

Theory of space-charge polarization and electrode-discharge effects

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A combined, general treatment of intrinsic and extrinsic conduction in a liquid or solid is presented. Positive and negative species of mobile charge of arbitrary valences and mobilities are assumed present, together with homogeneous immobile charge in the extrinsic case. The general equations are specialized to a one-dimensional situation and then to that where both position-dependent static and much smaller sinusoidally time-varying components of charge, field, and current are simultaneously present. Sufficiently general boundary conditions are used that any condition from complete blocking to free discharge of positive and negative mobile carriers separately can occur at the electrodes. For the flat-band condition (zero static field; in the binary electrolyte case, coincidence of the zero charge potential and the equilibrium potential) exact equivalent circuits and an exact expression for the small-signal impedance are obtained. Relatively simple, closed-form expressions for the zero-frequency limiting values, C_{i0} and R_{i0} , of the two frequency-dependent elements which appear in the equivalent circuit, C_i and R_i , are derived even in general cases. The dependence of the normalized quantities C_{iN0} and R_{iN0} on detailed boundary conditions, mobility ratio, valence ratio, temperature, and impurity doping level is examined in detail, reserving examination of frequency and temperature dependence of C_{iN} and R_{iN} themselves for later publication. Even for complete blocking of charges of both sign, C_{i0} and R_{i0} are not both intensive (interface) quantities unless the electrode separation contains many Debye lengths and the mobility and valence ratios are equal. When charges of one sign are completely blocked and those of the other partially or completely free to discharge, neither C_{i0} nor R_{i0} is generally intensive, and C_{i0} may be many orders of magnitude larger than the completely blocking, diffuse-double-layer value. The dependence of C_{iN0} and R_{iN0} on all the above parameters is quite different in the extrinsic conduction case depending upon whether the discharging species involves majority or minority carriers.

I. INTRODUCTION

The early ac space-charge polarization theories of Macdonald¹ and Friauf² have been applied to a wide variety of experimental situations.²⁻¹⁹ In many of these instances, however, the actual experimental conditions have not corresponded well with some of the underlying theoretical assumptions. Here, therefore, a more general theory will be developed which will apply to a wider class of materials of interest.

The theory of Ref. 1 assumed the presence of only a single species of positive charge carriers, concentration p , and a single species of negative charge carriers, concentration n . Arbitrary mobilities were assumed, together with an arbitrary amount of dissociation of n and p from a neutral center uniformly distributed in the material under equilibrium conditions. The treatment was one dimensional and involved plane-parallel electrodes separated by a distance l . The electrodes were taken completely blocking to the mobile charge carriers. Friauf's slightly later theory² made the same assumptions except that partial blocking²⁰ was included as well as complete blocking. Such partial blocking employed the Chang-Jaffé²¹ boundary conditions and can account for discharge of mobile carriers at the electrodes,²² often involving electrode reactions,^{10,22,23} a Faradaic process.²⁴

It was explicitly stated in Ref. 1 that it applied only to intrinsic and to complete impurity types of situations. For such conditions only two species of carriers are present. In the intrinsic case (e.g., dissociation of

a solute in a strong liquid electrolyte, ionization of an F center, intrinsic conduction in a semiconductor, etc.), it is assumed that both the charged center after dissociation and the charged dissociated species may be mobile. When the dissociated center is taken immobile, one has the usual complete-impurity situation. In such a case, which is the limit of extrinsic conduction when the extrinsic concentration divided by the intrinsic concentration approaches infinity, the minority carrier has a vanishingly small concentration.

Many authors who have applied the above theories to their data have found less than satisfactory agreement between theory and experiment. Frequently, however, they have applied either the two-mobile intrinsic results or the one-mobile complete impurity results to a general extrinsic conduction situation. As I shall show, such a misapplication can indeed lead to unsatisfactory results.

Let N_D and N_A denote the concentrations of uniformly distributed neutral donors and acceptors in a material. Then N_D^+ and N_A^- represent the concentration of charged centers after some dissociation has occurred. (See Sec. II for a symbol glossary.) Note especially that N_D and N_A can not only represent the concentrations of Group III and V atoms in a Group IV semiconductor, for example, but they can also represent the concentrations of neutral species which dissociate to multiply valent charged species. For example, consider the uniform addition of CaBr_2 to a KBr single crystal.¹⁸ One obtains Ca^{2+} ions in substitutional K^+ positions. In

thermal equilibrium, both positive and negative ion vacancies will be present, with the negative ion vacancies the minority species. Taking the smearing of ionic charge in an ionic crystal into account, one may regard the doped material as containing uniformly distributed, essentially immobile, univalent positive charges (from Ca^{2+}) and possibly mobile, univalent positive and negative species, the vacancies.

In the general extrinsic case where both donors and acceptors are simultaneously present, there will be at least four distinct charged species present. In most cases of practical interest, however, the concentration of either donors or acceptors strongly dominates that of the other. It will be sufficient to define $N_e \equiv N_D^+ - N_A^-$ as the net concentration of charged donor-acceptors. We shall assume these centers, charged or uncharged, are immobile compared to other charged species present. Note that full dissociation of impurity dopants is not assumed here since N_e represents just the charged part of the dissociated concentration, partial or full.

Those authors who have neglected the minority carriers in a strongly extrinsic situation have not always made a bad approximation when the electrodes are completely blocking. On the other hand, for the more probable experimental situation of partial blocking, neglect of minority carriers (the use of the complete-impurity-case theory instead of a general extrinsic theory) can indeed be a poor approximation. This is particularly the case when the minority carriers (even when present in very low concentration) are the only ones that can discharge and the majority carriers are completely blocked.^{25,26}

It is surprising that no general extrinsic theory has been given until now. Apparently, the need for it has been largely unrecognized because it was implicitly or intuitively felt that low-concentration minority carriers could have no important effect, even in a partial-blocking discharge situation. Ninomiya and Sonoike²⁷ have presented the elements of a partial-blocking, complete-impurity-case theory but give insufficient details of their calculation to allow its results to be adequately assessed. Beaumont and Jacobs⁷ have published a more complete treatment of such a theory and have found it insufficient to explain their general extrinsic situation. Baker and Buckle¹² generalized the theory of Ref. 1 to include arbitrary valences (especially appropriate in liquid electrolytes and fused salts), but their treatment has been severely criticized.²⁸ Considerable further analysis and extension of the completely and partially blocked intrinsic theories^{1,2} (for equal mobilities) has been recently published,^{22,23,28} and papers discussing the detailed frequency-response results of the present general theory for intrinsic²⁹ and extrinsic³⁰ conditions will be published separately.

All the ac theories discussed herein thus far assume a flat-band condition at equilibrium. No static external potential is applied; no direct current flows; and the

static components of charge are assumed to maintain their bulk thermal equilibrium values right up to the electrodes. Although the general ac theory is quite complicated even with these simplifying approximations, it is orders of magnitude more complicated when they are relaxed. Later I hope to publish results applying when these approximations are removed; for the present they will be omitted from the general equations developed but included in the final ac solution as usual.

All these theories are formally limited to apply only for a low-voltage region defined by $V_1^* \equiv eV_1/kT \lesssim 1$, where V_1 is the amplitude of the applied sinusoidal voltage; e is the proton charge; k is Boltzmann's constant; and T is the absolute temperature. Theory suggests that considerably different results should be obtained for $V_1^* \gg 1$, but experimental results frequently show little sensitivity to the value of V_1^* over a considerable range of $V_1^* > 1$. Many authors have tried to explain this puzzling result by positing either insulating or exhaustion-depletion regions in the material next to the electrodes or poor contacts, leading to actual air gaps.^{3,11,15,19,31-33} It seems safe to assert, however, that thus far the full reasons for the above behavior have not been unambiguously determined and they may, in fact, differ from case to case. In the present work, this same restriction will be applicable, although the theory may possibly apply reasonably adequately to some experimental results for which $V_1^* > 1$.

The present treatment and those discussed above are, of course, all idealizations which apply only under limited conditions. Some of the restrictions have been discussed, e.g., in Refs. 1, 22, 23, and 31. Here it is worthwhile to mention restriction to nondegenerate conditions, omission of charge carrier size effects, and omission of compact double layer effects, including specific adsorption, when the treatment is applied to electrolytes. The theoretical equations, which are developed herein primarily for the case of an arbitrary static applied potential difference together with a much smaller sinusoidal P.D., are more general than earlier ones because (a) any intrinsic-extrinsic condition is included; (b) static space-charge regions present near the electrodes even in the absence of any applied P.D. are accounted for; (c) mobile-charge mobilities and valences are taken arbitrary; and (d) arbitrary values of boundary-condition parameters are employed. The final ac-only solution of these equations presented herein retains the generality of (a), (c), and (d) but drops (b), since only in the resulting flat-band case can explicit, closed-form results be obtained.

