THE ELECTRICAL CONDUCTANCE OF SEMIPERMEABLE MEMBRANES

I. A FORMAL ANALYSIS

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ABSTRACT A kinetic analysis of membrane conductance under conditions of stationary flow is presented. The semipermeable membrane is idealized as a homogeneous laminar phase separating ionic solutions on either side. It is assumed, without consideration of the mechanisms involved, that some ion species permeate the membrane while others do not. The flux of a given species is taken to be linearly related to the gradient of its concentration and to the electric field. The resulting flow equations, when combined with Poisson's equation, permit the formulation of the conductance problem in terms of a set of non-linear differential equations. They describe the spatial variation of the electric displacement and contain the ion current densities as parameters. Their integration, subject to appropriate boundary conditions, fixes the values of these parameters and of the corresponding transmembrane potential. The solution of the conductance problem cannot, however, be carried through in analytic form. The numerical analysis of a number of special cases will be presented in subsequent publications.

INTRODUCTION

Non-equilibrium electrical phenomena associated with semipermeable membranes are usually discussed in terms of their conductance under conditions of either stationary or non-stationary current flow. The problem of stationary flow, with which we deal, is usually approached theoretically in either of two ways. The first approach, initiated by Staverman, (1952), and extended by Kedem and Katchalsky, (1958, 1963), applies the formalism of irreversible thermodynamics in which stationary flow is characterized by a set of generalized linear force flux relations. The method appears to be particularly useful for the phenomenological description of osmotic membrane systems in which the mutual interaction of the membrane, solvent, and solute must be considered.

We follow the second approach, exemplified by the work of Goldman, (1943). It utilizes a kinetic description in which the flow of a given ion species is taken to be proportional to the gradient of the electric potential and to the concentration gradient of that species alone. Or, more concisely, the flow of the species is proportional to the gradient of its electrochemical potential only. Furthermore, the ionic activity coefficients appearing in a thermodynamic statement of the electrochemical potentials are equated to unity. The dependence of these coefficients upon ion concentration, temperature, and dielectric constant of the solvent, which characterizes real electrolyte solutions, is thus ignored. The absolute activity of each ion species is, therefore, equated to its concentration under all conditions and in every phase of the membrane-solution system in which that species is postulated to be present. In following the kinetic approach we will also take the dissociation of electrolytes to be complete, as is appropriate for strong electrolytes. Details of structure play a more direct role in the kinetic development; in particular, simplifying assumptions regarding charge and field distributions in the vicinity of the membrane are required if an analytic expression for the conductance is to be achieved. We sacrifice this possibility in order to minimize such assumptions. Comparison of theoretical predictions with experiment should thus permit a more critical evaluation of the inherent limitations of the kinetic method as outlined above. Such assumptions as are required to render the problem tractable will be noted in the text as the need for them arises.

The results of numerical calculations, carried out for a number of special cases, will be presented in tabular and graphical form in subsequent publications.

THE FORMAL ANALYSIS

1. *The Membrane Model.*

The idealized membrane is regarded as a homogeneous laminar phase separating ionic solution phases on either side. Specifically, we assume that: (*a*) The membrane is a plane sheet of specified thickness, but of infinite extent in all directions parallel to its surfaces. Thus we deal with a one dimensional problem in which such quantities as electric potential, ion concentration, and their gradients are functions of a single coordinate, x. The x axis is perpendicular to the membrane surfaces. (*b*) The membrane is non-osmotic; *i.e.*, is impermeable to the solvent in the surrounding solutions. (*c*) No bound charge other than that arising from polarization is present within the membrane. (*d*) Ions are classified, without consideration of the mechanisms involved, as permeant or impermeant. Permeant ions have finite mobilities different from zero within the membrane. Impermeant ions have zero mobility within the membrane and are excluded therefrom. (*e*) All ions have infinite mobility in the exterior phases; *i.e.*, the surrounding solutions offer no impedance to ion motion. (*f*) The solution phases are of infinite extent. Thus the ion concentrations at large distances from the membrane are unaffected by a stationary current flow, always maintaining their equilibrium values.

2. *Notation and Sign Conventions.*

Ion concentrations. The concentration of the i^{th} positive ion species will be designated by c_i^+ (x) or simply c_i^+ with its dependence upon position being understood. The quantity, c^+, written without the subscript, will represent the total concentration of all positive ion species at a given point. We define similar variables, c_i^- and c^-, for negative ions. In general, for quantities to which a summation over ion species would be appropriate, the absence of the subscript will imply the summation.

Current density. That portion of the total current density attributable to the motion of positive ions is labeled j^+. The quantity, j^+, will be a positive number if positive charge moves to the right, in the direction of increasing x, and will be negative for flow to the left. Similarly, j^- will denote the contribution of negative ions to the total current density; j^- will, however, be a negative number if negative charge moves to the right and positive for flow to the left. The total current density, j, is clearly equal to $j^+ + j^-$. We note also that the current densities corresponding to a given state of stationary flow are constants independent of position.

Electric potential and field. The electric potential is given by ψ. The electric field is

$$E = -\frac{d\psi}{dx} \tag{1}$$

and is positive or negative if ψ is decreasing to the right or left, respectively.

Electron charge and ion valence. The specific electron charge, e, is always positive. The valence of a positive ion species will be designated by z_i^+, a positive integer, and that of a negative ion species by z_i^-, a negative integer.

3. *The Flow Equations.*

We consider first the general problem of current flow through any homogeneous medium due to the motion of ions of a particular species under the influence of: (a) an electric field or potential gradient, and (b) a gradient in the concentration of that species alone.

For positive ions the current density due to an electric potential gradient is

$$j_i^+(\text{electric}) = -ez_i^+\mu_i^+c_i^+\frac{d\psi}{dx} \tag{2}$$

where μ_i^+ is the mobility of the species. The diffusion current density is, by Fick's law,

$$j_i^+(\text{diffusion}) = -ez_i^+D_i^+\frac{dc_i^+}{dx} \tag{3}$$

where D_i^+ is the diffusion constant of the i^{th} positive ion species. The net current density

$$j_i^+ = -ez_i^+\left[\mu_i^+c_i^+\frac{d\psi}{dx} + D_i^+\frac{dc_i^+}{dx}\right] \tag{4}$$

is obtained by adding equations (2) and (3).

