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Transport of Ions of One Kind through Thin Membranes

II. Nonequilibrium Steady-State Behavior

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Summary. The equation for steady-state movement of ions of one kind through planar membranes has been solved. Numerical results are given, as well as profiles of potential, field and concentration. For small deviations from the equilibrium potential, an essentially constant intrinsic membrane conductance is obtained, which can be calculated from equilibrium properties. For larger deviations from equilibrium, the intrinsic membrane conductance is still essentially constant for symmetrical interfacial concentrations of the permeable ion, but varies significantly with potential for asymmetric interfacial concentrations, especially if these concentrations are small. In the latter case, one can often use the constant field approximation, for which explicit expressions are presented.

In a preceding paper (de Levie & Moreira, 1972, hereafter called Part I), we have discussed the equilibrium solutions of the basic equation for transport of ions of one kind through a thin membrane,

$$\frac{dE}{dS}+\frac{1}{2}E^2=i\,s+A. \tag{1}$$

We will now consider the more general case in which current flows. Some formal solutions of Eq. (1) were obtained by Skinner (1955) and will be used as our point of departure. Alternative derivations were subsequently given by Wright (1961) and by Sinharay and Meltzer (1964). By analogy with the treatment in Part I, three separate cases must be considered; namely, $is+A \gtreqless 0$.

Introduction of the new variables

$$y \equiv -\frac{E}{(y\,i)^{\frac{1}{3}}} \tag{2}$$

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and

$$z \equiv \frac{is+A}{(2i^2)^{\frac{1}{3}}} \tag{3}$$

transforms Eq. (1) into the Ricatti equation

$$\frac{dy}{dz} - y^2 + z = 0. \tag{4}$$

When $z > 0$, the solution of Eq. (4) is

$$y = -z^{\frac{1}{2}} \frac{C_1 I_{\frac{2}{3}}(\alpha) + C_2 I_{-\frac{2}{3}}(\alpha)}{C_1 I_{-\frac{1}{3}}(\alpha) + C_2 I_{\frac{1}{3}}(\alpha)} \tag{5}$$

$$\alpha \equiv \tfrac{2}{3} z^{\frac{3}{2}} = \frac{\sqrt{2}}{3i} (is+A)^{\frac{3}{2}} \tag{6}$$

whereas one obtains for $z < 0$

$$y = -(-z)^{\frac{1}{2}} \frac{C_1 J_{\frac{2}{3}}(\beta) - C_2 J_{-\frac{2}{3}}(\beta)}{C_1 J_{-\frac{1}{3}}(\beta) + C_2 J_{\frac{1}{3}}(\beta)} \tag{7}$$

$$\beta \equiv \tfrac{2}{3} (-z)^{\frac{3}{2}} = \frac{\sqrt{2}}{3i} (-is-A)^{\frac{3}{2}}. \tag{8}$$

In Eq. (7), $J_\nu(\beta)$ denotes a Bessel function of order ν and real argument β; likewise, in Eq. (5), $I_\nu(\alpha)$ represents a modified Bessel function of order ν and real argument α. The dimensionless field E follows directly from Eqs. (2) and (5) or (7), and the corresponding expressions for the dimensionless potential φ or the dimensionless concentration γ are obtained through use of the Poisson equation; *see* Eq. (I-6)[1].

The More Symmetrical Case, $is + A < 0$

From Eq. (7) we obtain

$$\varphi = -2 \ln \left(\frac{\beta}{\beta_0}\right)^{\frac{1}{3}} \frac{p J_{-\frac{1}{3}}(\beta) + J_{\frac{1}{3}}(\beta)}{p J_{-\frac{1}{3}}(\beta_0) + J_{\frac{1}{3}}(\beta_0)} \tag{9}$$

$$\beta_0 = \beta_{s=0} = \frac{(-2A)^{\frac{3}{2}}}{6i} \tag{10}$$

$$E = \frac{i}{|i|} \sqrt{2(-is-A)} \frac{p J_{\frac{2}{3}}(\beta) - J_{-\frac{2}{3}}(\beta)}{p J_{-\frac{1}{3}}(\beta) + J_{\frac{1}{3}}(\beta)} \tag{11}$$

$$\gamma = (-is-A) \left\{ \left(\frac{p J_{\frac{2}{3}}(\beta) - J_{-\frac{2}{3}}(\beta)}{p J_{-\frac{1}{3}}(\beta) + J_{\frac{1}{3}}(\beta)} \right)^2 + 1 \right\}. \tag{12}$$

For $s = 0$, Eq. (12) yields

$$\gamma_0 = -A \left\{ \left(\frac{p J_{\frac{2}{3}}(\beta_0) - J_{-\frac{2}{3}}(\beta_0)}{p J_{-\frac{1}{3}}(\beta_0) + J_{\frac{1}{3}}(\beta_0)} \right)^2 + 1 \right\}. \tag{13}$$

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[1] The notation Eq. (I-6) refers to Eq. (6) in Part I.

In Eq. (9) we have already implied that $\varphi=0$ for $s=0$. For $s=1$ we have

$$v=-2\ln\left(\frac{\beta_1}{\beta_0}\right)^{\frac{1}{3}}\frac{p\,J_{-\frac{1}{3}}(\beta_1)+J_{\frac{1}{3}}(\beta_1)}{p\,J_{-\frac{1}{3}}(\beta_0)+J_{\frac{1}{3}}(\beta_0)} \tag{14}$$

$$\beta_1=\beta_{s=1}=\frac{\sqrt{2}}{3i}(-i-A)^{\frac{3}{2}} \tag{15}$$

so that the integration constant p can be expressed as

$$p=\frac{\beta_0^{\frac{1}{3}}J_{\frac{1}{3}}(\beta_0)-e^{v/2}\beta_1^{\frac{1}{3}}J_{\frac{1}{3}}(\beta_1)}{e^{v/2}\beta_1^{\frac{1}{3}}J_{-\frac{1}{3}}(\beta_1)-\beta_0^{\frac{1}{3}}J_{-\frac{1}{3}}(\beta_0)}. \tag{16}$$

The Less Symmetrical Case, $is+A>0$

Eq. (5) now yields

$$\varphi=-2\ln\left(\frac{\alpha}{\alpha_0}\right)^{\frac{1}{3}}\frac{q\,I_{-\frac{1}{3}}(\alpha)+I_{\frac{1}{3}}(\alpha)}{q\,I_{-\frac{1}{3}}(\alpha_0)+I_{\frac{1}{3}}(\alpha_0)} \tag{17}$$

$$\alpha_0=\alpha_{s=0}=\frac{(2A)^{\frac{3}{2}}}{6i} \tag{18}$$

$$E=\frac{i}{|i|}\sqrt{2(is+A)}\,\frac{q\,I_{\frac{2}{3}}(\alpha)+I_{-\frac{2}{3}}(\alpha)}{q\,I_{-\frac{1}{3}}(\alpha)+I_{\frac{1}{3}}(\alpha)} \tag{19}$$

$$\gamma=(is+A)\left\{\left(\frac{q\,I_{\frac{2}{3}}(\alpha)+I_{-\frac{2}{3}}(\alpha)}{q\,I_{-\frac{1}{3}}(\alpha)+I_{\frac{1}{3}}(\alpha)}\right)^2-1\right\} \tag{20}$$

$$\gamma_0=A\left\{\left(\frac{q\,I_{\frac{2}{3}}(\alpha_0)+I_{-\frac{2}{3}}(\alpha_0)}{q\,I_{-\frac{1}{3}}(\alpha_0)+I_{\frac{1}{3}}(\alpha_0)}\right)^2-1\right\} \tag{21}$$

