THE NUMERICAL SOLUTION OF THE TIME-DEPENDENT NERNST-PLANCK EQUATIONS

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ABSTRACT Calculations are reported of the time-dependent Nernst-Planck equations for a thin permeable membrane between electrolytic solutions. Charge neutrality is assumed for the time-dependent case. The response of such a membrane system to step current input is measured in terms of the time and space changes in concentration, electrical potential, and effective conductance. The report also includes discussion of boundary effects that occur when charge neutrality does not hold in the steady-state case.

1. INTRODUCTION

This paper presents a mathematical extension of the Nernst-Planck (1-3) analysis of ion transport in thin layers. As is well known, the Nernst-Planck equations have been used as a phenomenological model for electrolytic behavior in membranes. The steady-state concentrations and electric potential gradients given by the model serve satisfactorily as an electrical and chemical background or quiescent state. Applied to active biological membranes, the Nernst-Planck relations do not seem to provide a satisfactory description of the membrane response to excitation. It appears as though this response cannot be obtained from the balancing of diffusion and electric forces that the Nernst-Planck model represents. Several attempts have been made to add elements to the original electrolytic theory [fixed charge (1), porous convective flows (5)], but these have not as yet proved as successful as discarding the diffusion-dominated process altogether for the description of the time-dependent reactions. This has been done in the Hodgkin-Huxley (6) theory where the burden of the non-linear response is placed on empirically obtained relations for separate ion conductances.

Nevertheless, it has seemed of interest to learn what the time-dependent version of the Nernst-Planck equations provides. The direct motivation for the calculations presented here was the observation made to us by A. Mauro and A. Finkelstein of The Rockefeller Institute, New York, that, while steady-state solutions for the Nernst-Planck equations had been available and discussed for many years (8-10), it appeared that no transient solutions had been given.[1] We would like to present these results in the spirit of providing a more complete view of the time-dependent character of the Nernst-Planck system.

If one considers a thin permeable membrane separating two electrolytic solutions, the steady-state ion concentrations and potential gradient can be found by solving a system of non-linear ordinary differential equations. For the case in which (*a*) the concentrations external to the membrane region are kept constant, (*b*) there is no fixed charge in the membrane region, and, furthermore, (*c*) charge neutrality is assumed both inside and outside of this region, a formal solution for the differential equations can be set out. When there are several ion species, one must still solve a transcendental equation to relate ion concentrations and the electrical field, but this can be done numerically without difficulty.

For the transient case, however, even with these three strong assumptions, the inherent non-linearity of the partial differential equation system prevents an easy analytical solution. The following question is to be answered: how does the system go from one of the steady states described in the preceding paragraph to another steady state and what characterization can be given of the electrical properties of the membrane during this transition?

The membrane of thickness l is taken to be mechanically completely permeable, but no other physical properties are attributed to it. This means that it is simply an interval in space. In fact, since we shall be considering only a one dimensional problem, the membrane will be just the interval $0 \le \bar{x} \le l$.

The equations governing ion flux and charge are given first in the form usually found in the cited works (1-3) (all the constants used and all dimensions are listed in Appendix 1):

$$\bar{\Phi}_i^{\pm} = -\bar{\mu}_i^{\pm}\left[\frac{RT}{F}\frac{\partial \bar{C}_i^{\pm}}{\partial \bar{x}} \mp \bar{C}_i^{\pm}\bar{E}\right] \tag{1.1}$$

$$\bar{E} = -\frac{\partial \bar{\psi}}{\partial x}. \tag{1.2}$$

Here, the $\bar{\Phi}_i^{\pm}$ are the fluxes of cations (+) and anions (−), the $\bar{C}_i^{\pm}$ are the concentrations of the $j = 1, 2, \cdots, n^{\pm}$ species, and $\bar{\psi}$ is the electric potential. The continuity equations and Poisson's equation are the field equations:

$$\frac{\partial \bar{C}_i^{\pm}}{\partial t} = -\frac{\partial \bar{\Phi}_i^{\pm}}{\partial \bar{x}} \tag{1.3}$$

$$\frac{\epsilon \cdot 10^9}{4\pi c^2}\frac{\partial \bar{E}}{\partial \bar{x}} = \bar{\rho} = F\sum_i (\bar{C}_i^{+} - \bar{C}_i^{-}). \tag{1.4}$$

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[1] We are very grateful to Dr. Mauro and Dr. Finkelstein for introducing this problem to us and for providing us with much helpful guidance.

It is also useful to write out an expression for the total current. We define the current to be

$$\bar{I} = F\Big(\sum_i \bar{\Phi}_i^+ - \sum_i \bar{\Phi}_i^-\Big) + \frac{\epsilon\cdot 10^9}{4\pi c^2}\frac{\partial \bar{E}}{\partial \bar{t}}, \tag{1.5}$$

the last term being the displacement current.[2]

Using

$$\bar{U} = \sum_i \bar{\mu}_i^+ \bar{C}_i^+, \qquad \bar{V} = \sum_i \bar{\mu}_i^- \bar{C}_i^- \tag{1.6}$$

the relation between current, electric potential, and the concentrations can be written

$$\frac{\epsilon\cdot 10^9}{4\pi c^2}\frac{\partial \bar{E}}{\partial \bar{t}} = \bar{I} - F\bar{E}(\bar{U} + \bar{V}) + RT\frac{\partial}{\partial x}(\bar{U} - \bar{V}). \tag{1.7}$$