II. LIST OF SYMBOLS

A. Major Subscripts

- | | |
|-----|--|
| e | Denotes thermal equilibrium |
| f | Denotes field-free conditions and thus a position-independent quantity |

i	Designates an intrinsic or "interface" quantity; also used as index with $i=n$ or p	N	$(n/z_n n_{ef}); (29)$
n	Designates quantity associated with negative, mobile charged species	ΔN	$(N - N_e); (43)$
p	Designates quantity associated with positive, mobile charged species	N_A	Concentration of uniformly distributed immobile neutral acceptors
r	Value of a quantity at the reference temperature T_r	N_D	Concentration of uniformly distributed immobile neutral donors
M	Designates the value of a quantity evaluated at the electrode, where $Y=M$ and $x=l$	N_e	$(N_D^+ - N_A^-)$; concentration of net, charged, dissociated impurities
\bar{M}	Designates the value of a quantity evaluated at the $Y = -M$ electrode	P	$(p/z_p p_{ef}); (28)$
N	Normalization of impedances and resistances with R_∞ , of admittances and conductances with $G_\infty \equiv R_\infty^{-1}$, and of capacitances with C_g	ΔP	$(P - P_e); (41)$
P	A parallel quantity	R_D	G_D^{-1}
S	A series quantity	R_E	Frequency-independent series resistance·unit area; G_E^{-1}
T	Stands for "total"	R_i	"Interface" series resistance·unit area; associated with Z_i ; (88)
0	Designates either a static quantity or the zero-frequency limit of a frequency-dependent quantity	R_S	$(R_E + R_i)$
1	Designates the amplitude of a sinusoidally varying quantity	R_∞	G_∞^{-1}
∞	The value of a quantity in the limit of high frequencies (i.e., $\Omega \gg 1$)	T	Absolute temperature
		V	Applied voltage
		V_D	Diffusion potential
		X	Normalized length; x/L_D ; (25)
		Y	$(X - M)$; (39)
		Y_i	Z_i^{-1}
		Y_T	Total admittance/unit area of the system; (83)
		Y_2	$(Y_T - G_\infty - i\omega C_g)$; (84)
		Z_i	"Interface" impedance·unit area; (88), (A49)
		Z_T	Y_T^{-1}

B. Major Superscripts

\cdot	Indicates differentiation with respect to τ
$'$	Indicates differentiation with respect to X or Y
$*$	Normalization of potentials with kT/e , fields with kT/eL_D , and concentrations with n_i or p_i
$-$	A negatively charged quantity
$+$	A positively charged quantity

C. Major Symbols in Text

A number in parentheses indicates the equation where the symbol is first used or defined.

C_g	Geometric capacitance/unit area; $\epsilon/4\pi l$; (30)	a	$(\delta_p^2/\epsilon_p) + (\delta_n^2/\epsilon_n)$; (A4)
C_i	"Interface" capacitance/unit area; the series capacitance associated with Z_i ; (89)	c	$(\delta_n/\epsilon_n) - (\delta_p/\epsilon_p)$; (A6)
C_P	Total parallel capacitance/unit area; associated with Y_T ; (87). Note: $C_{P0} \equiv C_0 \equiv C_{i0} + C_g$	e	Protonic charge
D_i	Diffusion coefficient; for positive carriers $i=p$, for negative $i=n$; (8)	h	Enthalpy; (106), (108)
E	Electric field; (3)	k	Boltzmann's constant
G_D	Frequency-independent parallel discharge conductance/unit area; (85); see also Fig. 1	l	Distance of separation of plane, parallel electrodes
G_E	$(G_\infty - G_D) \equiv R_E^{-1}$; see Fig. 1	n	Concentration of mobile negative charges
G_n	$(G_\infty - G_p)$; (11)	p	Concentration of positive mobile charges
G_p	$(G_\infty - G_n)$; (10)	r	$M[\coth(M)]$
G_P	Total parallel conductance/unit area; associated with Y_T ; (86). Note: $G_{P0} \equiv G_D$, $G_{P\infty} \equiv G_\infty$	r_e	Designation of common value of r_p and r_n when they are equal
G_∞	Bulk conductance/unit area; (12)	r_n	Dimensionless discharge parameter for negative charges; (43)
I	Total current/unit area; (7), (37)	r_p	Dimensionless discharge parameter for positive charges; (41)
L_i	Intrinsic Debye length; (13)	t	Time
L_D	General Debye length; (22)	x	Distance measured from left electrode
M	$(l/2L_D)$; (38)	z_n	Valence number for negative mobile charges; (6)
M_i	$(l/2L_i)$	z_p	Valence number for positive mobile charges; (5)
		Ω	Normalized radial frequency; $\omega\tau_D$
		δ_n	$(1 + \pi_f^{-1})^{-1}$; (21)
		δ_p	$(1 + \pi_f)^{-1}$; (20)
		ϵ	Dielectric constant of the bulk material
		ϵ_n	G_n/G_∞ ; (18)
		ϵ_p	G_p/G_∞ ; (17)
		μ_i	Mobility; $i=n$ or p ; (3), (4)
		ν	$N_e/(z_n^2 n_{ef} + z_p^2 p_{ef})$; (24)
		ξ	$(1 + \chi^2)^{1/2}$; (72)
		π_e	$\pi_m(n^*/p^*)$; (16)

- π_f $\pi_z(n^*/p^*)$; (19)
 π_m Mobility ratio; μ_n/μ_p ; (16)
 π_z Valence number ratio; z_n/z_p ; (19)
 τ Normalized time; ωt ; (27)
 τ_D Dielectric relaxation time; $C_\epsilon R_\infty$; (31)
 χ $N_e/2z_n n_i = N_e/2z_p p_i$; (15)
 ψ Potential; taken zero at left electrode
 ω Radial frequency of the applied sinusoidal voltage

D. Case Designation

$(A, B; C, D; E, F) = (r_p, r_n; \pi_m, \pi_z; \chi, M)$. When $\chi=0$, $M=M_i$. When $\chi \neq 0$ and a specific value of M (e.g., $F=10^3$) is underlined, then the value is of M_i rather than M .

III. GENERAL EQUATIONS

Consider a homogeneous material held at constant, spatially uniform temperature between two plane-parallel electrodes separated by a distance l . All the subsequent analysis will deal with unit area of this system. Now assume that the uniformly distributed, charged, net doping concentration, $N_e \equiv N_D^+ - N_A^-$, represents immobile charge and is time independent. Finally, assume that the mobile charge concentrations always have their steady state or thermal equilibrium values in both intrinsic and extrinsic cases. This assumption of zero recombination time usefully simplifies the results. In the intrinsic situation, nonzero recombination time has been shown to have only a minor effect¹ when dissociation is incomplete and none, of course, for complete dissociation. The present treatment applies for any nonzero degree of dissociation.

The usual, nondegenerate-material, transport equations are

$$\partial p / \partial t = -\nabla \cdot \mathbf{j}_p, \quad (1)$$

$$\partial n / \partial t = -\nabla \cdot \mathbf{j}_n, \quad (2)$$

$$\mathbf{j}_p \equiv (\mu_p p \mathbf{E} - D_p \nabla p), \quad (3)$$

$$\mathbf{j}_n \equiv -(\mu_n n \mathbf{E} + D_n \nabla n), \quad (4)$$

$$\mathbf{I}_p \equiv e z_p \mathbf{j}_p, \quad (5)$$

$$\mathbf{I}_n \equiv -e z_n \mathbf{j}_n, \quad (6)$$

and

$$\mathbf{I} = \mathbf{I}_n + \mathbf{I}_p + (\epsilon/4\pi) (\partial \mathbf{E} / \partial t). \quad (7)$$

Here \mathbf{E} is the electric field and \mathbf{I}_p and \mathbf{I}_n are the positive and negative charge carrier current densities. In order that the present analysis apply to both a general intrinsic as well as extrinsic situation, the valence numbers z_p and z_n (>0) for the positive and negative charge carriers have been introduced here. For the usual extrinsic situation in solids, $z_n = z_p = 1$. The $z_n \neq z_p$ situation is, however, a common one for strong electrolytes, with situations of interest satisfying $0.2 < z_n/z_p < 5$.