$$v=-2\ln\left(\frac{\alpha_1}{\alpha_0}\right)^{\frac{1}{3}}\frac{q\,I_{-\frac{1}{3}}(\alpha_1)+I_{\frac{1}{3}}(\alpha_1)}{q\,I_{-\frac{1}{3}}(\alpha_0)+I_{\frac{1}{3}}(\alpha_0)} \tag{22}$$

$$\alpha_1=\alpha_{s=1}=\frac{\sqrt{2}}{3i}(i+A)^{\frac{3}{2}} \tag{23}$$

$$q=\frac{\alpha_0^{\frac{1}{3}}I_{\frac{1}{3}}(\alpha_0)-e^{v/2}\alpha_1^{\frac{1}{3}}I_{\frac{1}{3}}(\alpha_1)}{e^{v/2}\alpha_1^{\frac{1}{3}}I_{-\frac{1}{3}}(\alpha_1)-\alpha_0^{\frac{1}{3}}I_{-\frac{1}{3}}(\alpha_0)}. \tag{24}$$

The Intermediate Cases Including $is+A=0$

The solution for $is+A=0$ is identical to that given in Part I under $A=0$, and need not be repeated here. It might be noticed that the crossover between the three sets of solutions for $is+A\lesseqgtr 0$ will, in general, occur at some place inside the membrane, since the condition $is+A=0$ can only be met at one particular value of s when $i\neq 0$. At that value of s, Eqs. (I-44) to (I-46) apply. At such a cross-over in the mathematical description, the potential, the field and the ionic concentration must all be continuous functions of s.

When $A<0$ but $A+i>0$, it is convenient to combine Eqs. (17) and (22) into

$$\varphi=v-2\ln\left(\frac{\alpha}{\alpha_1}\right)^{\frac{1}{3}}\frac{q\,I_{-\frac{1}{3}}(\alpha)+I_{\frac{1}{3}}(\alpha)}{q\,I_{-\frac{1}{3}}(\alpha_1)+I_{\frac{1}{3}}(\alpha_1)}. \tag{25}$$

As s approaches $-A/i$ and α and β go to zero, continuity of φ as expressed by Eqs. (9) and (25) yields

$$v=-2\ln\left(\frac{\alpha_1}{\beta_0}\right)^{\frac{1}{3}}\frac{p}{q}\,\frac{q\,I_{-\frac{1}{3}}(\alpha_1)+I_{\frac{1}{3}}(\alpha_1)}{p\,J_{-\frac{1}{3}}(\beta_0)+J_{\frac{1}{3}}(\beta_0)}. \tag{26}$$

Likewise, continuity of the fields expressed by Eqs. (11) and (19) requires

$$p=-q \tag{27}$$

and insertion of this result into Eq. (26) yields

$$p=\frac{\left(\frac{\alpha_1}{\beta_0}\right)^{\frac{1}{3}}e^{v/2}\,I_{\frac{1}{3}}(\alpha_1)+J_{\frac{1}{3}}(\beta_0)}{\left(\frac{\alpha_1}{\beta_0}\right)^{\frac{1}{3}}e^{v/2}\,I_{-\frac{1}{3}}(\alpha_1)-J_{-\frac{1}{3}}(\beta_0)}. \tag{28}$$

When $A>0$ but $A+i<0$, we combine Eqs. (9) and (14) into

$$\varphi=v-2\ln\left(\frac{\beta}{\beta_1}\right)^{\frac{1}{3}}\frac{p\,J_{-\frac{1}{3}}(\beta)+J_{\frac{1}{3}}(\beta)}{p\,J_{-\frac{1}{3}}(\beta_1)+J_{\frac{1}{3}}(\beta_1)}. \tag{29}$$

Comparison of Eqs. (17) and (29) at $s=A/i$ (so that $\alpha, \beta\to 0$) results in

$$v=-2\ln\left(\frac{\beta_1}{\alpha_0}\right)^{\frac{1}{3}}\frac{q}{p}\,\frac{p\,J_{-\frac{1}{3}}(\beta_1)+J_{\frac{1}{3}}(\beta_1)}{q\,I_{-\frac{1}{3}}(\alpha_0)+I_{\frac{1}{3}}(\alpha_0)} \tag{30}$$

which can be combined with Eq. (27) to yield

$$p=\frac{\left(\frac{\alpha_0}{\beta_1}\right)^{\frac{1}{3}}e^{-v/2}\,I_{\frac{1}{3}}(\alpha_0)+J_{\frac{1}{3}}(\beta_1)}{\left(\frac{\alpha_0}{\beta_1}\right)^{\frac{1}{3}}e^{-v/2}\,I_{-\frac{1}{3}}(\alpha_0)-J_{-\frac{1}{3}}(\beta_1)}. \tag{31}$$

Numerical Evaluation

As in Part I, solutions are sought for fixed interfacial concentrations γ_0 and γ_1. For given values of γ_0, γ_1 and i, and an initial estimate for A, all needed (normal and modified) Bessel functions are first calculated,

Table 1. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = \gamma_1 = 0.01$ [a]

i	A	v	g	g_{cf}
0	−0.0099 8752	0	0.0100	0.0100
$2 \cdot 10^{-8}$	−0.0099 8753	0.0000 0201	0.0100	0.0100
$2 \cdot 10^{-7}$	−0.0099 8762	0.0000 2002	0.0100	0.0100
$2 \cdot 10^{-6}$	−0.0099 8801	0.0002 0016	0.0100	0.0100
$2 \cdot 10^{-5}$	−0.0099 9552	0.0020 0257	0.0100	0.0100
$2 \cdot 10^{-4}$	−0.0098 8719	0.0200 1666	0.0100	0.0100
$2 \cdot 10^{-3}$	0.0090 4579	0.2001 6645	0.0100	0.0100
$2 \cdot 10^{-2}$	1.9831 4297	2.0015 6435	0.0100	0.0100
0.2	199.9801 086	20.0044 9920	0.0100	0.0100
0.5	1,249.9806 66	50.0047 9949	0.0100	0.0100

[a] Equilibrium data are shown for comparison under $i=0$, and the conductances calculated with the constant-field approximation are listed under g_{cf}.

Table 2. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = 0.0001$, $\gamma_1 = 0.01$ [a]

i	A	v	g	g_{cf}
$-5 \cdot 10^{-2}$	12.3590 1426	−4.9683 1627	0.00522	0.00522
$-2 \cdot 10^{-2}$	1.2845 0794	−1.6005 1222	0.00322	0.00322
$-1 \cdot 10^{-2}$	0.0001 4814	−0.0205 6984	0.00216	0.00216
$-2 \cdot 10^{-3}$	3.0663 8925	2.4773 2725	0.00094	0.00094
$-2 \cdot 10^{-4}$	8.9108 3423	4.2220 9103	0.00052	0.00052
0	10.6016 4689	4.6051 7019	0.00047	0.00047
$2 \cdot 10^{-5}$	10.8031 5590	4.6487 1887	0.00046	0.00046

[a] *See* footnote a, Table 1.