The problem is now to solve equations (1.3), (1.4), and (1.5) subject to given conditions on the initial state and on the boundaries of the membrane. The solution will consist of the changes that occur in the $\bar{C}_i^+$ and $\bar{E}$ for a given change in $\bar{I}$. It will be obtained by numerical computation and represents the chief contribution of this paper. In carrying out the computation, we assume that charge neutrality holds. In order to carefully understand this assumption, we have found it useful to express the preceding equations in dimensionless form (see Appendix 1 for the normalizing quantities). When this is done, we have

$$\Phi_i^\pm = -\mu_i^\pm\left[\frac{\partial C_i^\pm}{\partial x} \mp C_i^\pm E\right] \tag{1.1$'$}$$

$$E = -\frac{\partial \Psi}{\partial x} \tag{1.2$'$}$$

$$\frac{\partial C_i^\pm}{\partial t} = -\frac{\partial \Phi_i^\pm}{\partial x} \tag{1.3$'$}$$

$$\kappa\frac{\partial E}{\partial x} = \rho = \sum_i (C_i^+ - C_i^-) = C^+ - C^- \tag{1.4$'$}$$

$$\kappa\frac{\partial E}{\partial t} = I - E(U + V) + \frac{\partial}{\partial x}(U - V). \tag{1.7$'$}$$

As can be seen, the parameters in the original equation reduce to the normalized mobilities, $\mu_i^\pm$, and the constant κ. κ is a ratio of scaling times,

$$\kappa = \frac{T_e}{T_d} \tag{1.8}$$

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[2] Although the displacement current does not appear in Planck's formulation, it can be seen from equations (1.4)′ and (1.7)′ that it enters to the same order of magnitude as the excess charge.

where

$$T_e = \frac{\epsilon \cdot 10^9}{4\pi c^2 F\bar{C}(0)^+ \bar{\mu}_{\mathrm{Cl}}^-}$$

is an electric relaxation time and

$$T_d = \frac{l^2}{\bar{\mu}_{\mathrm{Cl}}^- RT/F}$$

is a diffusion time. Since the original physical time has been made dimensionless with respect to T_d, we are looking at the system on the diffusion time scale. In general, for the kind of ion motion we are concerned with, T_e will be much smaller than T_d. For example, for typical values[3] $\kappa = 1.65 \times 10^{-14} \times l^{-2}$. Thus, for membranes with $l = 10^{-6}$ cm, $\kappa = 1.65 \times 10^{-2}$ whereas for laboratory membranes with $l = 10^{-2}$, $\kappa = 1.65 \times 10^{-10}$.

It is now clear that charge neutrality is embodied in the size of κ. For κ small we may neglect the left-hand sides of equations (1.4)′ and (1.7)′. Notice that this does not involve an assumption on $\partial E/\partial x$ or $\partial E/\partial t$. In fact, if either of these derivatives is very large at any place or time, we may balance out the smallness of κ. One may think of the case $\kappa = 0$ as being the first step in a perturbation expansion in κ. It is actually a singular perturbation. A discussion of such a development is given in Appendix 2.

2. THE NUMERICAL RESULTS FOR $\kappa = 0$

The steady-state solutions of equations (1.1)′, (1.2)′, (1.3)′, (1.4)′, and (1.7)′ have been discussed and calculated rather extensively (8-10). The numerical calculation we have carried out uses a solution of the steady-state problem as an initial state for the time-dependent case. The steady state chosen is a solution for an initial constant value of the current I and for given values of the concentrations at $x = 0$ and $x = 1$. It is convenient to remind the reader here that, if we define $C = C^+ + C^- = \Sigma_j C_j^+ + \Sigma_j C_j^-$, then for $\kappa = 0$

$$C = [C(1) - C(0)]x + C(0) \tag{2.1}$$

$$E = G/C \tag{2.2}$$

$$\Psi(x) = -\frac{G}{C(1) - C(0)} \ln \frac{C}{C(0)} \tag{2.3}$$

where $C(1)$ and $C(0)$ are the values at $x = 1$ and $x = 0$, respectively, and G is a constant determined from a transcendental equation involving I (see Appendix 2).

The programming details of the time-dependent solution will not be entered into here except to remark that finite-difference approximations were used for the deriva-

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[3] $c^2F/10^9 = 0.8685 \times 10^{17}$ volt-cm/farad, $\bar{C}^+(0) = 11 \times 10^{-5}$ mol-ions/cm³, $\bar{\mu}_{\mathrm{Cl}}^- = 0.676 \times 10^{-3}$ cm²/volt sec.

tives with respect to x and t and a predictor-corrector scheme was used for integrating with respect to t. A further description appears in Appendix 3.

A series of calculations was performed with the arrangement:[4]

0.1 N NaCl + 0.01 N HCl | membrane | 0.01 N NaCl + 0.1 N HCl using the mobilities

$$\bar{\mu}_{Cl} = 0.000676, \quad \bar{\mu}_{Na} = 0.000456, \quad \bar{\mu}_{H} = 0.003242 \, \frac{\text{cm/sec.}}{\text{volt/cm}}.$$

A step-function current was used, going from $I = 0$ to ΔI to 0 to $-\Delta I$ to 0 for $\Delta I = 0.1$ and $\Delta I = 0.5$ amp/cm^2. Only samples of the results are exhibited because of space limitations. A report containing more graphs is available (4). In all cases the concentration profiles were set at steady-state values before each change of current, and the changes in concentrations, electric fields, and membrane voltages were calculated and printed at various times after the current change. In all cases, the total concentrations were taken to satisfy $C(0) = C(1)$ so that one has only a special case of the steady-state solution mentioned above. Figs. 1*a* and 1*b* show the time development of the concentration profiles[5] when the current is stepped from 0.0 to 0.5 and from 0.5 to 0.0, respectively. With $\Delta I = 0.1$, the changes were, as one would expect, much milder.