In addition to the above equations, we shall need the general Einstein relation²⁸

$$D_i = (kT/e z_i) \mu_i, \quad (8)$$

where $i=n$ or p , and the Poisson equation

$$\nabla \cdot \mathbf{E} = (4\pi e/\epsilon) (z_p p - z_n n + N_e). \quad (9)$$

In these equations, D_i and μ_i are diffusion coefficients and mobilities (taken independent of concentration as usual) and ϵ is the dielectric constant of the basic material (including no mobile-charge effects).

For simplification of subsequent work, it will be convenient to introduce many normalized quantities. Consider first the zero-current equilibrium condition and denote the negative mobile-charge concentration by n_e and the positive by p_e . In general, n_e and p_e are position dependent. In the field-free flat-band situation, these static quantities, which are then the unperturbed bulk values, will be designated by n_{ef} and p_{ef} . We may now write

$$G_p \equiv (e/l) (z_p \mu_p p_{ef}), \quad (10)$$

$$G_n \equiv (e/l) (z_n \mu_n n_{ef}), \quad (11)$$

$$G_\infty \equiv R_\infty^{-1} \equiv G_n + G_p, \quad (12)$$

where R_∞ is the high-frequency-limiting resistance-unit area of the unperturbed two-electrode system.

Now denote the bulk values of intrinsic charge carrier concentrations by n_i and p_i . They are connected by the intrinsic electroneutrality condition, $z_n n_i = z_p p_i$. For a completely intrinsic material $n_{ef} \equiv n_i$ and $p_{ef} \equiv p_i$. The intrinsic Debye length is

$$L_i \equiv [\epsilon kT / 4\pi e^2 (z_n^2 n_i + z_p^2 p_i)]^{1/2}. \quad (13)$$

Next, the following normalized quantities will prove useful:

$$n^* \equiv (n_{ef}/n_i), \quad p^* \equiv (p_{ef}/p_i), \quad (14)$$

and

$$\chi \equiv [(z_n + z_p)/2] [N_e / (z_n^2 n_i + z_p^2 p_i)] \\ \equiv [N_e / (z_n n_i + z_p p_i)]. \quad (15)$$

When $\chi=0$, the material is completely intrinsic and $p^* = n^* = 1$. Note that when $z_n = z_p = 1$, $n_i = p_i$ and $\chi = N_e/2n_i$.

We shall also need

$$\pi_m \equiv (\mu_n/\mu_p), \quad \pi_e \equiv \pi_m (n^*/p^*), \quad (16)$$

$$\epsilon_p \equiv (G_p/G_\infty) \equiv (1 + \pi_e)^{-1}, \quad (17)$$

$$\epsilon_n \equiv (G_n/G_\infty) \equiv (1 + \pi_e^{-1})^{-1}, \quad (18)$$

$$\pi_z \equiv (z_n/z_p), \quad \pi_f \equiv \pi_z (n^*/p^*), \quad (19)$$

$$\delta_p \equiv [z_p p^* / (z_p p^* + z_n n^*)] \equiv (1 + \pi_f)^{-1}, \quad (20)$$

and

$$\delta_n \equiv [z_n n^* / (z_p p^* + z_n n^*)] \equiv (1 + \pi_f^{-1})^{-1}. \quad (21)$$

Note that $\epsilon_n + \epsilon_p = \delta_n + \delta_p = 1$. Since the general Debye length L_D is given by

$$L_D \equiv [\epsilon kT / 4\pi e^2 (z_n^2 n_{ef} + z_p^2 p_{ef})]^{1/2}, \quad (22)$$

one readily finds that

$$(L_i/L_D) = [(p^* + \pi_z n^*) / (1 + \pi_z)]^{1/2}. \quad (23)$$

Also let

$$\begin{aligned} \nu &\equiv [N_e/(z_n^2 n_{ef} + z_p^2 p_{ef})] \\ &\equiv [2\chi/(z_n + z_p)](L_D/L_i)^2. \end{aligned} \quad (24)$$

Now let us specialize to a one-dimensional situation with x measured from the left electrode and $0 \leq x \leq l$. Let

$$X \equiv (x/L_D), \quad (25)$$

$$E^* \equiv (eL_D/kT)E, \quad (26)$$

$$\tau \equiv \omega t, \quad (27)$$

$$P \equiv (p/z_p p_{ef}), \quad (28)$$

$$N \equiv (n/z_n n_{ef}), \quad (29)$$

and

$$\Omega \equiv \omega C_g R_\infty. \quad (30)$$

Here $C_g \equiv \epsilon/4\pi l$ is the geometric capacitance per unit area and ω is the radial frequency of a sinusoidal excitation. The dielectric relaxation time,

$$\tau_D \equiv \epsilon/[4\pi e(z_n \mu_n n_{ef} + z_p \mu_p p_{ef})], \quad (31)$$

is just $C_g R_\infty$; thus $\Omega \equiv \omega \tau_D$. Most measurable space-charge and discharge effects of interest occur in the range $0 \leq \Omega < 1$.

We are now finally in a position to rewrite the equations in normalized form. To do so, first combine Eqs. (1) and (3), (2) and (4), and use (8) and (9). Denote partial differentiation with respect to τ by a dot over the quantity being differentiated and that with respect to X by a superscript prime. We obtain

$$P'' = \Omega \delta_p \epsilon_p^{-1} \dot{P} + z_p [E^* P' + (\delta_p P - \delta_n N + \nu) P], \quad (32)$$

$$N'' = \Omega \delta_n \epsilon_n^{-1} \dot{N} - z_n [E^* N' + (\delta_p P - \delta_n N + \nu) N], \quad (33)$$

$$E^{*'} = \delta_p P - \delta_n N + \nu, \quad (34)$$

$$I_p = (2kT/e) G_\infty \epsilon_p M (z_p P E^* - P'), \quad (35)$$

$$I_n = (2kT/e) G_\infty \epsilon_n M (z_n N E^* + N'), \quad (36)$$

and

$$I = I_n + I_p + (2kT/e) (G_\infty \Omega M) \dot{E}^*, \quad (37)$$

where the important quantity M is

$$M \equiv (l/2L_D) \quad (38)$$

the number of general Debye lengths contained in $(l/2)$. The corresponding intrinsic quantity is $M_i \equiv l/2L_i$. The general neutrality condition in normalized form follows from Eq. (34) with $E^{*'}(X) \equiv 0$ for all X .

If we now define

$$Y \equiv X - M, \quad (39)$$

we may write for the normalized potential, $\psi^* \equiv e\psi/kT$, taken to be zero at $Y = -M$,

$$\psi^*(Y) = - \int_{-M}^Y E^*(Y) dY. \quad (40)$$

Let us now employ \bar{M} and M subscripts to denote quantities evaluated at $Y = -M$ and M , respectively. Thus, $\psi^*(M) \equiv \psi_M^*$. The normalized applied potential is therefore just $V^* = \psi_M^* - \psi_{\bar{M}}^* = \psi_M^*$, and V^* may be a function of time. We shall first be interested in the steady-state response of the system to a V^* of the form $V^* = V_0^* + V_1^* \sin \tau$. Here V_0^* and V_1^* are time independent. In the general case, $|V_0^*|$ and V_1^* may be $\gg 1$, and V_1^* need not be smaller than $|V_0^*|$.

In order to obtain the total current I as an explicit function of the applied potential, boundary conditions are required. Although their parameters may possibly be frequency dependent and may vary with time in general, only time- and frequency-independent parameters will be considered here. Further, the boundary condition parameters, if not even the form of the conditions themselves, will generally depend on static levels,^{34,35} such as the value of V_0^* , and the parameter values may sometimes even need to be different at the two electrodes.³⁵

Even if the two electrodes are identical, the equilibrium condition does not generally correspond to zero charge on the surfaces. Because of the difference between electrode material and the material between them, and because of a possible difference in the free energy of formation of positive and negative mobile carriers,³⁶ there will usually be present a contact or diffusion potential V_D which perturbs the concentrations of mobile charges in the neighborhood of the electrodes even under zero-current conditions. Then $n_e \neq n_{ef}$ and $p_e \neq p_{ef}$. Thus, an important part of a complete solution of the present equations should be the specification of the equilibrium perturbation, as part of the initial and boundary conditions of the problem. Such perturbations have been considered in certain space-charge situations^{37,38} but have not usually been taken into account when there are two species of mobile carriers present. Although they have been included to some extent in a recent V_0^* , $V_1^* \neq 0$ theory,³⁹ its many approximations and assumptions raise doubts of its adequacy and usefulness.⁴⁰ A more complete theory requires adding to the equations considered herein relations which specify the dependence of positive and negative surface charge (when it is distinct from electrode charge) on applied potential difference.⁴⁰

Since the present equations are nonlinear, their solution for a general applied potential and for electrodes which may be different must be carried out numerically. It should be noted that diffusion-potential perturbation and, when appropriate, concentration-dependent diffusion coefficients may be much more readily incorporated into such a solution than into a completely analytic one.