Table 3. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = \gamma_1 = 1$

i	A	v	g	g_{cf}
0	−0.8925 2241	0	0.9262	1.0000
$2 \cdot 10^{-6}$	−0.8925 2346	0.0000 0216	0.9262	1.0000
$2 \cdot 10^{-5}$	−0.8925 3246	0.0000 2159	0.9262	1.0000
$2 \cdot 10^{-4}$	−0.8926 2244	0.0002 1594	0.9262	1.0000
$2 \cdot 10^{-3}$	−0.8935 2068	0.0021 5938	0.9262	1.0000
$2 \cdot 10^{-2}$	−0.9022 8974	0.0215 9346	0.9262	1.0000
0.2	−0.9692 5327	0.2159 2348	0.9263	1.0000
0.5	−0.9716 7021	0.5396 6331	0.9265	1.0000
1	−0.8121 7183	1.0783 1486	0.9274	1.0000
2	0.4133 5989	2.1492 8486	0.9305	1.0000
5	10.5985 2129	5.2928 9089	0.9447	1.0000

Table 4. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = 0.01$, $\gamma_1 = 1$

i	A	v	g	g_{cf}
−5.0	15.4820 7947	−5.2398 9384	0.5079	0.5224
−4.0	9.9380 9324	−4.1588 6941	0.4564	0.4691
−3.0	5.3889 0496	−3.0165 2353	0.3936	0.4038
−2.0	1.9238 8696	−1.7402 7215	0.3152	0.3224
−1.0	0.0252 6656	−0.1009 2322	0.2125	0.2162
−0.75	0.0381 8944	0.4545 5317	0.1807	0.1835
−0.50	0.5240 2852	1.1533 7100	0.1449	0.1468
−0.25	2.1538 9682	2.1699 3468	0.1027	0.1038
−0.10	4.9379 3728	3.2113 9748	0.0717	0.0724
−0.02	8.6851 0150	4.2189 7507	0.0518	0.0522
0	10.3931 1056	4.6051 7019	0.0462	0.0465
0.002	10.5966 9499	4.6490 5591	0.0456	0.0459
0.02	12.8150 6805	5.1028 5192	0.0402	0.0405
0.10	50.4072 7144	10.0563 3909	0.0183	0.0184
0.20	199.9801 887	20.0069 7134	0.0130	0.0130

Table 5. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = \gamma_1 = 100$

i	A	v	g	g_{cf}
0	−11.8844 8548	0	18.7822	100.00
$2 \cdot 10^{-4}$	−11.8845 9040	0.0000 1065	18.7823	100.00
$2 \cdot 10^{-3}$	−11.8854 9043	0.0001 0648	18.7823	100.00
$2 \cdot 10^{-2}$	−11.8944 9043	0.0010 6483	18.7823	100.00
$2 \cdot 10^{-1}$	−11.9844 9051	0.0106 4911	18.7809	100.00
2	−12.8780 0157	0.1064 7913	18.7830	100.00
20	−21.2413 6327	1.0604 3586	18.8602	100.00
50	−33.0326 9491	2.5995 5250	19.2341	100.00
100	−48.1174 6254	4.9352 7511	20.2623	100.00
200	−68.4789 5759	8.8315 1456	22.6462	100.00

Table 6. Dimensionless current i, voltage v, conductance g and integration constant A calculated for $\gamma_0 = 1$, $\gamma_1 = 100$

i	A	v	g	g_{cf}
−100	51.9467 0732	−4.3077 0494	11.2197	21.6220
−75	34.0278 0983	−2.9761 7399	9.8927	18.3549
−50	17.5846 0106	−1.4122 1875	8.3093	14.6841
−20	1.8128 0956	1.1398 4478	5.7715	9.4002
−2	0.4440 8012	4.0236 9371	3.4395	5.2213
−0.2	1.8595 4357	4.5413 3467	3.1331	4.7101
0	2.0647 1068	4.6051 7019	3.0981	4.6517
0.02	2.0858 4696	4.6116 3312	3.0946	4.6458

using the criteria $A \lessgtr 0$ and $A+i \lessgtr 0$. Asymptotic expansions are used for arguments with absolute magnitudes larger than 40, otherwise the normal ascending series are used. Subsequently, v is calculated by a Newton-Raphson iteration for γ_1, using the appropriate formalism (e.g., Eqs. (12) and (16) for the case $A<0$, $A+i<0$) and this value of v is then used to calculate $(\gamma_0)_{\text{calc}}$. When $(\gamma_0)_{\text{calc}} < \gamma_0$, A is incremented (and likewise A is decremented when $(\gamma_0)_{\text{calc}} > \gamma_0$) and the calculation repeated, until

$$|(\gamma_0)_{\text{calc}} - \gamma_0| < 10^{-8}\, \gamma_0.$$

(In the few cases in which $(d^2\gamma/ds^2)_{s=0} < 0$, the change in A is in the direction opposite to that mentioned above.) Most calculations were restricted to the experimentally accessible range $-5 \lesssim v \lesssim +5$, and were performed on an IBM 360-40 computer of the Georgetown University Computation Center.

Some numerical results are shown in Tables 1 through 6. These represent calculations with either symmetrical (1, 3, 5) or asymmetrical (2, 4, 6) interfacial concentrations, and at either low (1, 2), medium (3, 4) or high (5, 6) ionic concentrations. Some corresponding profiles of dimensionless concentration, electric field and potential across the membrane are shown in Figs. 1 through 4.

We will first discuss those results for which the excursions from equilibrium are small, subsequently those obtained at low ionic concentrations, and finally the general results at medium and high concentrations.

Results for Small Deviations from Equilibrium

For all currents for which v is close to its equilibrium value, $v_{\text{eq}} = \ln \gamma_1/\gamma_0$, the dimensionless potential v varies with i in an essentially linear fashion. After subtraction of v_{eq}, a direct proportionality is obtained. Thus, for small deviations from equilibrium, the intrinsic current-voltage curve of the membrane is linear when we consider the quantity $v - v_{\text{eq}}$ as the effective dimensionless voltage, analogous to the dimensionless overvoltage $-nF\eta/RT$ in conventional electrochemistry. We use the term "intrinsic" here to denote that the interfacial concentrations γ_0 and γ_1 are considered to be constant. Note that mass transport in the aqueous solutions adjacent to the membrane can greatly affect the overall current-voltage curves (LeBlanc, 1969, 1971) as can the double layers in those aqueous solutions (McLaughlin, Szabo, Eisenman & Ciani, 1970; McLaughlin, Szabo & Eisenman, 1971). Such complications are not considered here, but will be taken up in Part III.

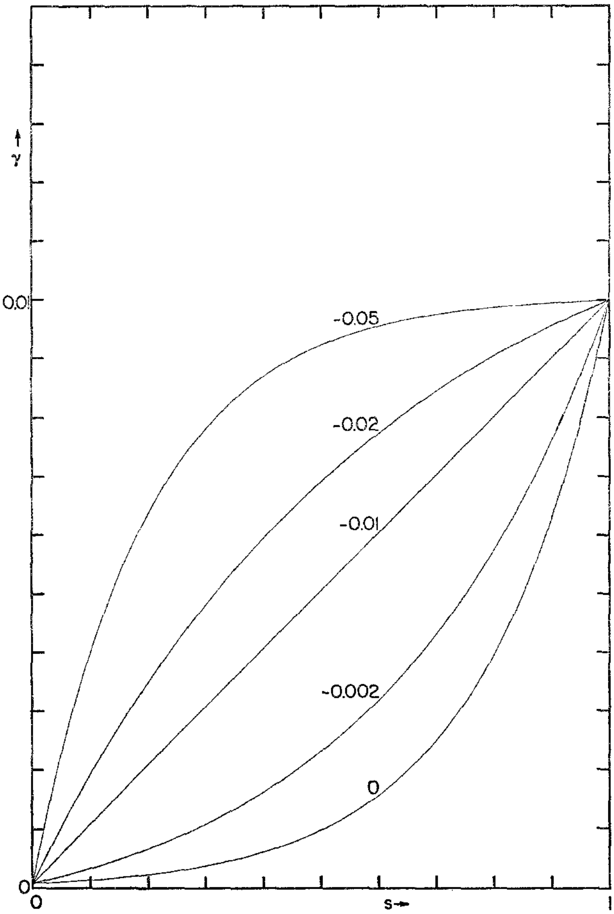

Fig. 1 A

Fig. 1. Profiles of dimensionless concentration γ, field E and potential φ across the membrane ($0 \leqq s \leqq 1$) for $\gamma_0 = 10^{-4}$, $\gamma_1 = 10^{-2}$ and various values of i as indicated with each curve. The curves were calculated from the data in Table 2, but are indistinguishable from curves calculated using the constant-field approximation, Eqs. (47)–(55)