Fig. 2 shows the corresponding changes, over time, of the electric field,

$$E(x, t) = \frac{I}{U + V} + \frac{\frac{\partial}{\partial x}(U - V)}{U + V}. \tag{2.4}$$

U and V are the weighted mobilities

$$\begin{aligned} U &= \mu_{Na^+}C_{Na^+} + \mu_{H^+}C_{H^+} \\ V &= \mu_{Cl^-}C_{Cl^-}. \end{aligned} \tag{2.5}$$

Since the concentrations do not change in the first instant of time after a change ΔI in current, U and V at $t = -0$ and $t = +0$ are the same. The instantaneous change in E is then found from equation (2.4) to be

$$E(x, +0) - E(x, -0) = \frac{\Delta I}{U + V}, \tag{2.6}$$

where $U + V$ have the steady-state values at $t = -0$.

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[4] Calculations have also been carried out for a sodium, potassium, chloride system, and curves are available. The effects show up more strongly for the case with hydrogen, however, and for this reason this case was used here. The computer program has been prepared to accept 10 cations and 10 anions.

[5] All quantities in the graphs are given in dimensional units, omitting the bars over the symbols.

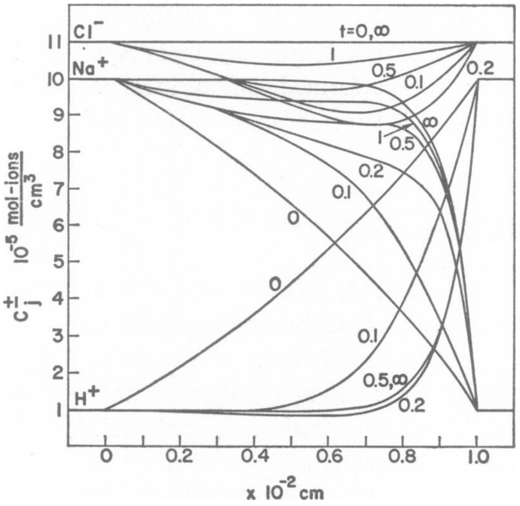

FIGURE 1*a* Concentrations for I(−0) = 0, I(+0) = 0.5 amp/cm², *t* in seconds.

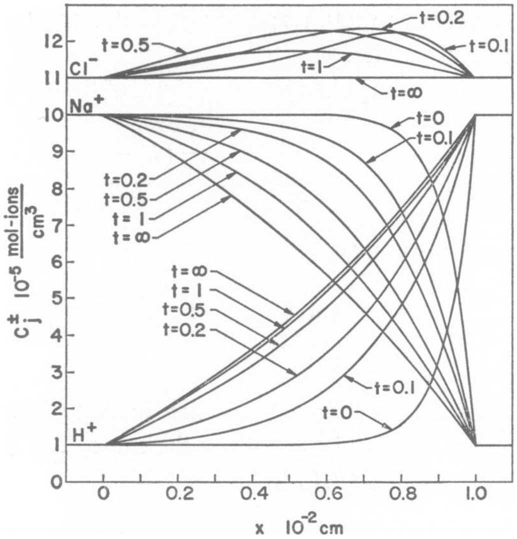

FIGURE 1*b* Concentrations for I(−0) = 0.5, I(+0) = 0 amp/cm², *t* in seconds.

The second term of equation (2.4),

$$E_l(x, t) = \frac{\frac{\partial}{\partial x}(U - V)}{U + V}, \tag{2.7}$$

referred to by Planck as the "local electromotive force," is the same as E for the cases where $I = 0$. This term is exhibited in Fig. 3 for the case in which I goes from

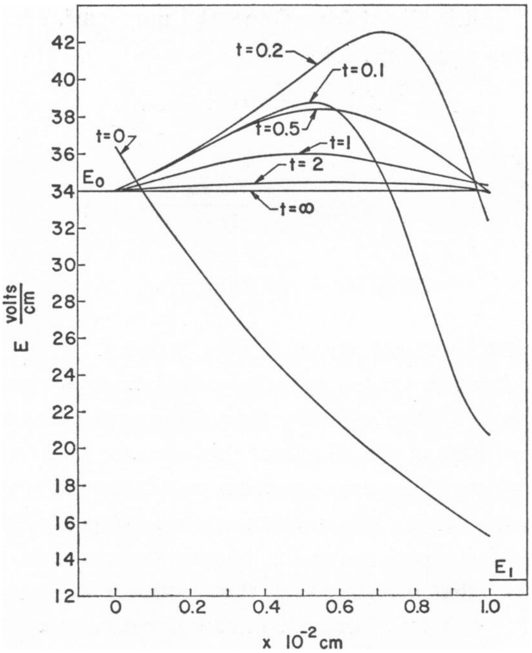

Figure 2 Electric field E in volts/cm for $I(-0) = 0$, $I(+0) = 0.5$ amp/cm², t in seconds.

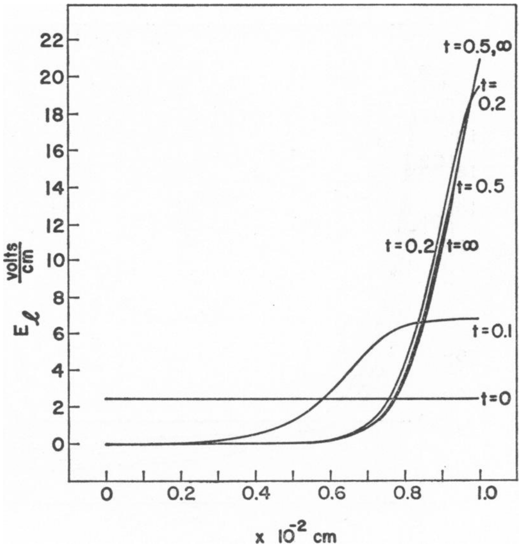

Figure 3 $E_l = (U_x - V_x)/(U + V)$ in volts/cm for $I(-0) = 0$, $I(+0) = 0.5$ amp/cm², t in seconds.