Now $j_i^+ = 0$ in equilibrium. Furthermore, the equilibrium ion concentration will vary with position according to Maxwell-Boltzmann statistics, or

$$c_i^+ = c_i^+(x_0) \exp\left[-\frac{ez_i^+\{\psi - \psi(x_0)\}}{kT}\right] \tag{5}$$

where, k, is the Boltzmann constant and, T, is the absolute temperature. Here $c_i^+(x_0)$ and $\psi(x_0)$ are the concentration and potential, respectively, at any fixed reference point, x_0, within the homogeneous medium. Differentiation of equation (5) and substitution of the result into equation (4) gives, for equilibrium,

$$-ez_i^+c_i^+\frac{d\psi}{dx}\left[\mu_i^+ - \frac{ez_i^+D_i^+}{kT}\right] = 0 \tag{6}$$

This result can hold in general only if the bracketed quantity vanishes, or

$$\frac{z_i^+D_i^+}{\mu_i^+} = \frac{kT}{e}. \tag{7}$$

This is the Einstein relation in a form applicable to the positive ions. The quantities μ_i^+ and D_i^+ are constants (at fixed temperature and pressure) which characterize the interaction of the ions with the medium, hence, though derived for the equilibrium case, equation (7) will be assumed to hold under non-equilibrium conditions as well. We proceed, with due regard for the sign conventions given above, to the corresponding derivations for negative ions. Starting from

$$j_i^-(\text{electric}) = ez_i^-\mu_i^-c_i^-\frac{d\psi}{dx} \tag{8}$$

$$j_i^-(\text{diffusion}) = -ez_i^-D_i^-\frac{dc_i^-}{dx} \tag{9}$$

and

$$j_i^- = ez_i^-\left[\mu_i^-c_i^-\frac{d\psi}{dx} - D_i^-\frac{dc_i^-}{dx}\right] \tag{10}$$

we obtain the appropriate Einstein relation

$$-\frac{z_i^-D_i^-}{\mu_i^-} = \frac{kT}{e} \tag{11}$$

The two flow equations, (4) and (10), may now be rewritten together in the condensed form

$$\frac{j_i^\pm}{\mu_i^\pm} = \mp kT\frac{dc_i^\pm}{dx} \pm ez_i^\pm c_i^\pm E \tag{12}$$

The equation obtained by retaining only the upper sign of ± or ∓, designated (12, u), results from substitution of equations (1) and (7) into equation (4). The equation obtained by retaining only the lower sign, designated (12, *l*), results from substitution of equations (1) and (11) into equation (10). This condensed notation, and the indicated mode of reference to either of the equations thus combined, will be used extensively for the sake of brevity.

4. *The Fundamental Equation.*

Our goal is the combination of Poisson's equation

$$\frac{K}{4\pi e}\frac{dE}{dx} = \sum_i z_i^+ c_i^+ + \sum_i z_i^- c_i^- \tag{13}$$

with the flow equations in such a way as to remove all explicit dependence upon the ion concentrations. Here K is the static dielectric constant of the homogeneous medium. The summations are over all positive and negative ion species which are present. We begin by defining the quantities, Γ_i^+ and Γ_i^-, by

$$\Gamma_i^{\pm} = \frac{j_i^+}{\mu_i^+} \pm \frac{j_i^-}{\mu_i^-} \tag{14}$$

We note that, for equations written in condensed form the appearance of the + or − sign alone is to mean that the sign is the same in both equations. Now add (12, *u*) and (12, *l*) to obtain (15, *u*), and subtract (12, *l*) from (12, *u*) to obtain (15, *l*). The results, using (14, *u*) and (14, *l*) respectively, are

$$\Gamma_i^{\pm} = -kT\frac{d}{dx}(c_i^+ \mp c_i^-) + e(z_i^+ c_i^+ \mp z_i^- c_i^-)E \tag{15}$$

It will prove convenient to rewrite (15, *u*) and (15, *l*) in the forms (16, *u*) and (16, *l*) respectively, as shown

$$\begin{aligned} 2\Gamma_i^{\pm} &+ \left(\frac{1}{z_i^+} \pm \frac{1}{z_i^-}\right)kT\frac{d}{dx}(z_i^+ c_i^+ - z_i^- c_i^-) \\ &+ \left(\frac{1}{z_i^+} \mp \frac{1}{z_i^-}\right)kT\frac{d}{dx}(z_i^+ c_i^+ + z_i^- c_i^-) = 2e(z_i^+ c_i^+ \mp z_i^- c_i^-)E \end{aligned} \tag{16}$$

Note that expansion of the factors on the left-hand side, followed by cancellation, division by two and rearrangement of terms, leads from (16, *u* or *l*) directly back to (15, *u* or *l*).

We now eliminate $(z_i^+ c_i^+ - z_i^- c_i^-)$ between (16, *u*) and (16, *l*). This may be done by dividing (16, *u*) by E, then differentiating it with respect to x. The first and second derivatives of $(z_i^+ c_i^+ - z_i^- c_i^-)$ which appear may be eliminated by substitution from (16, *l*) and (16, *l*) differentiated. The single equation resulting, after some rearrangement, is

$$\frac{e}{kT}\Gamma_i^- E^2 + \frac{1}{2}\left[\left(\frac{1}{z_i^+} + \frac{1}{z_i^-}\right)\Gamma_i^- - \left(\frac{1}{z_i^+} - \frac{1}{z_i^-}\right)\Gamma_i^+\right]\frac{dE}{dx}$$

$$= \frac{kT}{z_i^+ z_i^-}\left[E\frac{d^2}{dx^2}(z_i^+c_i^+ + z_i^-c_i^-) - \frac{dE}{dx}\frac{d}{dx}(z_i^+c_i^+ + z_i^-c_i^-)\right]$$
$$- e\left(\frac{1}{z_i^+} + \frac{1}{z_i^-}\right)E^2\frac{d}{dx}(z_i^+c_i^+ + z_i^-c_i^-) + \frac{e^2}{kT}E^3(z_i^+c_i^+ + z_i^-c_i^-) \qquad (17)$$

The manipulations leading to equation (17) imply a purely formal pairing of positive and negative ion species. The final step in the elimination of explicit dependence upon concentration would presumably involve summation of all ion pair equations, each having the form of equation (17), followed by substitution from equation (13). For the most general case difficulty is encountered due to the presence of the valences as factors in the first two terms on the right in equation (17). We avoid the difficulty by imposing a restrictive assumption to the effect that, within the homogeneous medium, all positive ions have the same valence; *i.e.*, $z_i^+ = z^+$ for all species. Similarly we will require that $z_i^- = z^-$, a constant for all negative ion species. We make these substitutions into equation (17) and now the summation referred to above is over the concentrations and current density to mobility ratios of the ions pairs only. Thus we have not sacrificed the capacity to deal with the situation in which a multiplicity of ion species is present; the restriction is with respect to their valences only. The summation may now be carried out, using the convention of part 2, above, by simply dropping the remaining subscripts in equation (17). Similarly equation (13) becomes

$$\frac{K}{4\pi e}\frac{dE}{dx} = z^+c^+ + z^-c^- \qquad (18)$$

We substitute equation (18) into equation (17), written without subscripts, and express the result in terms of the electric displacement, $D = KE$, rather than E. It is

$$\frac{e}{K^2kT}\Gamma^- D^2 + \frac{1}{2K}\left[\left(\frac{1}{z^+} + \frac{1}{z^-}\right)\Gamma^- - \left(\frac{1}{z^+} - \frac{1}{z^-}\right)\Gamma^+\right]\frac{dD}{dx}$$
$$= \frac{kT}{4\pi Kz^+z^-e}\left[D\frac{d^3D}{dx^3} - \frac{dD}{dx}\frac{d^2D}{dx^2}\right]$$
$$- \frac{1}{4\pi K^2}\left(\frac{1}{z^+} + \frac{1}{z^-}\right)D^2\frac{d^2D}{dx^2} + \frac{1}{4\pi K^3}\left(\frac{e}{kT}\right)D^3\frac{dD}{dx} \qquad (19)$$

The relationship of equation (19) to the Poisson-Boltzmann equation in one dimension will be discussed in Appendix A.