Since the intrinsic current-voltage curve is linear for $v - v_{\mathrm{eq}} \ll 1$, it is useful to define a dimensionless intrinsic membrane conductance as

$$g \equiv \frac{i}{v - v_{\mathrm{eq}}}. \tag{32}$$

Clearly, for small deviations from equilibrium, we have

$$g \approx g_{\mathrm{eq}} \tag{33}$$

and it is worthwhile to consider the equilibrium behavior of g in more detail.

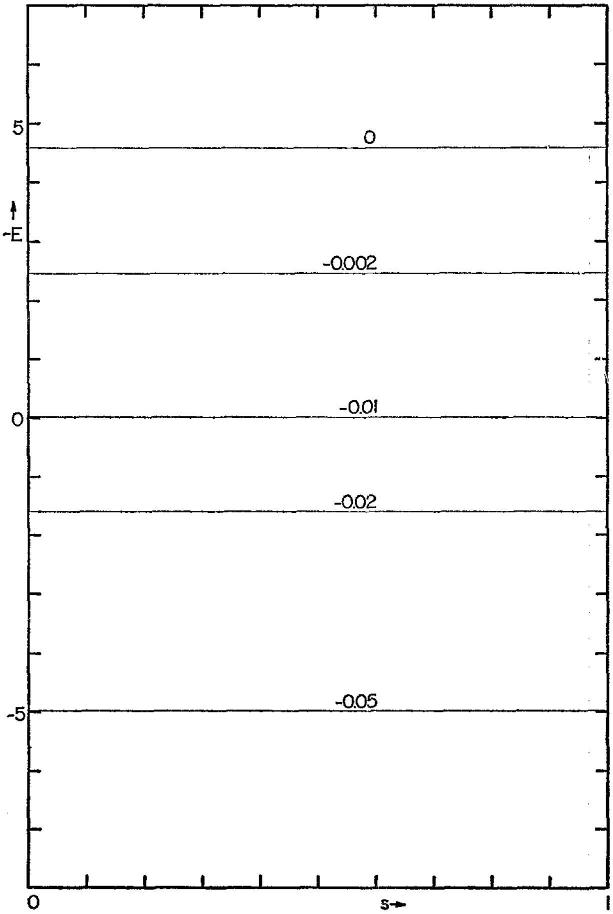

Fig. 1 B

The Intrinsic Equilibrium Conductance

We write the Nernst-Planck relation, Eq. (I-1), in dimensionless form as

$$i = -\frac{d\gamma}{ds} + \gamma \frac{d\varphi}{ds} \tag{34}$$

or, after rearrangement,

$$\frac{i}{\gamma} ds = -d \ln \gamma + d\varphi. \tag{35}$$

Since i is independent of s, integration yields

$$i \int_0^1 \frac{ds}{\gamma} = -\ln \frac{\gamma_1}{\gamma_0} + v = v - v_{\text{eq}} \tag{36}$$

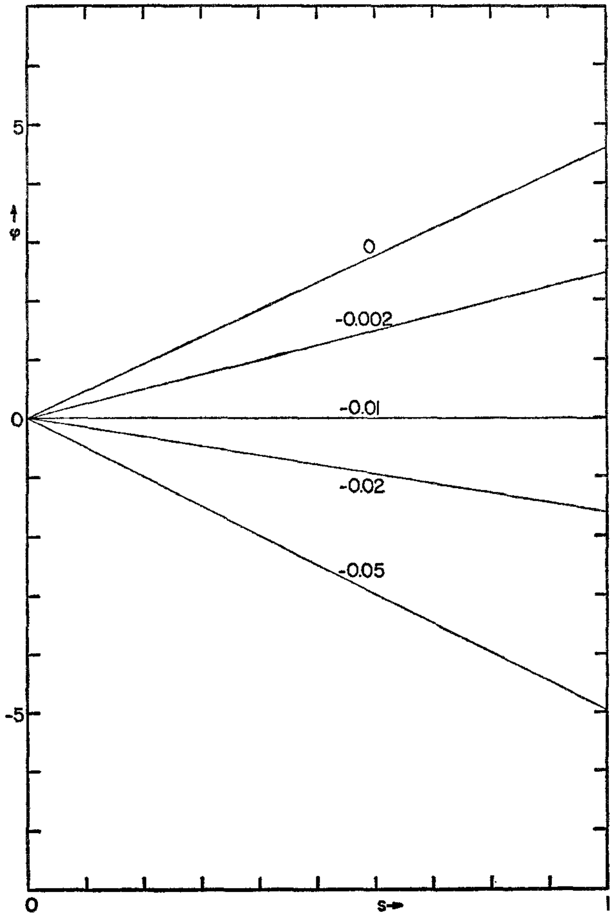

Fig. 1 C

so that the intrinsic membrane conductance can be defined, in dimensionless form, as

$$g \equiv \frac{i}{v - v_{\text{eq}}} = \frac{1}{\int\limits_0^1 \frac{ds}{\gamma}}. \tag{37}$$

This result (Teorell, 1953; Eisenman, Ciani & Szabo, 1968) clearly shows that g remains finite and well-defined when $v - v_{\text{eq}}$ and consequently i approach zero. Pertinent new aspects for the steady-state current-voltage behavior are that $g \approx g_{\text{eq}}$ for $|v - v_{\text{eq}}| \ll 1$ and that g_{eq} can be obtained directly from the equations given in Part I. Integration of Eq. (I-30) yields for the more symmetrical case ($A < 0$)

$$g_{\text{eq}} = \frac{2b^2(p^2+1)}{\int\limits_0^1 (p \sin bs + \cos bs)^2 \, ds} = \frac{4b\gamma_0}{2b(1+p^2) + (1-p^2)\sin 2b + 4p \sin^2 b} \tag{38}$$

