosh \Psi + b$$
, (A.16)

where b is the constant of integration which is readily evaluated, subject to (A.11), to give

$$b = -1$$
 (A.17)

Hence, (A.16) becomes

$$p^2/2 = \cosh \Psi - 1$$
 (A.18)

The Chapman-Gouy equation relates the surface potential to the surface charge density fixed on the wall. Hence, we have, from (A.12), (A.13), and (A.18),

$$\frac{1}{2} (4\pi\sigma F/D_{O}RT\kappa)^{2} = \cosh\Psi_{a} - 1 , \qquad (A.19)$$

where Ψ_{a} is the value of Ψ at the wall. By rearrangement, (A.19) becomes

$$\sigma^2 = 4 (2 \epsilon RT \overline{c}) (\cosh \Psi_a - 1)/2$$
 (A.20)

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where ε is the electric permittivity

$$\varepsilon = D_0 / 4\pi . \tag{A.21}$$

From (A.20), there follows, then,

$$\sigma = 2 (2 \epsilon RTc)^{1/2} \sinh (\Psi_a/2)$$
, (A.22)

where we have used

$$\sinh (\Psi_a/2) = \sqrt{(\cosh \Psi_a - 1)/2}$$
 (A.23)

Equation (A.22) is the Chapman-Gouy equation.

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$$r = \frac{5}{4} \cdot \left(1 + \frac{3}{4} + \frac{3}$$

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APPENDIX B

DERIVATION OF EQUATIONS (4.87) AND (4.88)

In the following we derive equations (4.87) and (4.88). From the recurrence formula,

$$d \xi I_1 / d\xi = \xi I_0 , \qquad (B.1)$$

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we have, in (4.87),

$$\int_{0}^{\xi} \xi I_{0}^{3} d\xi = \int_{0}^{\xi} I_{0}^{2} (\xi I_{0}) d\xi = \int_{0}^{\xi} I_{0}^{2} d\xi I_{1} .$$
 (B.2)

By integration by parts, there results

$$\int_{0}^{\xi} \xi I_{0}^{3} d\xi = \xi I_{1} I_{0}^{2} - 2 \int_{0}^{\xi} \xi I_{1} I_{0}^{d} I_{0}$$
(B.3)

Note, however, that

$$dI_{0}/d\xi = I_{1}, \qquad (B.4)$$

whence

$$\int_{0}^{\xi} \xi I_{1} I_{0} dI_{0} = \int_{0}^{\xi} \xi I_{1} I_{0} (dI_{0}/d\xi) d\xi = \int_{0}^{\xi} \xi I_{1}^{2} I_{0} d\xi \quad (B.5)$$

Substitution of (B.5) into (B.3) yields, by rearrangement, equation (4.87),

$$\int_{0}^{\xi} \xi \mathbf{I}_{0} \mathbf{I}_{1}^{2} d\xi = \xi \mathbf{I}_{0}^{2} \mathbf{I}_{1}^{2} - \int_{0}^{\xi} \xi \mathbf{I}_{0}^{3} d\xi^{2}$$
(B.6)

To obtain equation (4.88), we write

$$\int_{0}^{\xi} \xi \mathbf{I}_{0}^{2} d\xi = \int_{0}^{\xi} \mathbf{I}_{0}^{2} d(\xi^{2}/2)$$
(B.7)

By integration by parts, there results

$$\int_{0}^{\xi} \xi I_{0}^{2} d\xi = \xi^{2} I_{0}^{2} / 2 - \int_{0}^{\xi} \xi^{2} I_{0} dI_{0}$$
(B.8)

From (B.4), we have

$$\int_{0}^{\xi} \xi^{2} \mathbf{I}_{0} d\mathbf{I}_{0} = \int_{0}^{\xi} \xi^{2} \mathbf{I}_{0} (d\mathbf{I}_{0}/d\xi) d\xi = \int_{0}^{\xi} (\xi\mathbf{I}_{0}) (\xi\mathbf{I}_{1}) d\xi$$
$$= \int_{0}^{\xi} (\xi\mathbf{I}_{1}) d (\xi\mathbf{I}_{1}) = \xi^{2} \mathbf{I}_{1}^{2}/2 , \qquad (B.9)$$

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where we have used (B.1). Substitution of (B.9) into (B.8) yields equation (4.88),

$$\int_{0}^{\xi} \xi I_{0}^{2} d\xi = \xi^{2} (I_{0}^{2} - I_{1}^{2})/2$$
(B.10)