Equation (19) is fundamental to our development. It is, however, non-linear and of third order. What follows is, in effect, nothing more than a systematic effort to reduce its order while at the same time supplying constants of integration appropriate to the membrane problem.

As a first step we return to equation (16) and, as above, replace z_i^+ by z^+ and z_i^- by z^-. The summation over paired species is then carried out by dropping the remaining subscripts. It will be convenient to introduce three positive quantities q^+, q^-, and z, related to z^+ and z^- by the following equations

$$z^{\pm} = \pm 2q^{\pm}z \tag{20}$$

and

$$z^2 = -z^+z^- \tag{21}$$

The three quantities are not independent since they are defined in terms of only two independent quantities. Multiply (20, u) by (20, l), matching side for side, then substitute from equation (21) and cancel to obtain

$$q^+q^- = \tfrac{1}{4} \tag{22}$$

Now, using these relations, (16, u) and (16, l) with subscripts dropped become (23, u) and (23, l) respectively of

$$\Gamma^{\pm} \mp 2(q^+ \mp q^-)kT\frac{d}{dx}(q^+c^+ + q^-c^-) \\ \pm \frac{1}{4\pi}(q^+ \pm q^-)\frac{kT}{ez}\frac{d^2D}{dx^2} = \frac{2ez}{K}D(q^+c^+ \pm q^-c^-) \tag{23}$$

where we have substituted from Poisson's equation, written as

$$\frac{1}{8\pi ez}\frac{dD}{dx} = q^+c^+ - q^-c^- \tag{24}$$

on the left in equation (23). Now substitute from equation (24) on the right in (23, l) and integrate from an arbitrarily chosen reference point, x_0, to any other point, x, within the homogeneous medium. The result, after rearrangement, is

$$2(q^+ + q^-)ez(q^+c^+ + q^-c^-) = 2(q^+ + q^-)ez(q^+c^+(x_0) + q^-c^-(x_0)) \\ + \tfrac{1}{4}(q^+ - q^-)\left[\frac{dD}{dx} - \frac{dD(x_0)}{dx}\right] + \frac{1}{8\pi K}\left(\frac{ez}{kT}\right)[D^2 - D(x_0)^2] - \left(\frac{ez}{kT}\right)\Gamma^-[x - x_0] \tag{25}$$

where $dD(x_0)/dx$ is to be interpreted as $(dD(x)/dx)_{x=x_0}$; *i.e.*, the gradient of the displacement evaluated at $x = x_0$. This notation will be used consistently. Now multiply (23, u) by $(q^+ + q^-)$ and (23, l), with the displacement gradient substituted from equation (24) on its right, by $(q^+ - q^-)$. Then substitute into (23, u) from equation (25) and (23, l) to eliminate $(q^+c^+ + q^-c^-)$ and its derivative respectively. The result may be written

$$\frac{d^2zD}{dx^2} = \left[\frac{2}{K^2}\left(\frac{e}{2kT}\right)^2\{(zD)^2 - (zD(x_0))^2\} + (q^+ - q^-)\frac{2}{K}\left(\frac{e}{2kT}\right)\left\{2\frac{dzD}{dx} - \frac{dzD(x_0)}{dx}\right\}\right. \\ \left. + (q^+ + q^-)\frac{8\pi}{K}\frac{e^2z^2}{kT}\{q^+c^+(x_0) + q^-c^-(x_0)\} - \frac{4\pi}{K}\left(\frac{ez}{kT}\right)^2\Gamma^-\{x - x_0\}\right]zD \\ - 4\pi z\left(\frac{ez}{kT}\right)[(q^+ + q^-)\Gamma^+ + (q^+ - q^-)\Gamma^-] \tag{26}$$

5. *The Membrane Problem.*

We will shortly apply equation (26), valid for any homogeneous medium, to the membrane problem in which we deal with three such media "in series" as illustrated in Fig. 1. The origin of the x axis is placed at the left membrane surface; the right surface intersects the axis at x_1, which thus measures the membrane thickness. Equating of the dielectric constants of the media in regions I and III to the same value, K_1, is not an essential simplification; we make it, however, since in situations of biological interest both of the media in question will invariably be aqueous ionic solutions. We note in this connection our tacit assumption that the dielectric constant of the homogeneous medium is strictly constant. Observations such as those of Little, (1958), indicate a reduction of the dielectric constant of aqueous electrolyte solutions as the solute concentration is increased. The effect is not large and we do not consider it further. The dielectric constant of the membrane medium is K_2 where in general $K_2 \neq K_1$. We set $\Gamma^+ = \Gamma^- = 0$ in regions I and III under all conditions on the basis of equation (14), the assumption of part 1(e), and the fact that the current densities, limited by the membrane resistance, will always be finite. The equalities will hold in region II only in equilibrium.

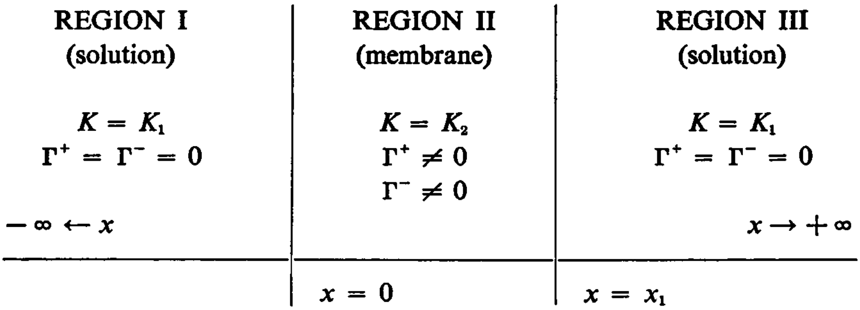

FIGURE 1 The model membrane.