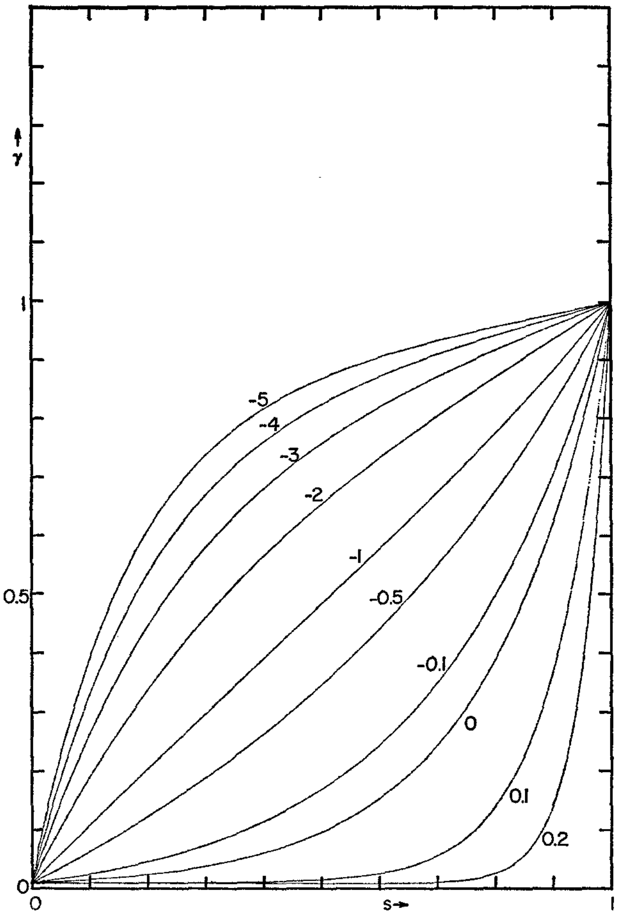

Fig. 2 A

Fig. 2. Profiles of dimensionless concentration γ, field E and potential φ across the membrane ($0 \leqq s \leqq 1$) for $\gamma_0 = 10^{-2}$, $\gamma_1 = 1$ and various values of i as indicated with each curve. The curves were calculated from the data in Table 4

whereas one obtains for the less symmetrical case ($A > 0$)

$$g_{\mathrm{eq}} = \frac{2a^2(q^2-1)}{\int\limits_0^1 (q \sinh as + \cosh as)^2 \, ds} = \frac{4a\gamma_0}{2a(1-q^2)+(1+q^2)\sinh 2a + 4q \sinh^2 a}. \tag{39}$$

For the special case $A = 0$ one finds

$$g_{\mathrm{eq}} = \frac{2}{\int\limits_0^1 (s+r)^2 \, ds} = \frac{6}{3r^2+3r+1}. \tag{40}$$

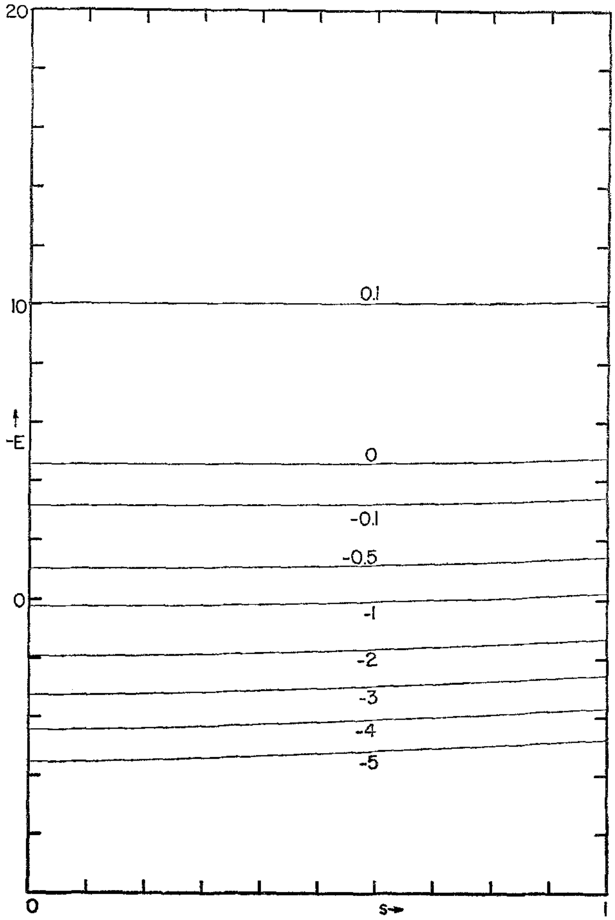

Fig. 2 B

The dependence of g_{eq} on γ_0 at constant equilibrium potential is shown in Fig. 5, and some numerical values are listed in Table 7. Clearly, g_{eq} is directly proportional to γ_0 as long as neither γ_0 nor γ_1 exceed 0.1, a result which also follows from the use of Eq. (I-55) which is applicable at such low concentrations:

$$g_{eq} = \frac{\gamma_0}{\int\limits_0^1 \gamma_0^s \gamma_1^{-s}\, ds} = \frac{\gamma_0 v_{eq}}{1 - e^{-v_{eq}}} = \frac{\gamma_0 \gamma_1 \ln \gamma_1/\gamma_0}{\gamma_1 - \gamma_0}. \tag{41}$$

For $\gamma_0 \approx \gamma_1 \leqq 0.1$, either this result or use of Eq. (I-59) leads to

$$g_{eq} = \gamma_0. \tag{42}$$

Conversion of this result into dimensional form yields

$$\frac{G}{c_0} = \frac{n^2 F^2 D}{RTd} \tag{43}$$

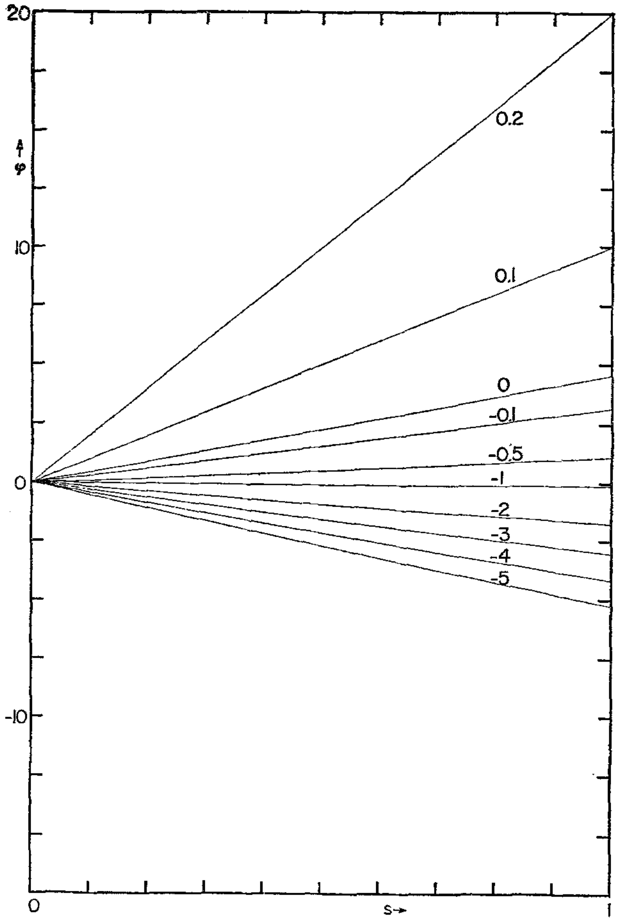

Fig. 2 C

which suggests a numerical value of the order of 10^7 cm Ω^{-1} mole^{-1} at room temperature if one assumes $D = 10^{-6}$ cm^2 sec^{-1} and $d = 50$ Å. In Eq. (36), G denotes the intrinsic equilibrium conductance, in Ω^{-1} cm^{-2}, and c_0 the interfacial concentration of ions just inside the membrane, in moles cm^{-3}. Note that, at least in principle, Eq. (42) allows us to estimate the single-ion partition coefficient from the intrinsic membrane conductance, the bulk ionic concentration in the aqueous phase in contact with the membrane, and the membrane charge density.