Finding boundary conditions which will yield $I(V)$ curves in good agreement with specific data at different temperatures, even for the static case of $V = V_0$, is a difficult task, certainly one not yet fully accomplished

for most materials. Until experimental dc response over an appreciable potential range for at least a single temperature can be derived quite closely theoretically, one cannot hope to achieve an adequately general ac theory. Nevertheless, using simple boundary conditions, small-signal ac response for the linear regime around equilibrium is still of interest for comparison with experiment and, since it can be obtained analytically in closed form, is also valuable as a check solution for comparison with later, more complicated numerical solutions of the problem.

Thus, the Chang-Jaffé boundary conditions^{2,7,21} will be used herein, as in most comparable earlier work. These conditions involve the time-independent parameters r_p and r_n ; relate conduction currents and concentrations; and may be written at the boundaries, $Y = \pm M$, as

$$I_{p\bar{M}} = -r_p(ez_p D_p/l)(\bar{p}_M - \bar{p}_{e\bar{M}}) \\ = -r_p(kT/e)(G_{\infty}\epsilon_p)\Delta P_{\bar{M}}, \quad (41)$$

$$I_{pM} = r_p(ez_p D_p/l)(\bar{p}_M - \bar{p}_{eM}) \\ = r_p(kT/e)(G_{\infty}\epsilon_p)\Delta P_M, \quad (42)$$

$$I_{n\bar{M}} = r_n(ez_n D_n/l)(\bar{n}_M - \bar{n}_{e\bar{M}}) \\ = r_n(kT/e)(G_{\infty}\epsilon_n)\Delta N_{\bar{M}}, \quad (43)$$

and

$$I_{nM} = -r_n(ez_n D_n/l)(\bar{n}_M - \bar{n}_{eM}) \\ = -r_n(kT/e)(G_{\infty}\epsilon_n)\Delta N_M. \quad (44)$$

In these equations, $\Delta P_{\bar{M}} \equiv P_{\bar{M}} - P_{e\bar{M}}$, $\Delta N_{\bar{M}} \equiv N_{\bar{M}} - N_{e\bar{M}}$, etc., and r_p and r_n are dimensionless discharge parameters which can be related to a symmetrical free energy barrier at the electrodes² and to specific electrode reaction rate constants.⁷ They thus may be expected to increase with increasing temperature. When r_p and r_n are zero, the electrodes are completely blocking (ideally polarized in electrochemical parlance). Alternatively, when r_p and r_n are infinite, the electrode reactions have infinite rates; there is no blocking at all; and $\Delta P_{\bar{M}} = \Delta P_M = \Delta N_{\bar{M}} = \Delta N_M = 0$.

These boundary conditions, while not completely general, nevertheless span the entire range from complete blocking to no blocking for each species of charge carrier in a simple and natural way. They may be applied whether the mobile charges are electrons and holes, ions, vacancies, or interstitials. In the electrolyte case, they are particularly appropriate for first-order redox reactions, where one or more electrons may participate in the reaction, depending on the valence of the reacting ion. Note that $r_p = r_n = 0$ corresponds to an infinite potential barrier to mobile charges at the electrodes. The values $r_p = r_n = \infty$ are actually not consistent with the potential barrier picture, a reasonable result since reaction rates are never actually infinite.

Since there is no practical difference in response between finite, physically possible values of 10^3 or more for r_p or r_n and infinite values, however, the latter will frequently be used as convenient limiting conditions.

Next, Eqs. (35) and (36), evaluated at $Y = \pm M$, may be used with (41)–(44) to obtain explicit boundary relations. Further, since $I(Y)$ is independent of Y in a one-dimensional situation, $I' = 0$ and thus $I_{\bar{M}} = I_M$. This equality leads to

$$(r_n\epsilon_n/2M)(\Delta N_M + \Delta N_{\bar{M}}) - (r_p\epsilon_p/2M)(\Delta P_M + \Delta P_{\bar{M}}) \\ = \Omega(\dot{E}_M^* - \dot{E}_{\bar{M}}^*). \quad (45)$$

Both sides of this equation are identically zero in equilibrium. For the $V^* = V_0^*$ static condition with I_0 zero or nonzero, (45) becomes

$$(r_n\epsilon_n)(\Delta N_{0M} + \Delta N_{0\bar{M}}) - (r_p\epsilon_p)(\Delta P_{0M} + \Delta P_{0\bar{M}}) = 0. \quad (46)$$

When ΔN and ΔP are antisymmetric functions centered about $Y = 0$, $I_{p\bar{M}} = I_{pM}$, $I_{n\bar{M}} = I_{nM}$, and $\dot{E}_{\bar{M}}^* = \dot{E}_M^*$. Further, when the electrodes are identical, it is necessary that $E_{e\bar{M}}^* = -E_{eM}^*$.

IV. STATIC AND PERTURBATIVE EQUATIONS

Let us assume that $V^* = V_0^* + V_1^*e^{ir}$ and that $V_1^* < 1$. Then other quantities such as P and N may be split into static and time-varying parts also. Because of the above condition on V_1^* , it will be a good approximation to neglect all harmonics in P , I , etc., and in all products, thus linearizing all time-varying terms in the equations.¹ The response induced by $V_1^*e^{ir}$ represents a small perturbation on the state of the system associated with a given value of V_0^* . Under such conditions, an ordinary impedance may be defined which will be a function of V_0^* . For use in future work, the pertinent equations of the problem will be separated into static (V_0^*) and perturbative (V_1^*) parts, although the present solution is for $V_0^* = V_D^* = 0$ only.

The static equations, which apply independently of the size of V_1^* , are

$$P_0'' = z_p[E_0^*P_0' + (\delta_p P_0 - \delta_n N_0 + \nu)P_0], \quad (47)$$

$$N_0'' = -z_n[E_0^*N_0' + (\delta_p P_0 - \delta_n N_0 + \nu)N_0], \quad (48)$$

$$E_0' = \delta_p P_0 - \delta_n N_0 + \nu, \quad (49)$$

$$I_{p0} = (2kT/e)G_{\infty}\epsilon_p M(z_p P_0 E_0^* - P_0'), \quad (50)$$

$$I_{n0} = (2kT/e)G_{\infty}\epsilon_n M(z_n N_0 E_0^* + N_0'), \quad (51)$$

$$I_0 = I_{p0} + I_{n0}, \quad (52)$$

$$z_p P_{0\bar{M}} E_{0\bar{M}}^* - P_{0\bar{M}}' = -(r_p/2M)\Delta P_{0\bar{M}}, \quad (53)$$

$$z_p P_{0M} E_{0M}^* - P_{0M}' = (r_p/2M)\Delta P_{0M}, \quad (54)$$

$$z_n N_{0\bar{M}} E_{0\bar{M}}^* + N_{0\bar{M}}' = (r_n/2M)\Delta N_{0\bar{M}}, \quad (55)$$

$$z_n N_{0M} E_{0M}^* + N_{0M}' = -(r_n/2M)\Delta N_{0M}, \quad (56)$$

and

$$V_0^* = - \int_{-M}^M E_0^*(Y) dY. \quad (57)$$

When $V^* = V_0^* = 0$, $I_0 = 0$, and the static solution reduces to the equilibrium condition independently of r_p and r_n values. Note, however, that for complete blocking where $r_p = r_n = 0$, $I_0 = I_{0M} = I_{0M} = 0$ for any applied V_0^* ; thus the final equilibrium state reached in this case after all transients have disappeared will not correspond to the original one unless $V_0^* = 0$. When $|V_0^*| > 0$ and r_p and/or r_n are/is nonzero, the final condition is the static steady state but is not a condition of equilibrium.