0.0 to 0.5 amp/cm², and in Fig. 4 from 0 to −0.5 amp/cm². The membrane voltage obtained by integrating equation (2.4), is

$$-\Psi_1(t) = I\cdot R(t) + \Psi_{emf}(t) \tag{2.8}$$

where

$$R(t) = \int_0^1 \frac{dx}{U + V} \tag{2.9}$$

$$\Psi_{emf}(t) = \int_0^1 E_l(x, t)\, dx. \tag{2.10}$$

Voltages $-\Psi_1(t)$ and $\Psi_{emf}(t)$ are plotted in Figs. 5 and 6.

The system considered in these particular calculations is symmetrical except for the fact that H+ has a higher mobility than its counterpart Na+. Therefore, the present investigation displays the effects of this asymmetry in ionic mobilities. The most noteworthy feature of the concentration profiles is the temporary decrease in total ion concentration within the membrane following positive current changes (see Fig. 1*a*) and the increase following negative current changes (see Fig. 1*b*). Equation (2.6) shows that the change in the electric field at $t = 0$ is ΔI times the local conductance $(U + V)^{-1}$. For a positive current change, this produces an increase in the electric field which will cause a readjustment of the concentration profiles with Na+ increasing and H+ decreasing inside the membrane. Due to the higher mobility of H+, its outflux is greater than the influx of Na+ so that the total concentration inside the membrane decreases. Then, as E gradually adjusts itself, the

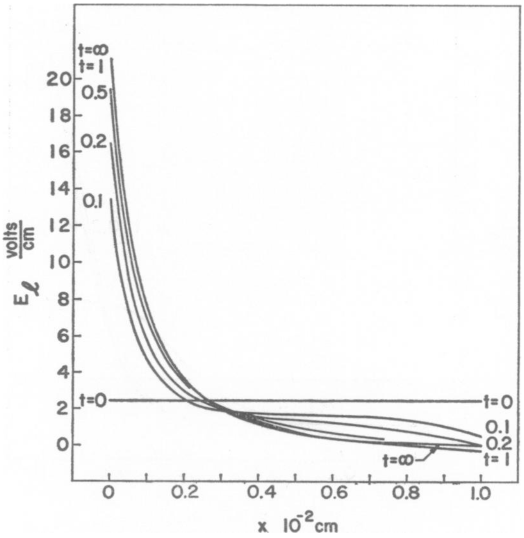

FIGURE 4 $E_l = (U_x - V_x)/(U + V)$ in volts/cm for I(−0) = 0, I(+0) = −0.5 amps/cm², t in seconds.

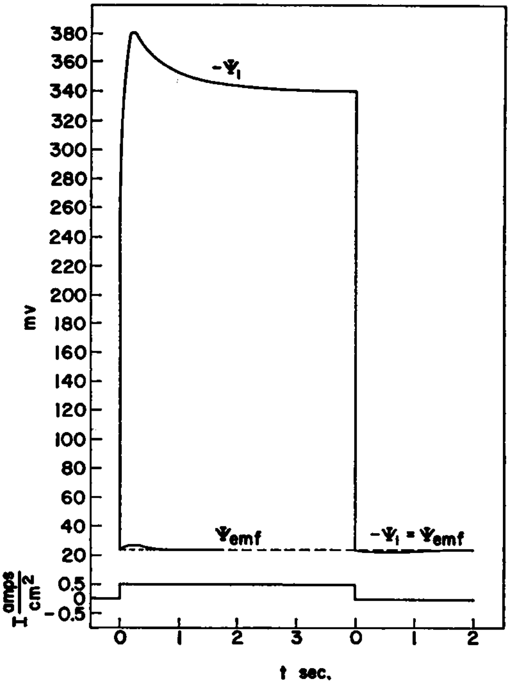

FIGURE 5 Membrane voltage — Ψ_I, and $\Psi_{emf} = \int(U_s - V_s)/(U + V)dx$, in millivolts, response to step-function current I = 0, 0.5, 0 amp/cm^2.

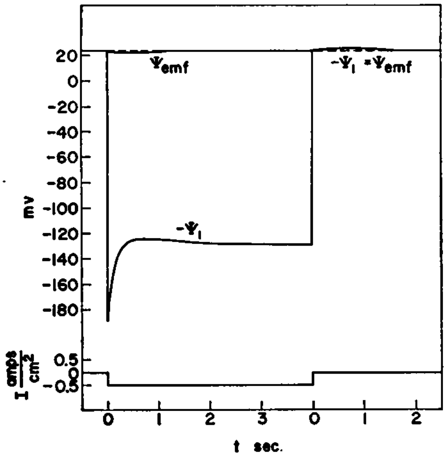

FIGURE 6 Membrane voltage — Ψ_I, and $\Psi_{emf} = \int (U_s - V_s)/(U + V)\, dx$ in millivolts, response to step-function current I = 0, —0.5, 0 amp/cm^2.

Cl^- concentration, temporarily distorted, resumes its steady-state constant profile, and the Na^+ and H^+ fluxes come into balance. In Fig. 5, the voltage curve obtained when I changes from 0 to 0.5 shows the typical inductive-capacitive–like response in going up past the steady-state voltage and approaching it from above. The $I = 0$ to -0.5 case in Fig. 6 is even more interesting. The voltage drops instantaneously to below its steady-state value, but then it rises up past the steady-state value and approaches it from above. The inductive-capacitive–like response has been anticipated and has been found experimentally by Teorell.[6] This behavior may make one suspect that a larger negative current pulse might produce an oscillatory response. It would be difficult to show this here since the concentrations would become so distorted with higher currents that the numerical approximations of the differential equations would require the use of smaller x and t intervals and, therefore, greater storage and machine time requirements. Furthermore, the physical model and the charge neutrality assumption would be less valid for such extreme cases.