We now introduce parameters needed to fix the ion concentrations in equilibrium at $x \rightarrow -\infty$ and $x \rightarrow +\infty$ in regions I and III respectively. By the assumption of part 1(f), they will then be fixed under conditions of stationary flow as well. The total concentration of all permeant positive ion species will be designated $c_{\text{per}}{}^+$. The total concentration of all impermeant positive ions will be given by $c_{\text{imp}}{}^+$. We introduce similar quantities, $c_{\text{per}}{}^-$ and $c_{\text{imp}}{}^-$ for negative ion species. This classification is exhaustive so, in region I

$$c_{\text{imp}}{}^{\pm}(-\infty) + c_{\text{per}}{}^{\pm}(-\infty) = c^{\pm}(-\infty) \tag{27}$$

We define dimensionless quantities, γ^+ and γ^-, by the relations

$$c_{\text{imp}}{}^{\pm}(-\infty) = \gamma^{\pm} c_{\text{per}}{}^{\pm}(-\infty) \tag{28}$$

Charge neutrality is required in the solution phases at large distance from the membrane surfaces, hence,

$$z^{+}c^{+}(-\infty) = -z^{-}c^{-}(-\infty) \tag{29}$$

or, from (20, u and l)

$$q^{+}c^{+}(-\infty) = q^{-}c^{-}(-\infty) = \tfrac{1}{2}c_1 \tag{30}$$

where we have introduced an "effective" concentration, c_1, defined by equation (30). Note that specification of the parameters q^+ or q^-, γ^+, γ^-, and c_1 is sufficient to fix all relevant ion concentrations at minus infinity.

For region III we have, as above,

$$c_{\text{imp}}^{\pm}(\infty) + c_{\text{per}}^{\pm}(\infty) = c^{\pm}(\infty) \tag{31}$$

and

$$q^{+}c^{+}(\infty) = q^{-}c^{-}(\infty) \tag{32}$$

Since both positive and negative permeant ions are assumed to be present it follows from the restriction imposed on ion valences in part 4 that the values of q^+ and q^- cannot change as we pass from region I to regions II and III. Hence we divide equation (32) by the first part of equation (30) to obtain

$$\frac{c^{+}(\infty)}{c^{+}(-\infty)} = \frac{c^{-}(\infty)}{c^{-}(-\infty)} = R \tag{33}$$

where, R, is another dimensionless parameter introduced to specify the ratios shown.

Finally, we define a parameter ψ_0 by

$$\psi_0 = [\psi(\infty) - \psi(-\infty)]_{\text{equilibrium}} \tag{34}$$

The well known Donnan equilibrium relations then give

$$c_{\text{per}}^{\pm}(\infty) = c_{\text{per}}^{\pm}(-\infty) \exp\left[-\frac{ez^{\pm}\psi_0}{kT}\right] \tag{35}$$

Equations (35, u) and (35, l) follow directly from (12, u) and (12, l) respectively by equating the left sides of the latter to zero, summing over permeant ion species only, substituting from equation (1) and finally integrating from $-\infty$ to $+\infty$. Upon defining another dimensionless parameter

$$\rho_0 = \frac{ez\psi_0}{kT} \tag{36}$$

we rewrite (35, u) and (35, l) as (37, u) and (37, l) respectively, or

$$c_{\text{per}}^{\pm}(\infty) = c_{\text{per}}^{\pm}(-\infty) \exp[\mp 2q^{\pm}\rho_0] \tag{37}$$

Six parameters, namely q^+ or q^-, γ^+, γ^-, c_1, R, and ρ_0 are sufficient to specify all relevant ion concentrations at $\pm\infty$ under the most general conditions which we can consider. All are dimensionless except c_1. They must all be positive except ρ_0 which will, however, generally be chosen positive also. Now manipulation of the above equations leads to expressions for $c_{\mathrm{imp}}^+ (\infty)$ and $c_{\mathrm{imp}}^- (\infty)$. They are

$$\frac{2q^{\pm}c_{\mathrm{imp}}^{\pm}(\infty)}{c_1} = \left[R - \frac{1}{(1+\gamma^{\pm})} \exp\left[\mp 2q^{\pm}\rho_0\right]\right] \tag{38}$$

The quantities on the left can never be negative hence the inequalities

$$\frac{1}{R(1+\gamma^{\pm})} \exp\left(\mp 2q^{\pm}\rho_0\right) \leq 1 \tag{39}$$

represent a further restriction upon the choice of the parameters.

In applying equation (26) to region I we will move the reference point x_0 to minus infinity and require that

$$D(x_0) \to 0 \tag{40}$$

and

$$\frac{dD(x_0)}{dx} \to 0 \tag{41}$$

as $x_0 \to -\infty$. Poisson's equation and the requirement of charge neutrality leads to equation (41). Since the concentrations go to constant values as $x_0 \to -\infty$ their gradients must vanish in this limit also. So from equation (12), with the left sides equal to zero as is appropriate in region I, we see that E must tend to zero as $x \to -\infty$. Hence equation (40) must also hold, at least provided K_1 is finite.

We now consider the quantity $8\pi(e^2z^2/kT)[q^+c^+(x_0) + q^-c^-(x_0)]$ which is incorporated into one of the terms of equation (26). As $x_0 \to -\infty$ it becomes a constant which we call λ^2 and which may be written, using equation (30), as

$$\lambda^2 = \frac{8\pi e^2z^2c_1}{kT} \tag{42}$$

Now $(1/\lambda)$ has the dimension of length and is in fact essentially the well known Debye relaxation length. We will find it convenient, however, to exclude the dielectric constant from the denominator in equation (42); therefore, we label the quantity λ^2 rather than the customary κ^2.

With the introduction of a characteristic length we will be able to express all subsequent results in dimensionless form. This will permit more compact notation. A far more important benefit of dimensionless notation lies in the fact that all possible "scaling," permitting widest applicability of numerical results, will automatically be incorporated into the development. We introduce a dimensionless variable corresponding to length

$$\xi = \frac{\lambda}{(K_2)^{1/2}}. \tag{43}$$

Substitution of x_1 for x in equation (43) gives ξ_1, a quantity proportional to the membrane thickness. The dimensionless variable corresponding to the electric displacement is

$$y = \frac{ezD}{2kT\lambda(K_2)^{1/2}} \tag{44}$$

For the potential

$$\rho = \frac{ez\psi}{kT} \tag{45}$$

For the currents

$$a^{\pm} = 2\pi\left(\frac{ez}{kT\lambda}\right)^2 \frac{(K_2)^{1/2}}{\lambda}\,\Gamma^{\pm} \tag{46}$$

Finally we introduce the dimensionless ratio

$$\alpha = K_2/K_1 \tag{47}$$

of the dimensionless dielectric constants, K_1 and K_2. Equations (43) through (47) have not been derived in the usual sense but have been obtained by inspection. This choice of dimensionless quantities is in fact not unique; it is based upon a desire to minimize numerical factors in subsequent equations.