The linearized perturbative equations are

$$P_1'' = i\Omega\delta_p\epsilon_p^{-1}P_1 + z_p[E_0^*P_1' + E_1^*P_0' + (\delta_pP_1 - \delta_nN_1)P_0 + (\delta_pP_0 - \delta_nN_0 + \nu)P_1], \quad (58)$$

$$N_1'' = i\Omega\delta_n\epsilon_n^{-1}N_1 - z_n[E_0^*N_1' + E_1^*N_0' + (\delta_pP_1 - \delta_nN_1)N_0 + (\delta_pP_0 - \delta_nN_0 + \nu)N_1], \quad (59)$$

$$E_1^* = \delta_pP_1 - \delta_nN_1, \quad (60)$$

$$I_{p1} = (2kT/e)G_{\infty}\epsilon_p M[z_p(P_0E_1^* + P_1E_0^*) - P_1'], \quad (61)$$

$$I_{n1} = (2kT/e)G_{\infty}\epsilon_n M[z_n(N_0E_1^* + N_1E_0^*) + N_1'], \quad (62)$$

$$I_1 = I_{p1} + I_{n1} + (2kT/e)(G_{\infty}i\Omega M)E_1^*, \quad (63)$$

$$z_p(P_0\bar{M}E_{1\bar{M}}^* + P_{1\bar{M}}E_{0\bar{M}}^*) - P_{1\bar{M}}' = -(r_p/2M)P_{1\bar{M}}, \quad (64)$$

$$z_p(P_{0M}E_{1M}^* + P_{1M}E_{0M}^*) - P_{1M}' = (r_p/2M)P_{1M}, \quad (65)$$

$$z_n(N_{0\bar{M}}E_{1\bar{M}}^* + N_{1\bar{M}}E_{0\bar{M}}^*) + N_{1\bar{M}}' = (r_n/2M)N_{1\bar{M}}, \quad (66)$$

$$z_n(N_{0M}E_{1M}^* + N_{1M}E_{0M}^*) + N_{1M}' = -(r_n/2M)N_{1M}, \quad (67)$$

and finally,

$$V_1^* = - \int_{-M}^M E_1^*(Y) dY. \quad (68)$$

Clearly, to solve Eqs. (47)–(68) one should first solve for the spatial dependence of the static quantities using (47)–(57) and the equilibrium solution, then use the results in (58)–(68). In general, such solutions can only be carried out numerically.

It will be convenient to indicate values of the six main parameters of the present problem in the following way: $(r_p, r_n; \pi_m, \pi_s; \chi, M_k)$. Here M_k may either be M or M_i as appropriate. For the situation $(0, 0; \pi_m, \pi_s; 0, M_i)$, the zero-frequency limiting capacitance of the linearized system may be calculated either from $V^* = V_0^* \rightarrow 0$ or from $V^* = V_1^* \sin\tau$ with $V_1^* < 1$ and $\tau \rightarrow 0$. Of course, for $V_0^* \geq 1$, the static solution yields a differential capacitance dependent on the value of V_0^* . Several special-case solutions of the basic equations have been obtained for the flat-band equilibrium condition, that of zero charge on the electrodes in equilib-

rium. For $V_0^* = 0$, some ac solutions have been obtained for the $(0, 0; \pi_m, 1; 0, M_i)$ case,^{1,2,22,23,28} for $(0, \infty; 1, 1; 0, M_i)$,^{22,23} and a partial solution² for $(r_p, r_n; \pi_m, 1; 0, M_i)$. Static solutions have been given²⁸ (a) for $(0, 0; \pi_m, \pi_s; 0, M_i)$ with $V_0^* \rightarrow 0$ and complete dissociation, and for $V_0^* \geq 1$ for the cases (b) $(0, 0; \pi_m, 1; 0, M_i)$ with complete dissociation⁴¹ and (c) $(0, 0; 0, 1; 0, M_i)$ with arbitrary dissociation.⁴² No static solutions for $V^* = V_0^* > 0$ and $(r_p, r_n; \pi_m, \pi_s; \chi, M)$ with $\chi \geq 0$ and r_p and r_n arbitrary or equal to $(0, \infty)$ or $(\infty, 0)$ have been obtained thus far to my knowledge, even when $V_D = 0$.

In the electrolyte case, $V_D = V_0 = 0$ corresponds to the equilibrium, zero-electrode-charge case. When V_D is not intrinsically zero, the usual situation, that potential (measured with respect to a reference electrode) which yields $I_0 = 0$ corresponds to the present $V_0 = 0$, the equilibrium condition. Thus, the present V_0 is the electrolyte overpotential. When discreteness-of-charge effects are considered, V_0 is known as the macropotential.⁴³ Here, such effects are neglected except insofar as they implicitly affect⁴⁰ the value of V_D .

When the electrodes are completely blocking (ideally polarized) and $V_D \neq 0$, the determination of that potential which corresponds to the present $V_0 = 0$ is more difficult since $I_0 \equiv 0$ independently of V_0 . If one is concerned with effects at a single working electrode, then $V_0 = 0$ corresponds to the condition of zero electrode charge. Of course the value of V_D is affected by electrode, solvent, and solute materials and by the presence or absence of specifically adsorbed charge.^{40,44} Note that even for complete blocking, where the electrodes themselves should have minimum effect on the equilibrium charge distributions near them, V_D is not usually zero because of specific ionic adsorption, charge in surface states, excess surface charge arising from possible differences in the free energies of formation of positive and negative charge carriers,³⁶ etc.

V. SPECIFIC SOLUTION

To make an analytic solution possible in the general $V_0^* = 0$ $(r_p, r_n; \pi_m, \pi_s; \chi, M)$ case, I shall now assume that $V_D^* = E_0^*(Y) = E_0^*(Y) \equiv 0$ for all Y . The static situation is then that for flat-band equilibrium. It follows that $P_0'' = N_0'' = P_0' = N_0' = I_0 \equiv 0$ for all Y as well. Under these conditions, $p_0 \rightarrow p_{ef}$, $P_0 \rightarrow P_{ef} \equiv z_p^{-1}$, $n_0 \rightarrow n_{ef}$, and $N_0 \rightarrow N_{ef} \equiv z_n^{-1}$. The general equilibrium neutrality condition which applies when $E_0^* = 0$ may now be written alternatively as

$$z_p p_{ef} - z_n n_{ef} + N_e = 0,$$

$$\delta_p P_{ef} - \delta_n N_{ef} + \nu = 0,$$

$$\delta_p p_i - \delta_n n_i + [(z_n n_i + z_p p_i)/2]\nu = 0,$$

or

$$p^* - n^* + 2\chi = 0, \quad (69)$$

where the final form follows on using

$$(z_p p^* + z_n n^*) / (z_n^2 n_{ef} + z_p^2 p_{ef}) \equiv [2 / (z_n n_i + z_p p_i)].$$

When the usual mass-action law appropriate for $z_p = z_n = 1$, $n_{ef} p_{ef} = n_i^2$, or $n^* p^* = 1$, is combined with (69) one obtains

$$p^* = \xi - \chi \quad (70)$$

and

$$n^* = \xi + \chi, \quad (71)$$

where

$$\xi \equiv (1 + \chi^2)^{1/2}. \quad (72)$$

Here, one should remember that $-\infty < \chi < \infty$ and that for $z_p = z_n = 1$, $\chi \equiv N_e / 2n_i$. For the intrinsic case, of course, $\chi = 0$ and $n^* = p^* = 1$ for any z_n and z_p values.

The flat-band condition leads to considerable simplification in Eqs. (58)–(67). We first obtain

$$P_1'' = a_{11} P_1 + a_{12} N_1, \quad (73)$$

$$N_1'' = a_{21} P_1 + a_{22} N_1, \quad (74)$$

where

$$a_{11} = \delta_p (1 + i\Omega \epsilon_p^{-1}), \quad (75)$$

$$a_{12} = -\delta_n, \quad a_{21} = -\delta_p, \quad (76)$$

and

$$a_{22} = \delta_n (1 + i\Omega \epsilon_n^{-1}). \quad (77)$$

These results will be used in the Appendix, Sec. I. Some of the other equations may now be rewritten as

$$I_{p1} = (2kT/e) G_\infty \epsilon_p M (E_1^* - P_1'). \quad (78)$$

$$I_{n1} = (2kT/e) G_\infty \epsilon_n M (E_1^* + N_1'), \quad (79)$$

$$E_{1M}^* - P_{1M}' = (r_p / 2M) P_{1M}, \quad (80)$$

and

$$E_{1M}^* + N_{1M}' = -(r_n / 2M) N_{1M}, \quad (81)$$

where the other two boundary conditions are superfluous since P_1 and N_1 are antisymmetric around $Y = 0$ for the present conditions.

An explicit numerical solution of some of these (or equivalent) equations, with $V_0^* \equiv 0$, has been obtained in the $(0, 0; 0, 1; 0, M_i)$ case by Stern and Weaver⁴⁶ for V_1^* possibly appreciably greater than unity. Unfortunately, diffusion effects were completely neglected, as were higher harmonics in current, concentration, etc. Thus, these results must be considered far from definitive. Because of the neglect of diffusion, they should not even reduce to the exact results for the above case found¹ for $V_1^* \leq 1$.