The graphs of the total membrane voltage plotted in Figs. 5 and 6 show that the total membrane electromotive force, Ψ_{emf}, is small compared to the resistance term in expression (2.8) for the total membrane voltage. *Therefore, nearly all of the electrical behavior of the membrane is given by the integrated resistance R(t).* The plot of the electric field in Fig. 2, however, shows that the electromotive force part of the electric field $E(x, t)$ makes a sizable contribution to the time changes of $E(x, t)$. It can be seen in Fig. 3 that, while $E_l(x, t)$ integrates to a total voltage close to its steady-state value for all t, it undergoes some rather significant local changes in the course of time and, for some ranges of x, makes a significant contribution to $E(x, t)$. This influences the integrated resistance *via* its effect on the concentration gradients.

Although the results described here are for the laboratory membrane of thickness $l = 10^{-2}$, it is easy to refer to the dimensionless equations to rescale all quantities and observe the results with a different l. The time is scaled with l^2, while the electric field and currents are scaled with l^{-1}. Hence, for a biological membrane with $l = 10^{-6}$ cm, and all other quantities (temperature, concentration, mobility) the same, 1 second would be replaced by 10^{-8} second while 1 amp would be replaced by 10^4 amps. The constant κ changes by 10^8 but is still small enough for the charge neutrality assumption to be valid. From these results, one can conclude that, for a membrane with no properties except the ability to maintain concentrations of salts at its surfaces, the Nernst-Planck equations predict capacitive-inductive responses. It is of some interest to compare the duration of time of these responses with the 1 to 2 nanoseconds response times found in nerve membranes. For the thicknesses of biological membranes, $l = 10^{-6}$ cm, it is seen that the duration of transient effects is 10 to 20 nsec., which is in effect, instantaneous in the millisecond time scale of the nerve membrane measurements.

Finally, it is shown (see Appendix 2) that, for the steady state, charge neutrality holds exactly for the case in which there are equal total concentrations at each boundary whereas with unequal concentrations it is valid for the entire membrane except for thin surface layers.

The computer program, as has been mentioned, can handle a larger number of

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[6] See Teorell, T., *Progr. Biophysics,* 1953, **3,** 341.

ion species. It can also be easily arranged that the mobilities be made functions of time and that the boundary conditions be altered.

APPENDIX 1

NUMERICAL VALUES OF CONSTANTS AND UNITS

The original dimensional system is normalized in the following manner:

$$t = \bar{t}/T_d$$

$$x = \bar{x}/l$$

$$C_i^{\pm} = \bar{C}_i^{\pm}/\bar{C}^{+}(0)$$

$$\Phi_i^{\pm} = \bar{\Phi}_i^{\pm}/f$$

$$\Psi = \bar{\Psi}\Big/\left(\frac{RT}{F}\right)$$

$$E = \bar{E}\Big/\left(\frac{RT}{Fl}\right).$$

The numerical values of the constants in the calculation are:

$$l = 10^{-2}\ \text{cm}$$

$$\bar{\mu}_{\text{Na}} = 0.000456\ \frac{\text{cm}^2}{\text{volt sec.}}$$

$$\bar{\mu}_{\text{H}} = 0.003242\ \frac{\text{cm}^2}{\text{volt sec.}}$$

$$\bar{\mu}_{\text{Cl}} = 0.000676\ \frac{\text{cm}^2}{\text{volt sec.}}$$

$$\bar{C}_{\text{Na}}(0) = 10^{-4},\quad \bar{C}_{\text{Na}}(l) = 10^{-5}\ \text{mol-ions/cm}^3$$

$$\bar{C}_{\text{H}}(0) = 10^{-5},\quad \bar{C}_{\text{H}}(l) = 10^{-4}\ \text{mol-ions/cm}^3$$

$$\bar{C}_{\text{Cl}}(0) = 11 \times 10^{-5},\quad \bar{C}_{\text{Cl}}(l) = 11 \times 10^{-5}\ \text{mol-ions/cm}^3$$

R = 8.3703 coul-volts/mol °K

T = 288°K

RT/F = 0.025 volt

c = 2.99776×10^{10} cm/sec. or esu/abcoul

F = 96,500 coul/farad

ϵ = 79 = dielectric constant of water

Numerical values of the units of the dimensionless equations are:

Mobility : $\bar{\mu}_{\mathrm{Cl}^-} = 0.676 \times 10^{-3}$ cm^2/volt sec.

Concentration : $\bar{C}^+(0) = 11 \times 10^{-5}$ mol-ions/cm^3

Electric potential : $RT/F = 25$ mv

Electric field : $RT/Fl = 2.5$ volts/cm

Ion flux : $f = \bar{\mu}_{\mathrm{Cl}^-}\bar{C}^+(0)\cdot(RT/Fl) = 18.59 \times 10^{-8} \dfrac{\text{mol-ions}}{\text{cm}^2\,\text{sec.}}$

Current : $\sigma = f \times F = 0.01793935$ amp/cm^2

Electric time : $T_e = \dfrac{\epsilon\cdot 10^9}{4\pi c^2 F\bar{C}^+(0)\bar{\mu}_{\mathrm{Cl}^-}} = 9.748924 \times 10^{-10}$ sec.

Diffusion time : $T_d = l^2/(\bar{\mu}_{\mathrm{Cl}^-}RT/F) = 5.91716$ sec.