To the reference point x_0 of equation (26) there clearly corresponds a dimensionless reference point, ξ_0. We rewrite equation (26) in dimensionless form as

$$\begin{aligned}\frac{d^2y}{d\xi^2} = 2y\Bigg[\left(\frac{K_2}{K}\right)^2\{y^2 - y(\xi_0)^2\} + \left(\frac{K_2}{K}\right)(q^+ - q^-)\left\{2\frac{dy}{d\xi} - \frac{dy(\xi_0)}{d\xi}\right\} \\ + \left(\frac{K_2}{K}\right)(q^+ + q^-)\left\{\frac{q^+c^+(\xi_0) + q^-c^-(\xi_0)}{2c_1}\right\} - \left(\frac{K_2}{K}\right)a^-\{\xi - \xi_0\}\Bigg] \\ - [(q^+ + q^-)a^+ + (q^+ - q^-)a^-]\end{aligned} \tag{48}$$

For region I we will require

$$y(\xi_0) \rightarrow 0 \tag{49}$$

and

$$\frac{dy(\xi_0)}{d\xi} \rightarrow 0 \tag{50}$$

as $\xi_0 \rightarrow -\infty$, analogous to equations (40) and (41). Clearly $a^+ = a^- = 0$ since $\Gamma^+ = \Gamma^- = 0$ in region I. Finally we substitute K_1 for K in equation (48) and it becomes

$$\frac{d^2y}{d\xi^2} = 2\alpha^2y^3 + 4\alpha(q^+ - q^-)y\frac{dy}{d\xi} + \alpha(q^+ + q^-)y \tag{51}$$

Equation (51) is therefore equation (26) applied to region I and written in dimensionless form. A first integral for equation (51), including an appropriate constant of integration, is

$$\left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-) - 2q^- \frac{dy}{d\xi}\right]^{2q^+} \left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-) + 2q^+ \frac{dy}{d\xi}\right]^{2q^-} = [\tfrac{1}{2}(q^+ + q^-)]^{2(q^+ + q^-)} \tag{52}$$

The physical significance of this result will be discussed in part 8 below. The formal integration of equation (51) will be outlined in Appendix B.

We now write equation (48) in a form appropriate to region II, setting $\xi_0 = 0$ and $K = K_2$. Noting from part 1(d) that only permeant ions are to be found within the membrane we have

$$\begin{aligned}\frac{d^2y}{d\xi^2} = 2y\Bigg[\{y^2 - y(0)^2\} + (q^+ - q^-)\left\{2\frac{dy}{d\xi} - \left(\frac{dy(0)}{d\xi}\right)_{\text{II}}\right\} \\ + (q^+ + q^-)\left\{\frac{q^+c_{\text{per}}{}^+(0) + q^-c_{\text{per}}{}^-(0)}{2c_1}\right\} - a^-\xi\Bigg] \\ - [(q^+ + q^-)a^+ + (q^+ - q^-)a^-]\end{aligned} \tag{53}$$

The quantity $(dy(0)/d\xi)_{\text{II}}$ is to be interpreted as the gradient of y evaluated in region II at a point ξ_0 which, although positive, differs from zero by a negligible amount. This notation, using roman numeral subscripts as appropriate, will be employed consistently in dealing with quantities which change in value discontinuously at the membrane-solution interfaces. Further development of equation (53) must await the treatment of membrane boundary conditions to be given in part 6 below.

Finally we apply equation (48), the dimensionless equivalent of equation (26), to region III. This time we move the reference point to plus infinity and require

$$y(\xi_0) \to 0 \tag{54}$$

and

$$\frac{dy(\xi_0)}{d\xi} \to 0 \tag{55}$$

as $\xi_0 \to +\infty$. From equations (30) and (33) we have

$$q^+c^+(\xi_0) + q^-c^-(\xi_0) \to Rc_1 \tag{56}$$

as $\xi_0 \to +\infty$. So, with $K = K_1$ and $a^+ = a^- = 0$, equation (48) becomes

$$\frac{d^2y}{d\xi^2} = 2\alpha^2y^3 + 4\alpha(q^+ - q^-)y\frac{dy}{d\xi} + \alpha(q^+ + q^-)Ry \tag{57}$$

A first integral for equation (57), including a constant of integration appropriate to region III, is

$$\left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-)R - 2q^- \frac{dy}{d\xi}\right]^{2q^+}\left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-)R + 2q^+ \frac{dy}{d\xi}\right]^{2q^-} = \left[\tfrac{1}{2}(q^+ + q^-)R\right]^{2(q^+ + q^-)} \tag{58}$$

This result is analogous to equation (52) and will also be discussed below.

6. *Membrane Boundary Conditions.*

The specification of the boundary conditions at the membrane-solution interfaces is based upon the following criteria: (*a*) All ion concentrations are finite at absolute temperatures greater than 0°K. Thus it follows from Gauss's law that the electric displacement and $y(\xi)$, its dimensionless equivalent, are continuous across the membrane-solution boundaries. (*b*) The concentration of impermeant ions drops discontinuously from a finite value to zero upon passing from either solution phase into the membrane. This follows from part 1(*d*). (*c*) The permeant ion concentration is a continuous function of position at the interfaces. From part 1(*d* and *e*) we note that the permeant ion mobilities are greater than zero in all three regions. It follows from the Einstein relations that their diffusion constants, at temperatures greater than 0°K, are greater than zero as well. Thus any discontinuity in the permeant ion concentration would imply an infinity gradient and an associated infinite diffusive flow unless countered by a suitable infinite discontinuity in the electric field and displacement. The latter possibility is ruled out by the conclusion of part 6(*a*) above. In this connection we again take note of the assumption made in the introduction that the absolute activities of the various ion species may be equated to their concentrations. This assumption is essential to our conclusion that the permeant ion concentration is continuous across the interfaces. Strictly speaking, it is the absolute activity of a permeant ion species which must be continuous across an interface in order to avoid a discontinuity in the electrochemical potential of that species which would result in an infinite electrochemical potential gradient and an associated infinite flow.