To obtain explicit expressions for the alternating current and impedance most simply, one may make use of the one-dimensional character of the present problem. Although the individual components of the current are functions of x , the total current amplitude

I_1 cannot be. Thus, averaging I_1 yields

$$I_1 = \frac{1}{2M} \int_{-M}^M \left[I_{p1}(Y) + I_{n1}(Y) + \left(\frac{2kTG_\infty i\Omega M}{e} \right) E_1^*(Y) \right] dY \\ = \left(\frac{kT}{e} \right) G_\infty \int_{-M}^M [(\epsilon_n N_1' - \epsilon_p P_1') + (\epsilon_p + \epsilon_n + i\Omega) E_1^*(Y)] dY. \quad (82)$$

For the presently chosen sign relation between V_1^* and the integral of E_1^* , Eq. (68), the total admittance Y_T is given by $Y_T \equiv I_1 / (-V_1)$. Let the subscript N denote normalization which involves dividing by G_∞ for admittances, by R_∞ for impedances, and by C_θ for separately considered capacitances. Note that C_θ and G_∞ are the components of the total system admittance in the high-frequency limit: $Y_{T\infty} \equiv G_\infty + i\omega C_\theta$. We may now write for the normalized admittance on evaluating (82)

$$Y_{TN} \equiv (-eI_1 / kTG_\infty V_1^*) \\ = 1 + i\Omega + (2/V_1^*) (\epsilon_p P_{1M} - \epsilon_n N_{1M}), \quad (83)$$

where the right hand side follows from (82) and (68) and the antisymmetry of P_1 and N_1 . Since $Y_{TN\infty} \equiv 1 + i\Omega$, the last part of the expression for Y_{TN} must go to zero as $\Omega \rightarrow \infty$.

For further work it is convenient to consider the admittance

$$Y_{2N} \equiv Y_{TN} - (1 + i\Omega) = (2/V_1^*) (\epsilon_p P_{1M} - \epsilon_n N_{1M}). \quad (84)$$

In Sec. II of the Appendix a complicated expression for Y_{2N} is derived from Eq. (84) in terms of functions of the basic input parameters $(r_p, r_n; \pi_m, \pi_z; \chi, M)$ and Ω . The $\Omega \rightarrow 0$ limit of Y_{2N} derived from this result is non-zero when r_p and r_n are not both zero. Let a subscript zero denote quantities evaluated when $\Omega \rightarrow 0$. Then one readily finds, from Eq. (A43) and $Y_{TN0} = Y_{2N0} + 1$,

$$Y_{TN0} = G_{DN} \equiv \frac{\epsilon_p r_p + \epsilon_n r_n + (r_p r_n / 2)}{2[1 + (r_p / 2)][1 + (r_n / 2)]}, \quad (85)$$

entirely independent of π_z ! Note that the discharge conductance G_D is zero for complete blocking ($r_p = r_n = 0$) and equal to G_∞ when $r_p = r_n = \infty$. For $(r_p, r_n) = (\infty, 0)$, $G_{DN} = \epsilon_p$, and for $(0, \infty)$ it reduces to ϵ_n . In the latter case, for example, $G_D = \epsilon_n G_\infty \equiv G_n$, just the conductance associated with the freely discharging charge carrier.

There is no zero subscript on G_D or G_{DN} because these quantities are frequency independent. Since $Y_{TN0} = G_{DN} \leq 1$ and $\text{Re}(Y_{TN\infty}) = 1$, it is clear that there is a direct, frequency-independent conducting discharge path between electrodes for all frequencies when r_p and r_n are not both zero. It turns out that the equivalent circuit of the whole system, when structured to involve a maximum number of frequency-independent elements,^{22,23} is as shown in Fig. 1(a). Here $G_E \equiv G_\infty - G_D$. Thus, $G_{EN} \equiv 1 - G_{DN}$. The only frequency dependence appears in the "interface" admittance Y_i .

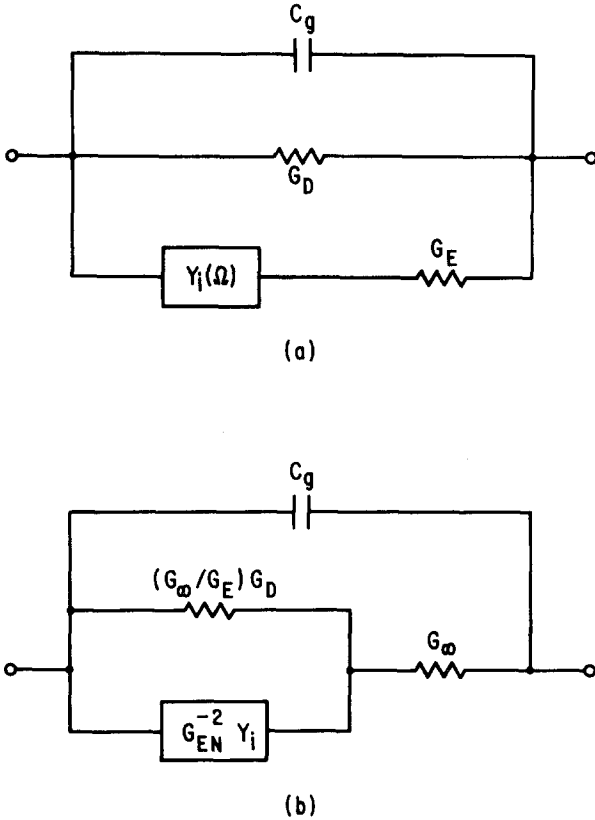


FIG. 1. Exact equivalent circuits involving the frequency-dependent admittance Y_i . The two circuits are electrically equivalent.

Its inverse Z_i may be separated into a frequency-dependent resistance R_i in series with a frequency-dependent capacitance C_i . As I shall show shortly, however, only for $M \gg 1$, $r_p = r_n$, and $\pi_m = \pi_z$ are the zero-frequency limits R_{i0} and C_{i0} both truly intensive interface quantities^{22,23} in the sense that only then are they both essentially independent of l . Note that since $Y_{i\infty} = \infty$, $\text{Re}(Y_{TN\infty}) = G_{DN} + G_{EN} \equiv 1$. Figure 1(b)

illustrates an alternate way of structuring the circuit, one with exactly the same over-all admittance at all frequencies. The sort of modification in these circuits necessary to take recombination of the charge carriers into account has been given previously¹ for $(0, 0; \pi_m, 1; 0, M_i)$.

In order to make direct contact with experiment, define the parallel components of the normalized total impedance as $G_{PN} \equiv G_P/G_\infty$ and $C_{PN} \equiv C_P/C_g$. Then since $Y_{TN} \equiv G_{PN} + i\Omega C_{PN}$,

$$G_{PN} = \text{Re}(Y_{TN}) \quad (86)$$

and

$$C_{PN} = \Omega^{-1} \text{Im}(Y_{TN}). \quad (87)$$

Note that these definitions of G_P and C_P differ somewhat from those used previously.²² It is here convenient to use the present definitions since G_P and C_P may be measured directly using an impedance bridge. Next note from the equivalent circuit that $C_{PN0} = 1 + C_{iN0}$. Generally, $C_{iN0} \gg 1$ in cases of interest.

From the equivalent circuit and Eq. (84), one can readily derive the following relation between Z_{iN} and Y_{2N} :

$$Z_{iN} \equiv R_{iN} + (i\Omega C_{iN})^{-1} = -Y_{2N}/[G_{EN}(G_{EN} + Y_{2N})]. \quad (88)$$

Since $\text{Re}(Y_{2N0}) \equiv -G_{EN}$, this equation involves a small difference between two large quantities when $\Omega \rightarrow 0$, and it is thus a poor choice for computation. Explicit equations for Z_{iN} [Eqs. (A48) and (A49)] which avoid this difficulty are derived in Sec. III of the Appendix.