At high concentrations, g_{eq} approaches the limiting value $4\pi^2$, regardless of the value of the equilibrium potential v_{eq}. This follows directly from substitution into Eq. (37) of the high-concentration approximations $b \to \pi$ and $p \to \frac{1}{\pi}\sqrt{\frac{\gamma_0}{2}}$ of Eqs. (I-61) and (I-62). Thus,

$$g_{\lim} = 4\pi^2 \tag{44}$$

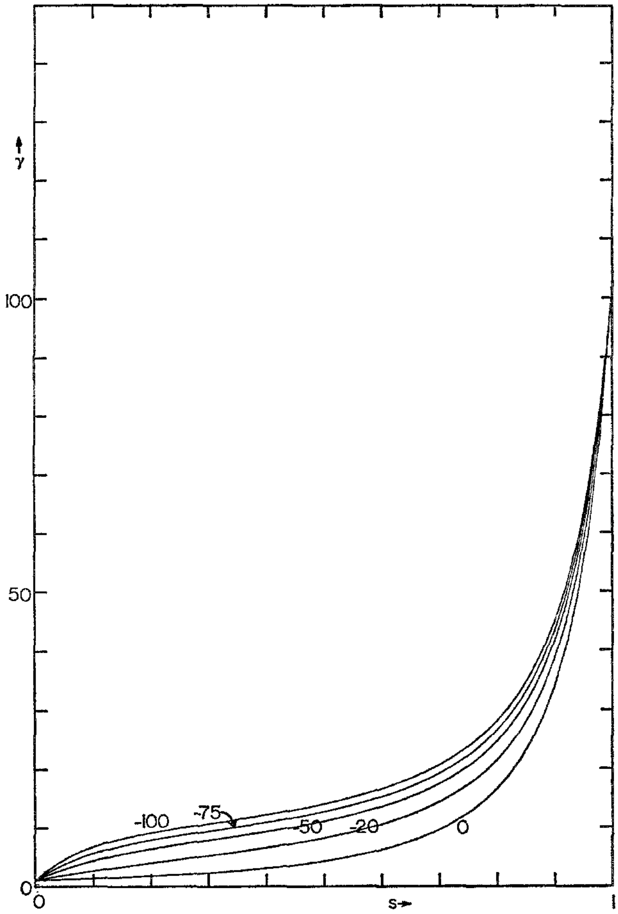

Fig. 3 A

Fig. 3. Profiles of dimensionless concentration γ, field E and potential φ across the membrane ($0 \leqq s \leqq 1$) for $\gamma_0 = 1$, $\gamma_1 = 10^2$ and various values of i as indicated with each curve. The curves were calculated from the data in Table 6

and

$$G_{\lim} = \frac{\pi D \varepsilon}{d^3} \tag{45}$$

which leads to an estimated limiting intrinsic membrane conductance of the order of $50\ \Omega^{-1}\ \mathrm{cm}^{-2}$ when one assumes $D = 10^{-6}\ \mathrm{cm}^2\ \mathrm{sec}^{-1}$, $\varepsilon_{\mathrm{rel}} = 2$ and $d = 50$ Å. The limiting conductance occurs because, at high ionic concentrations, an increase in γ_0 and γ_1 is accompanied by a compensating decrease in the thicknesses of the space charge layers inside the membrane.

Eqs. (43) and (45) were already obtained by Neumcke and Läuger (1970), who only considered the case $A < 0$.

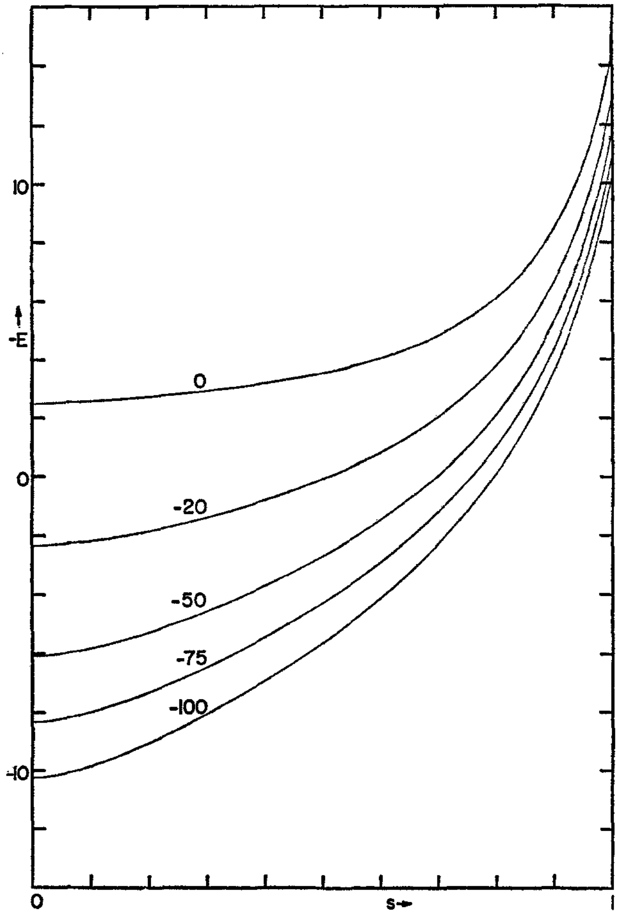

Fig. 3 B

Results for Low Ionic Concentrations: The Constant-Field Approximation

For low ionic concentrations ($\gamma \ll 1$), the mathematical treatment can be simplified greatly (Mott, 1939). We combine Eqs. (I-6) and (I-8) into

$$-\gamma+\tfrac{1}{2}E^2=is+A. \tag{46}$$

For small values of both γ and i we have

$$\tfrac{1}{2}E^2 \approx A \tag{47}$$

so that the field E is approximately constant, and integration of $d\varphi/ds=-E$ for constant E yields

$$v \equiv \varphi_1-\varphi_0 \approx -E. \tag{48}$$

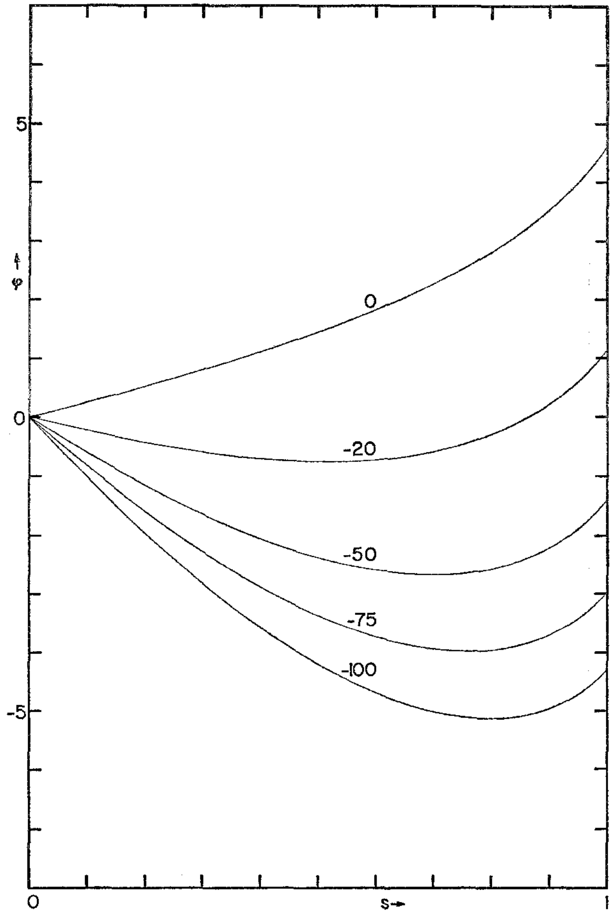

Fig. 3 C

We now combine this result with Eq. (34)