It is evident, however, that there will be a discontinuity in the electric displacement gradient owing to the discontinuity in the impermeant ion concentration at the interfaces. We write equation (24) in dimensionless form as

$$\frac{dy}{d\xi} = \frac{q^+c^+ - q^-c^-}{2c_1} \tag{59}$$

and apply it to the interface at $\xi = 0$ to obtain

$$\left(\frac{dy(0)}{d\xi}\right)_{\text{I}} = \left(\frac{q^+c_{\text{imp}}^+(0) - q^-c_{\text{imp}}^-(0)}{2c_1}\right)_{\text{I}} + \left(\frac{q^+c_{\text{per}}^+(0) - q^-c_{\text{per}}^-(0)}{2c_1}\right) \tag{60}$$

and

$$\left(\frac{dy(0)}{d\xi}\right)_{\text{II}} = \left(\frac{q^+c_{\text{per}}^+(0) - q^-c_{\text{per}}^-(0)}{2c_1}\right) \tag{61}$$

We turn now to the evaluation of the relevant concentrations. Application of equation (25) to region I yields

$$(q^+ + q^-)\left(\frac{q^+c^+ + q^-c^-}{2c_1}\right) = \alpha y^2 + \tfrac{1}{2}(q^+ + q^-) + (q^+ - q^-)\frac{dy}{d\xi} \tag{62}$$

in dimensionless form after letting $\xi_0 \rightarrow -\infty$, setting $K = K_1$, and $a^- = 0$. Multiply equation (59) by $(q^+ + q^-)$, then add it to equation (62) to obtain (63, u). Subtract it from equation (62) to obtain (63, l). The combined results are

$$2(q^+ + q^-)\left(\frac{q^\pm c^\pm}{2c_1}\right) = \alpha y^2 + \tfrac{1}{2}(q^+ + q^-) \pm 2q^\pm \frac{dy}{d\xi} \tag{63}$$

Now apply (12, u and l) to region I by setting the left sides equal to zero. Express them in dimensionless form, then multiply (12, u) by q^- and (12, l) by q^+. The results are (64, u and l) respectively, or

$$\mp q^\mp \frac{d}{d\xi}\left(\frac{c_i^\pm}{2c_1}\right) + \alpha\left(\frac{c_i^\pm}{2c_1}\right)y = 0 \tag{64}$$

These equations hold for each ion species separately and thus may be summed over permeant ions only, and over impermeant ions only. We carry out these summations for (64, u) and integrate the two equations to obtain the relation (65, u). In like fashion we obtain (65, l) from (64, l). We write

$$q^\mp \ln\left(\frac{c_{\text{imp}}^\pm(\xi)}{c_{\text{imp}}^\pm(-\infty)}\right) = q^\mp \ln\left(\frac{c_{\text{per}}^\pm(\xi)}{c_{\text{per}}^\pm(-\infty)}\right) = \pm\alpha\int_{-\infty}^{\xi} y\, d\xi \tag{65}$$

The first equality of (65, u and l) is sufficient to establish (66, u and l) respectively, or

$$\frac{c_{\text{imp}}^\pm(\xi)}{c_{\text{per}}^\pm(\xi)} = \frac{c_{\text{imp}}^\pm(-\infty)}{c_{\text{per}}^\pm(-\infty)} = \gamma^\pm \tag{66}$$

using (28, u and l). By combination of equations (66) and (63) we may obtain

$$\frac{q^\pm c_{\text{imp}}^\pm}{2c_1} = \frac{1}{2(q^+ + q^-)}\left(\frac{\gamma^\pm}{1+\gamma^\pm}\right)\left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-) \pm 2q^\pm\frac{dy}{d\xi}\right] \tag{67}$$

and

$$\frac{q^\pm c_{\text{per}}^\pm}{2c_1} = \frac{1}{2(q^+ + q^-)}\left(\frac{1}{1+\gamma^\pm}\right)\left[\alpha y^2 + \tfrac{1}{2}(q^+ + q^-) \pm 2q^\pm\frac{dy}{d\xi}\right] \tag{68}$$

These equations are valid throughout region I. Subtract equation (61) from equation (60), then use (67, u and l) to obtain

$$\begin{aligned}\left(\frac{dy(0)}{d\xi}\right)_{\text{I}} - \left(\frac{dy(0)}{d\xi}\right)_{\text{II}} &= \frac{1}{2(q^+ + q^-)}\left[\left\{\frac{\gamma^+}{1+\gamma^+} - \frac{\gamma^-}{1+\gamma^-}\right\}\alpha y(0)^2\right.\\ &\quad \left. + 2\left\{\frac{q^+\gamma^+}{1+\gamma^+} + \frac{q^-\gamma^-}{1+\gamma^-}\right\}\left(\frac{dy(0)}{d\xi}\right)_{\text{I}}\right] + \frac{1}{4}\left\{\frac{\gamma^+}{1+\gamma^+} - \frac{\gamma^-}{1+\gamma^-}\right\}\end{aligned} \tag{69}$$

Use of equation (25), written in dimensionless form and applied to region III, and Poisson's equation leads to

$$2(q^+ + q^-)\left(\frac{q^\pm c^\pm}{2c_1}\right) = \alpha y^2 + \frac{R}{2}(q^+ + q^-) \pm 2q^\pm \frac{dy}{d\xi} \tag{70}$$

analogous to equation (63) for region I. Proceeding as before from the flow equations, equation (64), which are identical in regions I and III, we obtain

$$\frac{q^\pm c_{\text{imp}}{}^\pm}{2c_1} = \frac{1}{2(q^+ + q^-)}\left[1 - \frac{1}{R(1 + \gamma^\pm)} \exp(\mp 2q^\pm \rho_0)\right] \cdot \left[\alpha y^2 + \frac{R}{2}(q^+ + q^-) \pm 2q^\pm \frac{dy}{d\xi}\right] \tag{71}$$

and

$$\frac{q^\pm c_{\text{per}}{}^\pm}{2c_1} = \frac{1}{2(q^+ + q^-)}\left[\frac{1}{R(1 + \gamma^\pm)} \exp(\mp 2q^\pm \rho_0)\right] \cdot \left[\alpha y^2 + \frac{R}{2}(q^+ + q^-) \pm 2q^\pm \frac{dy}{d\xi}\right] \tag{72}$$

which are valid throughout region III. Application of Poisson's equation at the boundary $\xi = \xi_1$, together with equation (71), then gives

$$\begin{aligned}\left(\frac{dy(\xi_1)}{d\xi}\right)_{\text{III}} - \left(\frac{dy(\xi_1)}{d\xi}\right)_{\text{II}} = -\frac{1}{2(q^+ + q^-)}&\left[\frac{1}{R}\left\{\frac{\exp(-2q^+\rho_0)}{(1 + \gamma^+)} - \frac{\exp(2q^-\rho_0)}{(1 + \gamma^-)}\right\}\alpha y(\xi_1)^2\right. \\ &\left. - 2\left\{q^+\left(1 - \frac{\exp(-2q^+\rho_0)}{R(1 + \gamma^+)}\right) + q^-\left(1 - \frac{\exp(2q^-\rho_0)}{R(1 + \gamma^-)}\right)\right\}\left(\frac{dy(\xi_1)}{d\xi}\right)_{\text{III}}\right] \\ &- \frac{1}{4}\left\{\frac{\exp(-2q^+\rho_0)}{(1 + \gamma^+)} - \frac{\exp(2q^-\rho_0)}{(1 + \gamma^-)}\right\}\end{aligned} \tag{73}$$

analogous to equation (69) for $\xi = 0$.