The value found for κ is

$$\kappa = \frac{T_e}{T_d} = 1.6476 \times 10^{-10}$$

APPENDIX 2

THE STEADY-STATE SOLUTIONS AND SINGULAR PERTURBATION TREATMENT

Summarizing the well known steady-state solution (8), we may write that for the boundary values

$$C_{i0}^\pm = C_i^\pm(0), \qquad C_{i1}^\pm = C_i^\pm(1)$$

the expressions for the concentrations are

$$C_i^\pm(x) = e^{\mp\Psi(x)}\left\{C_{i0}^\pm - \frac{\Phi_i^\pm}{\mu_i^\pm}\int_0^x e^{\pm\Psi(x')}\,dx'\right\} \tag{A.1}$$

where

$$\Phi_i^\pm = \mu_i^\pm\left(C_{i0}^\pm - C_{i1}^\pm e^{\pm\Psi_1}\right)\Big/\int_0^1 e^{\pm\Psi(x)}\,dx \tag{A.2}$$

are the constant (in x) fluxes: It is easy to show that, by summing over all the i's and using the definitions of C^+ and C^-,

$$\frac{dC^\pm}{dx} \mp C^\pm E = A^\pm \tag{A.3}$$

$$A^\pm = \sum_i \Phi_i^\pm/\mu_i^\pm. \tag{A.4}$$

Then, adding and subtracting the "+" and "−" equations of (A.3) and letting $C = C^+ + C^-$, we obtain

$$\frac{dC}{dx} - \kappa E \frac{dE}{dx} = A^+ + A^- = \alpha \tag{A.5}$$

and

$$\kappa \frac{d^2E}{dx^2} - CE = A^+ - A^- = -G. \tag{A.6}$$

Setting $\kappa = 0$ here gives the results already cited in section 2. The constant G can be related to the unknown value of Ψ at $x = 1$, Ψ_1, by

$$\Psi_1 = -\frac{G}{\alpha} \ln \frac{\alpha + \beta}{\beta}$$

where now $\alpha = C(1) - C(0)$ and $\beta = C(0)$. ($\Psi_0 = \Psi(0)$ can be arbitrarily set equal to zero.) The transcendental equation for Ψ_1 can be derived by writing the current in terms of the fluxes given in equation (A.2). For $\kappa = 0$ and with $C(0) = C(1)$, $(\alpha = 0)$, one has[7]

$$I = \Psi_1 \left[\frac{U_0 + V_1 - (U_1 - V_0)e^{\Psi_1}}{e^{\Psi_1} - 1} \right] \tag{A.7}$$

where U_0, U_1 and V_0, V_1 are the values of U and V at $x = 0$ and 1.

For $\kappa \neq 0$, the change which occurs may be examined by using the methods of singular perturbation theory. For κ small, it is convenient to write $\kappa = \epsilon^2$. The general solution for equation (A.5) is

$$C(x) = \alpha_\kappa x + \beta_\kappa + \frac{\kappa}{2} E^2, \tag{A.8}$$

with boundary conditions on C giving

$$\alpha_\kappa = \alpha - \frac{\epsilon^2}{2} (E_1^2 - E_0^2)$$

$$\beta_\kappa = \beta - \frac{\epsilon^2}{2} E_0^2,$$

where E_0 and E_1 are the values of E at $x = 0$ and $x = 1$ as these boundaries are approached from inside the region. They are not known *a priori.* We can rewrite equation (A.6) in the form

$$\epsilon^2 \frac{d^2E}{dx^2} - (\alpha x + \beta)E + \frac{\epsilon^2}{2} \{[E_0^2 + (E_1^2 - E_0^2)x]E - E^3\} + G = 0. \tag{A.9}$$

The non-linearity of this equation makes it difficult to solve exactly. It can be reduced to the equation of Painlevé (7), but the special solutions known for that equation are not particularly useful here. There would be no difficulty in giving a numerical solution, however, parametrically in terms of G. Since the equations for $C_i^\pm$ do not contain κ, the

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[7] This relation was derived by Goldman (9).

$C_j^{\pm}$ and $\Phi_j^{\pm}$ equations, given above, all hold for $\kappa \neq 0$. The only modification is that G must be found so that the E satisfying equation (A.9) with boundary conditions $dE/dx = 0$ at $x = 0$ and 1, when used in the current equation, gives the prescribed current. It should be pointed out here that, for $\alpha = 0$, $E = G/\beta$ is a solution of equation (A.9) for both $\kappa \neq 0$ and $\kappa = 0$ so the steady-state solution obtained in this case is the correct $\kappa \neq 0$ solution, with charge neutrality as a consequence rather than an assumption.

A suitable asymptotic representation (11) has the form

$$E = \sum_{n=0}^{\infty} \epsilon^n u_n + e^{-h(x)/\epsilon} \sum_{n=0}^{\infty} \epsilon^n v_n. \tag{A.10}$$

When this is substituted into equation (A.9), the terms of order $e^{-h(x)/\epsilon}$ require that

$$\left(\frac{dh}{dx}\right)^2 = \alpha x + \beta. \tag{A.11}$$

Both solutions of this equation may be employed with the requirement that

$$\begin{aligned} h^+(0) &= 0 \\ h^-(1) &= 0, \end{aligned} \tag{A.12}$$

where the + and − refer to the signed roots of equation (A.11). We may then write that

$$E = \sum_{n=0}^{\infty} \epsilon^n u_n + e^{-h^+(x)/\epsilon} \sum_{n=0}^{\infty} \epsilon^n v_n + e^{-h^-(x)/\epsilon} \sum_{n=0}^{\infty} \epsilon^n w_n \tag{A.13}$$

with

$$\begin{aligned} h^+(x) &= \frac{2}{3\alpha}\left[(\alpha x + \beta)^{3/2} - \beta^{3/2}\right] \\ h^-(x) &= \frac{2}{3\alpha}\left[(\alpha + \beta)^{3/2} - (\alpha x + \beta)^{3/2}\right]. \end{aligned} \tag{A.14}$$

As can be seen, h^+ and h^- are chosen so that the second and third series of terms in equation (A.13) become important in the neighborhood of $x = 0$ and $x = 1$, respectively. The size of the neighborhood is of the order of ϵ.