As shown in the Appendix, one can, after very considerable labor, derive exact expressions for $C_{iN0} \equiv -[\Omega \text{Im}(Z_{iN})]_{\Omega \rightarrow 0}^{-1}$ and $R_{iN0} \equiv \text{Re}(Z_{iN})_{\Omega \rightarrow 0}$. The general formula for C_{iN0} , Eq. (A80), may be written in the form

$$C_{iN0} = C_{aN} + C_{bN}, \quad (89)$$

where

$$C_{aN} \equiv \delta_n \delta_p M^2 (r_p - r_n)^2 / 12 \{ [1 + (r_p/2)] [1 + (r_n/2)] \}^2 \quad (90)$$

and

$$C_{bN} \equiv \frac{(r-1) \{ [1 + (r_p/2)] [1 + (r_n/2)] + [(r_n - r_p)/2] \{ \delta_p^2 [1 + (r_n/2)] - \delta_n^2 [1 + (r_p/2)] \} \}}{\{ [1 + (r_p/2)] [1 + (r_n/2)] \}^2}. \quad (91)$$

Here $r \equiv M[\coth(M)]$, essentially equal to M for $M \gtrsim 3$. For many situations of interest $C_{aN} \gg C_{bN}$.

When $r_p = r_n \equiv r_e$, C_{iN0} reduces to just

$$C_{iN0} = (r-1)/[1 + (r_e/2)]^2, \quad (92)$$

while for $(\infty, 0; \pi_m, \pi_z; \chi, M)$ and $(0, \infty; \pi_m, \pi_z; \chi, M)$ it becomes, respectively,

$$C_{iN0} = (\delta_n \delta_p M^2 / 3) + \delta_n^2 (r-1) \quad (93)$$

and

$$C_{iN0} = (\delta_n \delta_p M^2 / 3) + \delta_p^2 (r-1). \quad (94)$$

These results agree with those found previously in the $\pi_m = \pi_z = 1$, $\chi = 0$ cases.^{1,22,23,28} Since C_{iN0} does not involve ϵ_n or ϵ_p , it is independent of mobilities and π_m as it should be.

Now $C_{iN0} = (r-1)$ is the $r_e = 0$ completely blocking result previously found. Note that C_{PN0} then equals r

and, for $M \gtrsim 3$, $C_{p0} \cong \epsilon/8\pi L_D$, a completely intensive result arising from the usual double-layer interface capacitance (per unit area) of $\epsilon/4\pi L_D$ localized near each electrode.²⁸ Equation (92) shows that C_{iN0} may remain much greater than unity even when charges of both signs discharge identically and appreciably! C_{i0} is essentially intensive as long as $r \gg 1$.

Equations (93) and (94) indicate that C_{iN0} may be very much larger than the $r_e = 0$ result when charge of one sign is completely blocked and charge of the other sign is completely free to discharge. For example, for $(\infty, 0; \pi_m, 1; 0, 10^5)$, $C_{aN} \cong (10^{10}/12)$ and $C_{bN} \cong (10^5/4)$. Thus, $C_{iN0} \cong (10^{10}/12)$ is here nearly 10^6 times larger than the completely blocking result. Note especially that the dominant C_a part of C_{i0} is far from intensive.^{22,23} For the $(\infty, 0)$ case, for example, $C_a = (\epsilon l / 192\pi L_D^2)$, directly extensive. This possibly very large capacitance contribution, which increases directly with electrode separation and appears only when $r_p \neq r_n$, is thus specific to a differential discharge situation. It then arises when the diffusion length associated with the conduction process²² becomes comparable to l . This accounts for its unusual proportionality to l . Such proportionality

only appears, of course, in the low-frequency-limiting saturation region, and the larger l and hence C_a , the lower in frequency one must go to reach this region.

Although the general expression for R_{iN0} derived in the Appendix, which, like that for C_{iN0} , holds exactly for $0 \leq M < \infty$, is too unwieldy to write out explicitly, it reduces to manageable form in special cases. For example, for $r_p = r_n \equiv r_e$ we find

$$R_{iN0} = [1 + (r_e/2)]((a-1) + a(r-1)^{-1}[1 + (r_e/2)]) \times \{1 + [(M^2 \operatorname{csch}^2 M - r)/2(r-1)]\}, \quad (95)$$

where a is a quantity involving χ , π_m , and π_z and is given by $(\delta_p^2/\epsilon_p) + (\delta_n^2/\epsilon_n)$. It is unity for any χ when $\pi_m = \pi_z$. For the usual $M \gg 1$ case, R_{iN0} approaches $g_e[(a-1) + (ag_e/2M)]$, where $g_e \equiv [1 + (r_e/2)]$. Since R_∞/M is an intensive quantity, R_{i0} is only fully intensive in the present case when $a = 1$. It has not been clear until now that Z_{iN0} is only intensive in even the completely blocking case when $a = 1$, since only $\pi_m = \pi_z = 1$ results have been available previously.^{1,22,23,28}

For the $(\infty, 0; \pi_m, \pi_z; \chi, M)$ situation, one finds

$$R_{iN0} = \frac{\delta_n^2 \{ (a - 2c\delta_p)(r-1) + (a/2)(M^2 \operatorname{csch}^2 M - r) + (\delta_p\delta_n^{-1}M^2/3)[(M^2/15) + 2c\delta_n] \}}{[\delta_n^2(r-1) + (\delta_p\delta_n M^2/3)]^2}, \quad (96)$$

where $c \equiv (\delta_n/\epsilon_n) - (\delta_p/\epsilon_p)$. The corresponding result for $(0, \infty; \pi_m, \pi_z; \chi, M)$ is obtained on making the transformations $\delta_p \rightarrow \delta_n$, $\delta_n \rightarrow \delta_p$, $\epsilon_p \rightarrow \epsilon_n$, and $\epsilon_n \rightarrow \epsilon_p$.

Several special cases are of interest. Take $M \gtrsim 3$ and consider the cases (a) $\chi \ll -100$, (b) $\chi = 0$, and (c) $\chi \gg 100$ for $0 < \pi_m, \pi_z < \infty$. For Case (a), $(\infty, 0; \pi_m, \pi_z; \chi, M)$ yields

$$R_{iN0} \rightarrow (5\delta_n\delta_p)^{-1} \cong (4\xi^2/5\pi_z) \cong (4\chi^2/5\pi_z), \quad (97)$$

provided χ^2/π_z and χ^2 are both much greater than unity. On the other hand, for $(0, \infty; \pi_m, \pi_z; \chi, M)$, Case (a) leads to

$$R_{iN0} \rightarrow (r-2)/2(r-1)^2 \rightarrow (2M)^{-1}, \quad (98)$$

when the $(r-1)$ terms in (96) are dominant (i.e., $M^2 \ll 100\chi^2/\pi_z$). Thus (97) shows, as expected, that when the minority carrier is completely blocked, R_{iN0} becomes very large. When the majority carrier is blocked, however, $R_{iN0} \rightarrow 0$ as $M \rightarrow \infty$.

The expression for R_{iN0} only simplifies appreciably in Case (b) when $\pi_m = \pi_z = 1$. Then, both $(\infty, 0; 1, 1; 0, M)$ and $(0, \infty; 1, 1; 0, M)$ lead to

$$R_{iN0} \cong \frac{[(M^4/45) + (M/2) - 1]}{4\{[(M-1)/4] + (M^2/12)\}^2} \rightarrow \frac{4}{5}, \quad (99)$$

where again the last form follows for $M \gg 1$. The $(4/5)$ result is the same as that found previously, but the

$(M/2)$ term in the numerator differs slightly from the earlier result²² because of the present inclusion of all higher-order contributions to R_{iN0} .

Now Case (c), where the majority carriers are negative, yields, for $(\infty, 0; \pi_m, \pi_z; \chi, M)$,

$$R_{iN0} \rightarrow (r-2)/2(r-1)^2 \rightarrow (2M)^{-1}, \quad (100)$$

when $M^2 \ll 100\chi^2\pi_z$. The corresponding result for $(0, \infty; \pi_m, \pi_z; \chi, M)$ is

$$R_{iN0} \rightarrow (5\delta_n\delta_p)^{-1} \cong (4\xi^2\pi_z/5) \cong (4\chi^2\pi_z/5), \quad (101)$$

provided $\chi^2\pi_z$ and χ^2 are both much greater than unity.

Now C_{iN} and R_{iN} remain very nearly equal to C_{iN0} and R_{iN0} for $(0, 0; 1, 1; 0, M_i)$ up to $\Omega \lesssim 0.1$.^{22,28} For most other cases, however, C_{iN} and R_{iN} remain equal to their low-frequency-limiting values only for considerably smaller Ω . In the constant range, of course, the low-frequency-limiting forms of the equivalent circuits of Fig. 1 are sufficient to describe all the frequency response of the system of interest. Thus, for $(0, 0; 1, 1; 0, M_i)$, virtually everything interesting happens in this $C_{iN} \cong C_{iN0}$, $R_{iN} \cong R_{iN0}$ range. For this situation, $R_D = \infty$, $R_E = R_\infty$, $C_{i0} = (r-1)C_\phi$, and, for $M_i \gg 1$, $R_{i0} \ll R_\infty$, leading to a very simple equivalent circuit^{1,22,28} involving single-time-constant,²⁸ simple Debye dispersion.