Now using equations (61) and (68), we rewrite equation (53) as

$$\begin{aligned}\frac{d^2y}{d\xi^2} = 2y\Bigg[y^2 - \left\{1 - \frac{\alpha}{(q^+ + q^-)}\left(\frac{q^-}{1 + \gamma^+} + \frac{q^+}{1 + \gamma^-}\right)\right\}&y(0)^2 \\ + 2(q^+ - q^-)\frac{dy}{d\xi} + \frac{1}{2}\Bigg\{&\left(\frac{q^-}{1 + \gamma^+} + \frac{q^+}{1 + \gamma^-}\right) \\ + \frac{1}{(q^+ + q^-)}&\left(\frac{1}{1 + \gamma^+} - \frac{1}{1 + \gamma^-}\right)\left(\frac{dy(0)}{d\xi}\right)_{\text{I}}\Bigg\} - a^-\xi\Bigg] \\ - [(q^+ + q^-)a^+ &+ (q^+ - q^-)a^-]\end{aligned} \tag{74}$$

7. *Numerical Analysis.*

All information needed for solution of the conductance problem is now at hand. One could begin by choosing arbitrarily a value of $y(0)$, thereby fixing upon a particular stationary state of the system. Then $(dy(0)/d\xi)_{\text{I}}$ may be computed from equation (52) which will be a polynomial of second or higher degree in $(dy/d\xi)$ depending upon the values of q^+ and q^-. Care must be taken to choose from among the factors of this polynomial only those corresponding to physically significant solutions in region I as dictated by the requirements of equations (49) and (50). Next $(dy(0)/d\xi)_{\text{II}}$ is calculated from equation (69). Thus the initial value and slope needed to start the integration of equation (74) in region II are available. One must then find a pair of values for the parameters α^+ and α^- which will yield a pair of values for $y(\xi_1)$ and $(dy(\xi_1)/d\xi)_{\text{II}}$, upon completion of the integration, which satisfy the boundary conditions at ξ_1. This is checked by using the value of $y(\xi_1)$ determined by the integration to compute $(dy(\xi_1)/d\xi)_{\text{III}}$ using an appropriate factor of equation (58). Then $(dy(\xi_1)/d\xi)_{\text{II}}$ is computed from equation (73). The terminal slope in region II thus computed must agree with the terminal slope of the numerical solution. An auxiliary condition, obtained by applying the dimensionless equivalent of equation (25) to region II, may be used to facilitate the search for solutions. In the foregoing discussion it is assumed that all other parameters, which characterize the system in equilibrium, have been fixed in advance.

Now equation (1), in dimensionless form, is

$$\frac{d\rho}{d\xi} = -2\alpha y \tag{75}$$

in regions I and III, and

$$\frac{d\rho}{d\xi} = -2y \tag{76}$$

in region II. Hence numerical integration of the solutions for $y(\xi)$, once obtained as described above, yields the dimensionless equivalent of the transmembrane potential corresponding to α^+ and α^-. Final reduction of these quantities to potentials and current densities is dependent not only upon a knowledge of the equilibrium parameters of the system, but of the mobilities within the membrane of the permeant ions as well.

Consideration of certain special cases will lead to substantial simplification of the general formulation. If, for example, $z^+ = -z^-$ then $q^+ = q^- = \frac{1}{2}$, or $q^+ - q^- = 0$ and $q^+ + q^- = 1$. Then equations (74), (73), and (69) simplify and, in addition, the simplification of equations (52) and (58) leads to analytic solutions for $y(\xi)$ in regions I and III. The exclusion of impermeant ions from region I, accomplished by setting $\gamma^+ = \gamma^- = 0$, simplifies matters still further and leads in particular to the elimination of the discontinuity in the gradient of y at $\xi = 0$ as may be noted by inspection of equation (69).

Another special case of interest is that for which permeant ions of only one valence state, either positive or negative, are present. In this case it is possible to reduce equation (74) to first order although it still cannot be integrated analytically. We note that it is possible also to deal with a situation in which impermeant ions of opposite sign to the permeant ions, required for charge neutrality at large distances from the membrane, may be of different valence states in regions I and III. In this event the statements immediately preceding (33) no longer apply, and modifications of the development are required.

The points covered in part 7 above will be treated in detail in subsequent publications.

8. *Ion Products.*

Substitution of equation (75) into (64, *u* and *l*) permits the expression of the latter as (77, *u* and *l*) respectively, or

$$\mp\left(\frac{c_i^{\pm}}{2c_1}\right)\frac{d\theta_i^{\pm}}{d\xi} = 0 \tag{77}$$

where

$$\theta_i^{\pm} = \pm\rho + \ln\left(\frac{c_i^{\pm}}{2c_1}\right)^{2q^{\mp}} \tag{78}$$

is identifiable as the dimensionless equivalent of the electrochemical potentials of the various ion species present in regions I and III. It is clear that $\theta_i^{\pm}$ = constant) holds for each species throughout these regions. Summation of (64, *u*) over all positive ion species, and of (64, *l*) over all negative ion species, and substitution from (75) leads to results identical in form to those of equations (77) and (78) and which may in fact be obtained from the latter by simply dropping the subscripts. Summation of (78, *u*) and (78, *l*), without subscripts, gives

$$\left(\frac{c^{+}}{2c_1}\right)^{2q^{-}}\left(\frac{c^{-}}{2c_1}\right)^{2q^{+}} = \text{const.} \tag{79}$$

Clearly, with appropriate summation, similar products could be written for permeant ions only or impermeant ions only. Comparison of equation (79) with equations (63) and (70) indicates that equations (52) and (58) respectively are simply statements of the constancy of the generalized ion products.

We turn now to region II, sum (12, *u* and *l*) over permeant ion species only, put them in dimensionless form and substitute from equation (76) to obtain (80, *u* and *l*) respectively, or

$$2q^{\mp}(a^{+} \pm a^{-}) = \mp\left(\frac{c_{\text{per}}^{\pm}}{2c_1}\right)\frac{d\theta_{\text{per}}^{\pm}}{d\xi} \tag{80}$$

where

$$\theta_{\text{per}}^{\pm} = \pm\rho + \ln\left(\frac{c_{\text{per}}^{\pm}}{2c_1}\right)^{2q^{\mp}} \tag{81}$$

Multiply (80, u) by $-(c_{\text{per}}^{-}/2c_1)$ and (80, l) by $(c_{\text{per}}^{+}/2c_1)$, then add them to obtain

$$2a^{+}\left(\frac{q^{+}c_{\text{per}}^{+} - q^{-}c_{\text{per}}^{-}}{2c_1}\right) - 2a^{-}\left(\frac{q^{+}c_{\text{per}}^{+} + q^{-}c_{\text{per}}^{-}}{2c_1}\right)$$

$$= \left(\frac{c_{\text{per}}^{+}c_{\text{per}}^{-}}{4c_1^{2}}\right)\frac{d}{d\xi}\left(\theta_{\text{per}}^{+} + \theta_{\text{per}}^{-}\right)$$

$$= \left(\frac{c_{\text{per}}^{+}c_{\text{per}}^{-}}{4c_1^{2}}\right)\frac{d}{d\xi}\ln\left[\left(\frac{c_{\text{per}}^{+}}{2c_1}\right)^{2q^{-}}\left(\frac{c_{\text{per}}^{-}}{2c_1}\right)^{2q^{+}}\right] \tag{82}$$

In equilibrium the leftmost part of equation (82) vanishes and so the generalized ion product is constant throughout region II. In this case the product has the same value throughout all three regions since the permeant ion concentrations are continuous across the membrane boundaries. Note that this assertion is consistent with equation (37) as may be verified by raising both sides of (37, u) to the power $2q^{-}$, raising both sides of (37, l) to the power $2q^{+}$, then multiplying them to establish the equality of the permeant ion product at plus and minus infinity.