The expression (A.13) is now substituted into the differential equation (A.9), and one obtains, by equating terms of various orders, the following results. From terms of order ϵ^0:

$$u_0 = G/(\alpha x + \beta), \tag{A.15}$$

of order ϵ:

$$u_1 = 0, \tag{A.16}$$

of order ϵ^2:

$$u_2 = \frac{(d^2u_0/dx^2) + \frac{1}{2}(E_0{}^2 + (E_1{}^2 - E_0{}^2)x)u_0 - \frac{1}{2}u_0{}^3}{\alpha x + \beta}, \tag{A.17}$$

of order $\epsilon\, e^{-h_{\pm}(x)/\epsilon}$:

$$\frac{dv_0}{dx} + \frac{d^2h^+/dx^2}{2dh^+/dx}\, v_0 = 0, \qquad \frac{dw_0}{dx} + \frac{d^2h^-/dx^2}{2dh^-/dx}\, w_0 = 0. \tag{A.18}$$

The boundary conditions, $dE/dx = 0$ at $x = 0$ and 1, then require $v_0(0) = w_0(0) = 0$ and, since the solutions of equation (A.18) are

$$v_0 = \text{const} \times (dh^+/dx)^{-1/2}, \qquad w_0 = \text{const} \times (dh^-/dx)^{-1/2}, \tag{A.19}$$

these boundary conditions force $v_0(x)$ and $w_0(x)$ to be identically zero. One obtains from terms of order $\epsilon^2 e^{-h\pm(x)/\epsilon}$, the equations,

$$\frac{dv_1}{dx} + \frac{d^2h^+/dx^2}{2dh^+/dx} v_1 = 0, \qquad \frac{dw_1}{dx} + \frac{d^2h^-/dx^2}{2dh^-/dx} w_1 = 0, \tag{A.20}$$

with the conditions

$$v_1(0) = \left[\frac{du_0/dx}{dh^+/dx}\right]_{x=0} = -G\alpha b^{-5/2}$$

$$w_1(1) = \left[\frac{du_0/dx}{dh^-/dx}\right]_{x=1} = G\alpha(\alpha + \beta)^{-5/2}.$$

Thus,

$$v_1(x) = -\frac{G\alpha\beta^{-9/4}}{(\alpha x + \beta)^{1/4}}, \qquad w_1(x) = \frac{G\alpha(\alpha + \beta)^{-9/4}}{(\alpha x + \beta)^{1/4}}. \tag{A.21}$$

The asymptotic representation then becomes

$$E(x) = \frac{G}{\alpha x + \beta}\left\{1 + \epsilon^2 \frac{2\alpha^2(\alpha x+\beta)^{-2} + \frac{1}{2}(E_0{}^2 + (E_1{}^2 - E_0{}^2)x) - \frac{1}{2}G^2(\alpha x+\beta)^{-2}}{\alpha x+\beta} + O(\epsilon^4)\right\}$$
$$+ \left\{-\frac{\epsilon G\alpha}{\beta^{9/4}(\alpha x+\beta)^{1/4}} + O(\epsilon^2)\right\} e^{-h^+(x)/\epsilon} + \left\{\frac{\epsilon G\alpha}{(\alpha+\beta)^{9/4}(\alpha x+\beta)^{1/4}} + O(\epsilon^2)\right\} e^{-h^-(x)/\epsilon}. \tag{A.22}$$

For the evaluation of u_2, the values of E at the boundaries, E_0 and E_1, are required. These differ from the zero order approximation, u_0, at $x = 0$ and 1 by terms of order ϵ. Letting

$$E_0 = \frac{G}{\beta}, \qquad E_1 = \frac{G}{\alpha + \beta}$$

in equation (A.22) necessitates replacing $O(\epsilon^4)$ by $O(\epsilon^8)$ in the first part of equation (A.22). The first and second exponential terms in equation (A.22) are significant only near the left and right boundaries, respectively, and, for $x \approx 0$, the first exponential term can be written

$$-\frac{\sqrt{\kappa}\, G\alpha}{\beta^{5/2}} e^{-x/\sqrt{\kappa}}. \tag{A.23}$$

Letting $\kappa = \bar{\kappa}/l^2$ and $x = \bar{x}/l$, this can be written

$$-\frac{\sqrt{\kappa}\, G\alpha}{\beta^{5/2}} e^{-\bar{x}/\sqrt{\bar{\kappa}}}. \tag{A.24}$$

For the electrolytic solutions of the above problem,

$$\sqrt{\bar{\kappa}} = 1.2835 \times 10^{-7} \text{ cm} \tag{A.25}$$

so that the boundary layer would be approximately 30 A thick,[8] independent of the thickness of the membrane. The separation, in the boundary layer, between E and its approximation u_0 obtained with the charge neutrality assumption, is proportional to α, a measure of the asymmetry of the system and to G, a monotonic function of the current. The meaning of the result is exhibited in Fig. 7 for particular values of α, β, G, and l.

For the transient cases, even when $\alpha = 0$, the electric field E obtained by using the charge neutrality assumption, has a non-zero slope at the membrane surfaces. This indicates that there is a small layer where the correct E departs from the charge neutrality E to acquire the zero slope which it must have to satisfy the Poisson equation at the boundary. A perturbation treatment of this case would also exhibit this.