$$-i=\frac{d\gamma}{ds}-\gamma\frac{d\varphi}{ds}=\frac{d\gamma}{ds}+E\gamma=\frac{d\gamma}{ds}-v\gamma \tag{49}$$

which can be written as

$$d\ln\left(\gamma-\frac{i}{v}\right)=d(v\,s) \tag{50}$$

and can thus be integrated (Mott, 1939) to yield

$$\gamma=\left(\gamma_0-\frac{i}{v}\right)e^{v\,s}+\frac{i}{v}. \tag{51}$$

Substitution of $\gamma=\gamma_1$ at $s=1$ results in

$$\gamma_1=\left(\gamma_0-\frac{i}{v}\right)e^{v}+\frac{i}{v} \tag{52}$$

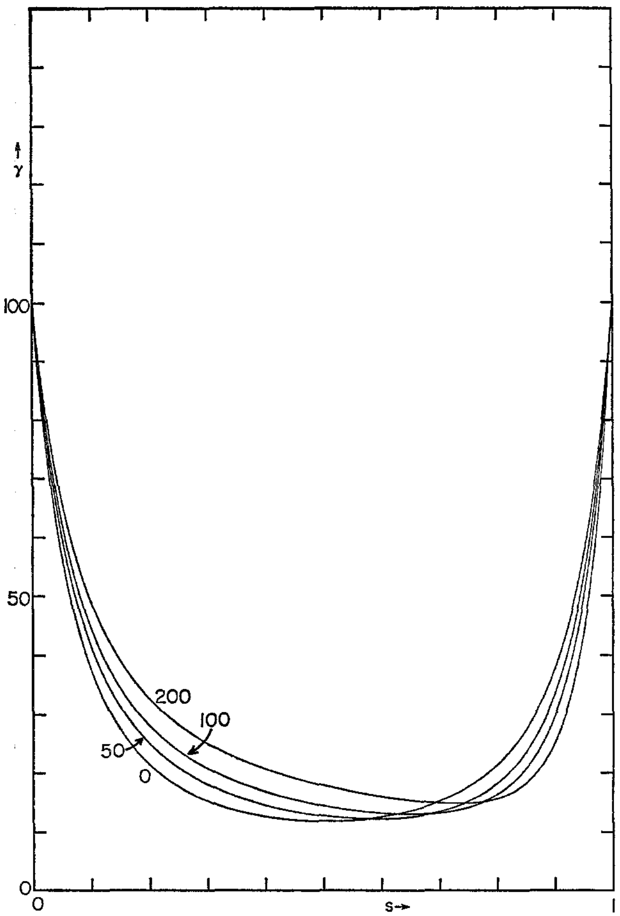

Fig. 4 A

Fig. 4. Profiles of dimensionless concentration γ, field E and potential φ across the membrane ($0 \leqq s \leqq 1$) for $\gamma_0 = \gamma_1 = 10^2$ and various values of i as indicated with each curve. The curves were calculated from the data in Table 5

from which i/v can be eliminated to obtain (Cole, 1965)

$$\gamma = \frac{(\gamma_0 - \gamma_1)\, e^{v s} + \gamma_1 - \gamma_0\, e^{v}}{1 - e^{v}}. \tag{53}$$

One readily verifies that the equilibrium condition $\gamma_1 = \gamma_0 e^{v}$ converts Eq. (53) into Eq. (I-55).

Finally, the intrinsic conductance g is obtained from

$$g = \frac{1}{\int_0^1 \frac{ds}{\gamma}} = \frac{(\gamma_1 - \gamma_0\, e^{v})\, v}{(1 - e^{v})(v - \ln \gamma_1/\gamma_0)}. \tag{54}$$

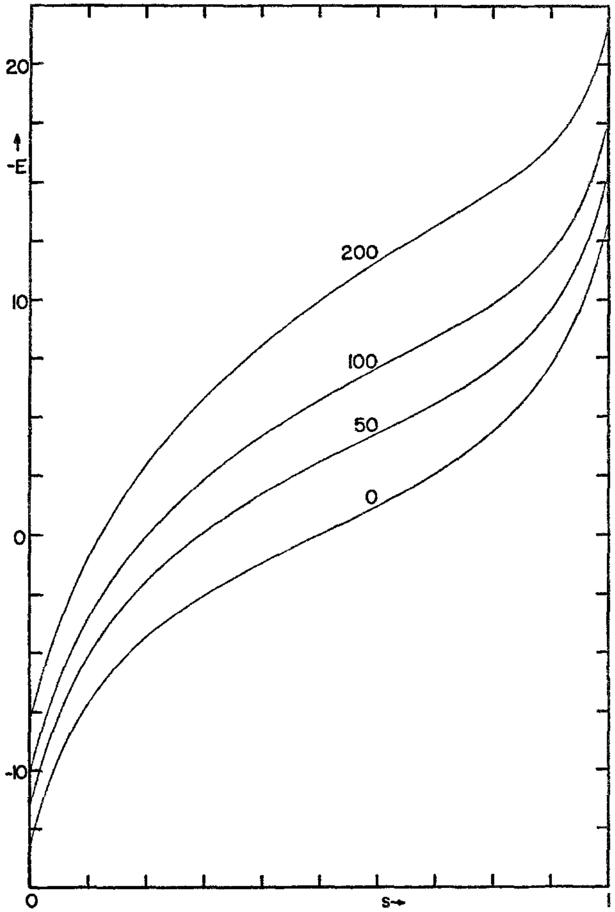

Fig. 4 B

The same result can also be derived from Eq. (52) since

$$\frac{i}{v}=\frac{\gamma_1-\gamma_0 e^v}{1-e^v} \tag{55}$$

so that

$$g=\frac{i}{v-v_{\mathrm{eq}}}=\frac{i}{v}\,\frac{v}{v-v_{\mathrm{eq}}}=\frac{\gamma_1-\gamma_0 e^v}{1-e^v}\,\frac{v}{v-\ln\gamma_1/\gamma_0}. \tag{54}$$

Using Eq. (55) one can calculate v for any given values of γ_0, γ_1 and i (e.g., with a Newton-Raphson approach), and subsequently find g from Eq. (54). Intrinsic conductances thus calculated are compared with the more exact computer calculations (which do not assume constancy of E) in Tables 1 through 6. For symmetrical boundary concentrations, $\gamma_0=\gamma_1$, Eq. (54) reduces to $g=\gamma_0$ [*compare* Eq. (42)] whereas for vanishingly small currents, g approaches $\gamma_0 v_{\mathrm{eq}}/(1-e^{-v_{\mathrm{eq}}})$ [*see* Eq. (41)].