Equation (82) indicates that the permeant ion product will not be constant in region II in the stationary state. It must, however, always maintain its equilibrium value on the membrane boundaries by virtue of the fact that the permeant ion product is always constant in regions I and III, and by the assumption of part 1(f). This result provides an additional useful guide to numerical analysis.

APPENDIX A

The Poisson-Boltzmann equation arises by inserting into Poisson's equation an expression for the charge density derived by application of Maxwell-Boltzmann statistics. Thus for a homogeneous medium of dielectric constant, K, containing ions of only two valence states we may write, for the equilibrium case,

$$\frac{1}{4\pi e}\frac{d^{2}\psi}{dx^{2}} = -\frac{1}{K}\left[z^{+}c^{+}(x_0)\exp\left\{-\frac{ez^{+}\psi}{kT}\right\} + z^{-}c^{-}(x_0)\exp\left\{-\frac{ez^{-}\psi}{kT}\right\}\right] \tag{83}$$

where ψ is a function of x only. We have taken for convenience $\psi(x_o) = 0$. Now substitute into the left side of equation (83) from equation (1), multiply by K and exp $(ez^{-}\psi/kT)$, then differentiate, thereby eliminating the constant $c^{-}(x_o)$. Then multiply by exp $(-ez^{-}\psi/kT)$ and again use equation (1) to obtain

$$\frac{1}{4\pi e}\left[\frac{d^{2}D}{dx^{2}} - \frac{ez^{-}}{kT}E\frac{dD}{dx}\right] = \frac{e(z^{+} - z^{-})}{kT}z^{+}c^{+}(x_0)E\exp\left(-\frac{ez^{+}\psi}{kT}\right) \tag{84}$$

Now divide by E, then multiply by exp $(ez^{+}\psi/kT)$ and differentiate, thereby eliminating $c^{+}(x_o)$. Finally multiply by exp $(-ez^{+}\psi/kT)$ and again use equation (1) to obtain, after rearrangement,

$$\frac{kT}{4\pi Kz^+ze^-}\left[D\frac{d^3D}{dx^3}-\frac{dD}{dx}\frac{d^2D}{dx^2}\right]$$

$$-\frac{1}{4\pi K^2}\left(\frac{1}{z^+}+\frac{1}{z^-}\right)D^2\frac{d^2D}{dx^2}+\frac{1}{4\pi K^3}\left(\frac{e}{kT}\right)D^3\frac{dD}{dx}=0 \qquad (85)$$

Equation (19) reduces to this result in the equilibrium case where $\Gamma^+ = \Gamma^- = 0$.

We are now in a position to more fully appreciate the difficulty of removing the restriction to no more than two ion valence states within the homogeneous medium which we imposed at the outset. The Poisson-Boltzmann equation may be generalized, again in one dimension, to

$$\frac{1}{4\pi e}\frac{d^2\psi}{dx^2}=-\frac{1}{K}\left[\sum_{i=1}^{N_1} z_i^+c_i^+(x_0)\exp\left(-\frac{ez_i^+\psi}{kT}\right)+\sum_{i=1}^{N_2} z_i^-c_i^-(x_0)\exp\left(-\frac{ez_i^-\psi}{kT}\right)\right] \qquad (86)$$

where $N = N_1 + N_2$ is the number of valence states present. We would now require N differentiations to remove the N constants $c_i^+ (x_o)$ and $c_i^- (x_o)$. As a result the differential equation for the displacement in the equilibrium case would be of order $N + 1$. Thus the differential equation for stationary flow, corresponding to equation (19) for the case $N = 2$, would be at least of order $N + 1$ also.

APPENDIX B

The problem of reducing the order of equations (51) and (57) may be generalized to that of finding a first integral for

$$\frac{d^2y}{d\xi^2}=g_1y^3+g_2y\frac{dy}{d\xi}+g_3y \qquad (87)$$

where g_1, g_2, and g_3 are unspecified constants. Introduce first a new variable $p = (dy/d\xi)$, noting that

$$\frac{d^2y}{d\xi^2}=\frac{dp}{d\xi}=p\frac{dp}{dy} \qquad (88)$$

Substitution of equations (88) into (87) gives

$$p\frac{dp}{dy}=g_1y^3+g_2yp+g_3y \qquad (89)$$

With the introduction of another variable $v = y^2$ and the observation that

$$\frac{dp}{dy}=\frac{dv}{dy}\frac{dp}{dv}=2y\frac{dp}{dv} \qquad (90)$$

we substitute equation (90) into (89) and divide by y to obtain

$$2p\frac{dp}{dv}=g_1v+g_2p+g_3 \qquad (91)$$

Finally, with the transformation

$$g_1u=g_1v+g_3 \qquad (92)$$

of the independent variable, equation (91) may be written in differential form as

$$(g_1 u + g_2 p)\, du - 2p\, dp = 0 \tag{93}$$

which is homogeneous and of first degree. Using standard methods (Cohen, 1933) we multiply equation (93) by the integrating factor $[u(g_1 u + g_2 p) - 2p^2]^{-1}$ so that it takes the form $dw = 0$, *i.e.*, it becomes an exact differential having a solution $w(p.\ u) = \text{const.}$ The evaluation of w also proceeds by standard methods (Cohen, 1933) referring to tables for evaluation of the necessary integrals. The results are not detailed here. We simply note that when $w(p, u)$ is found we may then proceed back up the chain of transformations above to a solution $w[y, dy/d\xi)] = \text{const.}$ of equation (89) which includes the parameters g_1, g_2, and g_3.

Taking g_1, g_2 and g_3 from equations (51) and (57) we find that their first integrals are equations (52) and (58) respectively, with the constant of integration appearing on the right. It is evaluated in each case by setting y and $(dy/d\xi)$ equal to zero, in accordance with equations (49), (50), (54), and (55) which summarize the boundary conditions at minus and plus infinity.

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