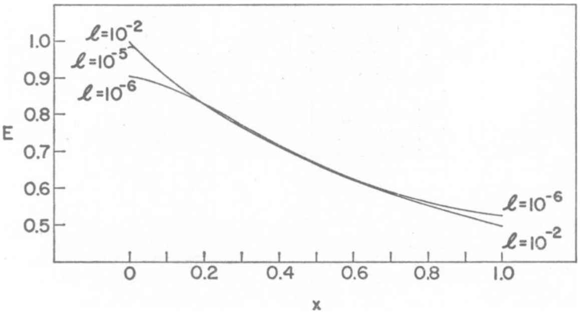

FIGURE 7 Plot of the singular perturbation theory estimate of $E(x)$ with $\alpha = \beta = G = 1$, in dimensionless units, for $l = 10^{-6}$, 10^{-5}, and 10^{-2}.

APPENDIX 3

NUMERICAL METHODS FOR TRANSIENT SOLUTIONS

For the time-dependent solutions, the equations to be solved are, letting primes and dots denote x and t derivatives, respectively,

$$\dot{C}_i^{\pm} = \mu_i^{\pm}(C_i^{\pm\prime\prime} \mp C_i^{\pm\prime}E \mp C_i^{\pm}E') \tag{A.26}$$

$$E = [I + U' - V']/(U + V) \tag{A.27}$$

where

$$U = \sum_{i=1}^{n^+} \mu_i^+ C_i^+ \tag{A.28}$$

$$V = \sum_{i=1}^{n^-} \mu_i^- C_i^-. \tag{A.29}$$

The finite difference equations are formed by defining equidistant points $x_i = ih$, $i = 0, 1, \ldots, N$ on the x-axis and approximating first and second derivatives by the formulas

$$f'(x) = (f(x_{i+1}) - f(x_{i-1}))/2h$$

$$f''(x) = (f(x_{i-1}) + f(x_{i+1}) - 2f(x_i))/h^2.$$

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[8] More precisely, at $\bar{x} = 30$ A the exponential term in equation (A. 16) will be 1/10 its value at the membrane surface, $x = 0$.

Thus, equation (A.26) can be expressed, letting $C_{jk}^{\pm}(x) = C_j^{\pm}(x, t_k)$, the index k denoting the time level,

$$\dot{C}_{jk}{}^{\pm}(x_i) = \mu_j{}^{\pm}\left[\frac{C_{jk}{}^{\pm}(x_{i+1}) - 2C_{jk}{}^{\pm}(x_i) + C_{jk}{}^{\pm}(x_{i-1})}{h^2}\right.$$

$$\left. \mp \frac{C_{jk}{}^{\pm}(x_{i+1}) - C_{jk}{}^{\pm}(x_{i-1})}{2h} E_k(x_i) \mp C_{jk}{}^{\pm}(x_i)E_k{}'(x_i)\right]. \qquad \text{(A.30)}$$

For the time-wise integration, the time-axis is divided into equal "major" time intervals $\Delta t = t_\kappa - t_{\kappa-1}$. Then, each Δt is divided into equal "minor" time intervals $\delta t = t_{k+1} - t_k$ with δt selected for each major time interval on the basis of the integration error of the integration formula. Each time step starts with an open integration,

$$C_{jk+1}{}^{\pm}(x_i) = C_{jk}{}^{\pm}(x_i) + \delta t\,\dot{C}_{jk}{}^{\pm}(x_i),$$

calculating $\dot{C}^{\pm}{}_{jk}$ with equation (A.30) using known data at time t_k. The resulting $C^{\pm}{}_{jk+1}$'s are used in equation (A.27) to determine an estimate of E_{k+1}. This E_{k+1} is used in a closed integration with the formula

$$C_{jk+1}{}^{\pm}(x_i) = C_{jk}{}^{\pm}(x_i) + \frac{\delta t}{2}\,[\dot{C}_{jk}{}^{\pm}(x_i) + \dot{C}_{jk+1}{}^{\pm}(x_i)], \qquad \text{(A.31)}$$

which is performed as follows: Putting all unknown $C^{\pm}{}_{jk+1}$'s on the left side of the equation puts equation (A.31) in the form of a tridiagonal system of equations in the $C^{\pm}{}_{jk+1}$'s:

$$-\frac{\delta t}{2}\,\mu_j{}^{\pm}\left[\frac{1}{h^2} \pm \frac{E_k(x_i)}{2h}\right]C_{jk+1}{}^{\pm}(x_{i-1}) + \left[1 + \frac{\delta t \mu_j{}^{\pm}}{2}\left(\frac{2}{h^2} \pm E'(x_i)\right)\right]C_{jk+1}{}^{\pm}(x_i)$$

$$-\frac{\delta t}{2}\,\mu_j{}^{\pm}\left[\frac{1}{h^2} \mp \frac{E_k(x_i)}{2h}\right]C_{jk+1}{}^{\pm}(x_{i+1}) = C_{jk}{}^{\pm}(x_i) + \frac{\delta t}{2}\,\dot{C}_{jk}{}^{\pm}(x_i). \qquad \text{(A.32)}$$

With the estimated E_{k+1} substituted in equation (A.32) these are solved for a new set of values of $C^{\pm}{}_{jk+1}$ which is then used to revise the estimate of E_{k+1}. This cycle is repeated until two successive estimates of the solution are sufficiently close by a convergence criterion on the $C^{\pm}{}_{jk+1}$'s.

The error in the integration formula (A.31) is

$$e_{jk}(x_i) = \frac{(\delta t)^2}{12}\,(\ddot{C}_{jk}{}^{\pm}(x_i) - \ddot{C}_{jk+1}{}^{\pm}(x_i)). \qquad \text{(A.33)}$$

The δt for the first major time interval is supplied to the program, but after that, δt is revised at the end of each major time interval.

The $\dot{C}^{\pm}{}_{jk}$'s at the last three k-levels of each major time interval are used to estimate the t-derivative terms in equation (A.33). Then, δt for the next major time interval is taken so that the maximum e_{jk} is less than a preassigned quantity. The time step δt was also taken to be so small that no more than three or four iterations on the closed integration were necessary.

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