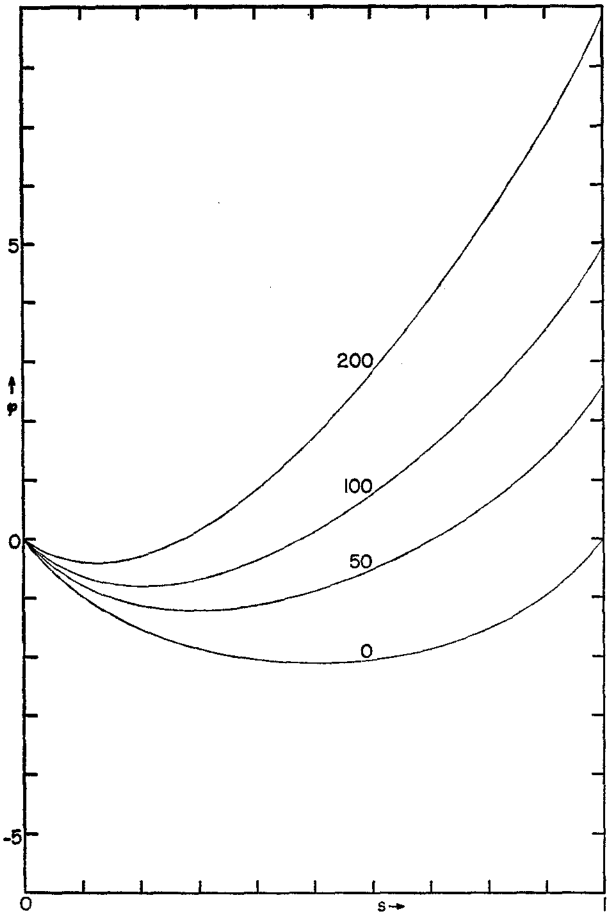

Fig. 4 C

The data in Tables 1 and 2 show that the constant-field approximation provides an excellent representation of the data for $\gamma \ll 1$, and the same conclusion can be drawn from Fig. 1. The constant-field approximation will still be adequate for most purposes when $\gamma \lesssim 1$ (*see* Tables 3 and 4 and Fig. 2).

Results for High Ionic Concentrations

For $\gamma \gg 1$, the constant-field approximation is no longer applicable. With symmetrical interfacial concentrations, $\gamma_0 = \gamma_1$, the intrinsic membrane conductance remains essentially constant and equal to its equilibrium value g_{eq} even though the concentration profiles are affected by the flow of current (*see* Fig. 4).

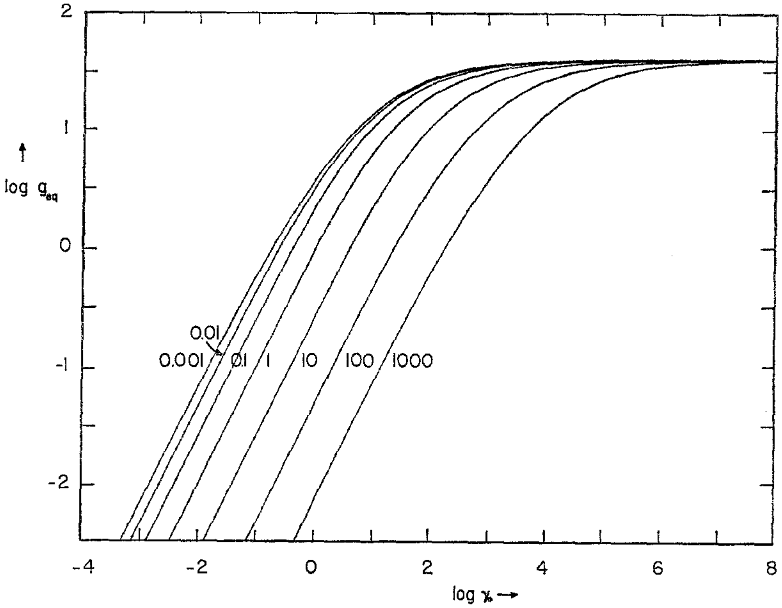

Fig. 5. The dimensionless equilibrium conductance g_{eq} as a function of γ_0 and of the ratio γ_0/γ_1 as indicated with each curve

For the asymmetric case (*see* Fig. 3), g is not constant but varies less (as a function of v) than at low concentrations. The data suggest that the intrinsic membrane conductance becomes essentially constant (and thus equal to the limiting value of g_{eq}) at sufficiently high ionic concentrations.

Discussion

The foregoing calculations and numerical examples have illustrated the essential features of the simple model used: ions of one kind permeating under the influence of a gradient in the electrochemical potential through a thin, homogeneous film. Eqs. (25)–(31) complete the earlier results of Skinner (1955) who did not consider the mixed cases and consequently appears to have reached an erroneous conclusion as to the origin of the negative impedances. Perusal of pairs of i and A listed in Tables 1–6 shows that all but Table 1 contain at least one example of the mixed case. (In Table 1, such a transition will occur between $i = 2 \times 10^{-4}$ and $i = 2 \times 10^{-3}$.) The application of a sufficiently high voltage (and the corresponding passage of current) to an otherwise symmetrical ionic distribution can render the membrane sufficiently "asymmetrical" to make A positive. Thus, the

Table 7. Values of the equilibrium membrane conductance g_{eq} calculated for constant γ_0 and varying ratio of γ_1/γ_0 using Eqs. (31) and (32)

γ_1/γ_0	$\gamma_0=10^{-2}$	$\gamma_0=10^{-1}$	$\gamma_0=1$	$\gamma_0=10$	$\gamma_0=10^2$	$\gamma_0=10^3$
0.01	0.0004 6513	0.0046 4800	0.0461 5418	0.4337 7317	3.0980 8927	12.4022 3693
0.02	0.0007 9828	0.0079 7484	0.0789 6747	0.7255 0458	4.7198 5287	15.9776 3189
0.05	0.0015 7642	0.0157 3909	0.1549 5957	1.3628 5600	7.6025 0495	20.6100 0404
0.1	0.0025 5778	0.0255 1942	0.2496 0551	2.0960 0182	10.2144 5125	23.7236 8698
0.2	0.0040 2212	0.0400 8973	0.3884 8779	3.0737 3016	12.9777 7635	26.3496 9421
0.5	0.0069 2741	0.0689 1168	0.6559 1194	4.7006 4113	16.4759 3685	29.0374 6529
1	0.0099 9168	0.0991 7759	0.9262 0613	6.0835 8816	18.7822 1613	30.5383 2372
2	0.0138 4670	0.1370 3219	1.2485 7301	7.4745 4558	20.7024 8202	31.6647 1112
5	0.0200 8131	0.1976 1079	1.7260 8848	9.1512 0491	22.6466 6629	32.7121 7294
10	0.0255 1942	0.2496 0551	2.0960 0182	10.2144 5125	23.7236 8698	33.2579 2979
20	0.0314 2272	0.3048 3138	2.4467 2275	11.0780 6777	24.5281 8380	33.6512 6987
50	0.0396 9863	0.3792 1869	2.8501 8333	11.9346 9113	25.2735 1336	34.0055 4447
100	0.0461 5418	0.4337 7317	3.0980 8927	12.4022 3693	25.6876 7660	34.1859 9467

symmetry considerations implied in the present paper as well as in Part I must be used with care.

For low ionic concentrations in the membrane ($\gamma \ll 1$), the constant-field approximation provides an excellent description of the electrical properties of the membrane. However, this approximation is not valid at $\gamma > 1$. Under symmetrical boundary conditions, $\gamma_0 = \gamma_1$, the conductance is essentially constant and equal to its equilibrium value, even for $\gamma \neq 1$. The equilibrium conductance exhibits a limiting value.

The present description of the "passive" electrical response of a conducting membrane is still quite incomplete. In Part III we will therefore incorporate the above results in a discussion of the membrane plus its adjacent solution layers, and in Part IV we will focus on the transient response.

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