Although there are far too many different types of

TABLE I. Limiting forms of frequency-independent resistive elements.

(r_p, r_n) situation	G_{DN}			G_{EN}			R_{DN}			R_{EN}		
	$\pi_e \ll 1$	$\pi_e = \pi_e$	$\pi_e \gg 1$	$\pi_e \ll 1$	$\pi_e = \pi_e$	$\pi_e \gg 1$	$\pi_e \ll 1$	$\pi_e = \pi_e$	$\pi_e \gg 1$	$\pi_e \ll 1$	$\pi_e = \pi_e$	$\pi_e \gg 1$
$(\infty, 0)$	~ 1	ϵ_p	~ 0	~ 0	ϵ_n	~ 1	~ 1	$1 + \pi_e$	$\sim \infty$	$\sim \infty$	$1 + \pi_e^{-1}$	~ 1
$(0, 0)$		0			1			∞			1	
$(0, \infty)$	~ 0	ϵ_n	~ 1	~ 1	ϵ_p	~ 0	$\sim \infty$	$1 + \pi_e^{-1}$	~ 1	~ 1	$1 + \pi_e$	$\sim \infty$

frequency response possible in the general $(r_p, r_n; \pi_m, \pi_z; \chi, M)$ case to list here, it is worthwhile mentioning that the $(r_p, \infty; 1, 1; 0, M_i)$ and $(\infty, r_n; 1, 1; 0, M_i)$ cases lead, for $M \gg 10$, to appreciable regions of approximate ω^{-k} response for C_p . Here $k=1.5$ for r_p or r_n equal to zero, and it decreases smoothly toward zero as r_p or r_n approaches infinity. Such response also appears under certain other (r_p, r_n) conditions when π_m and/or π_z are not unity and/or χ is not necessarily zero.

VI. DISCUSSION OF RESULTS

It is clear from symmetry that as far as the impedance of the present system is concerned certain specific situations are fully equivalent to others. If

$$(r_p, r_n; \pi_m, \pi_z; \chi, M) = (A, B; C, D; E, F),$$

where A is an arbitrary specific value of r_p , B of r_n , etc., then the situation described by $(B, A; C^{-1}, D^{-1}; -E, F)$ has the same impedance at all frequencies as does $(A, B; C, D; E, F)$. It also turns out that the usual normalized impedance of the $(0, 0; C, C; E, F)$ case is entirely independent of the values of $\pi_m = \pi_z = C$ and $\chi = E$. There is thus no difference between extrinsic and intrinsic normalized response for this particular completely blocking situation, although positive and negative charge carrier concentrations depend strongly on the value of χ . In addition, the important quantity a is independent of the sign of χ for the $(r_p, r_n; \pi_m, 1; \chi, M)$ case.

Since the normalized impedances Z_{TN} and Z_{iN} and some of their elements depend on seven parameters in the general case, and several of these parameters may depend strongly on temperature as well, it is impractical to investigate the effects of full variation of all parameters independently, even taking symmetry into account. Thus, frequency dependence for the intrinsic $(r_p, r_n; \pi_m, \pi_z; 0, M_i)$ case with variation of some of the input parameters will be explicitly considered from a binary electrolyte point of view in a subsequent paper,²⁹ and the frequency dependence of the intrinsic-extrinsic $(r_p, r_n; \pi_m, 1; \chi, M)$ case investigated in a further paper³⁰ emphasizing solid-state situations. As background for this subsequent work, the remainder of the present paper will principally illustrate the dependence of the $\Omega \rightarrow 0$ quantities C_{iN0} and R_{iN0} on some of the

input parameters of the problem for the above two cases of main physical interest. Thus, situations involving $\pi_z \neq 1$ and $\chi \neq 0$ concomitantly will not be further considered since they seem of little physical importance and are not covered by the present mass-action law.

First, Table I shows how the frequency-independent resistive elements of the equivalent circuit of Fig. 1(a) depend on various conditions. Clearly, when the discharging carrier is also the majority carrier, G_{DN} and R_{DN} may be essentially unity and $R_{EN} \sim \infty$. But since $\pi_e \equiv \pi_m(n^*/p^*)$ depends on both the mobility ratio and on the normalized concentration ratio, it is actually

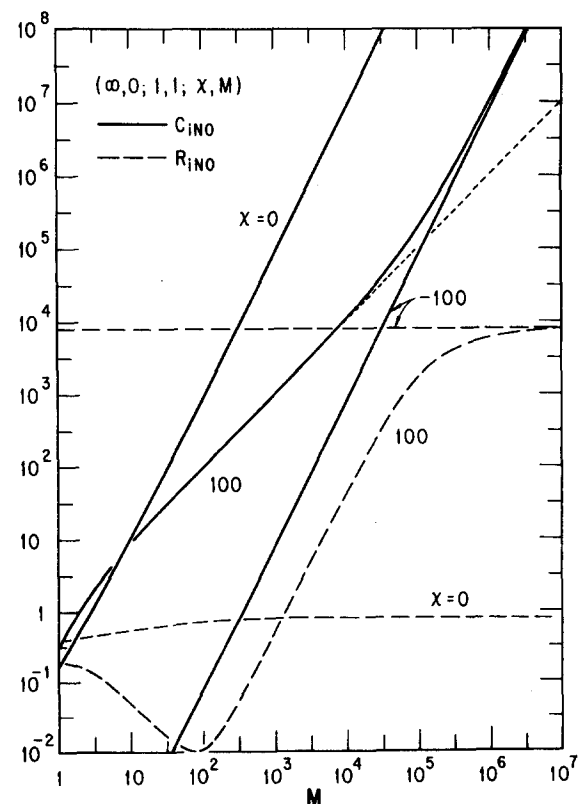
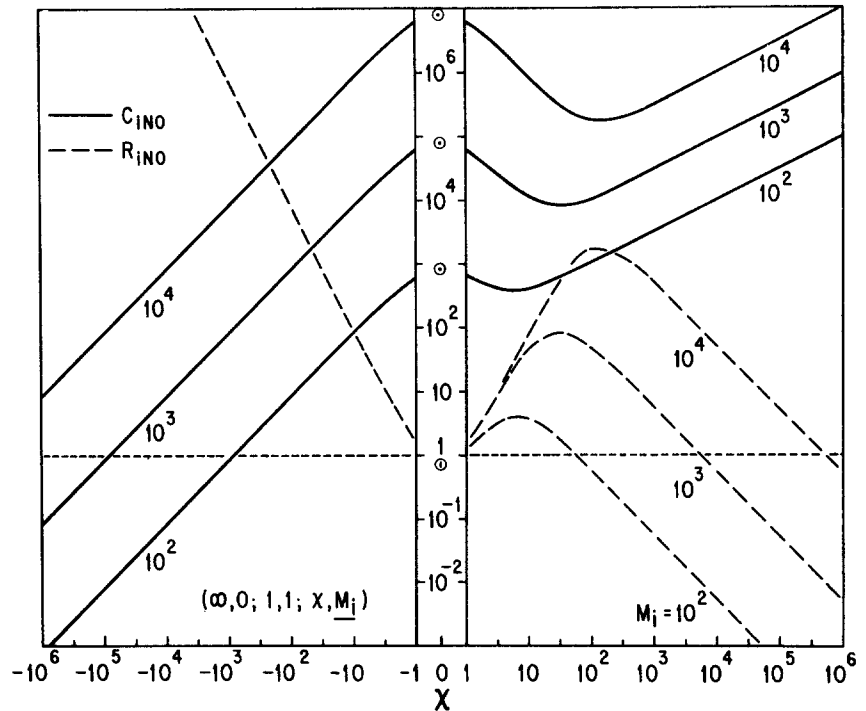


FIG. 2. The normalized quantities C_{iN0} and R_{iN0} versus M for several χ values for the $(\infty, 0; 1, 1; \chi, M)$ partially blocking situation. The line with short dashes applies to the $(0, 0; 1, 1; \chi, M)$ completely blocking situation.

FIG. 3. Log-log plots of C_{iN0} and R_{iN0} versus χ for fixed M_i values in the $(\infty, 0; 1, 1; \chi, \underline{M}_i)$ situation. Values for $\chi=0$ are shown by points in the center.



the ratio of $\mu_n n^*$ to $\mu_p p^*$, not just which type of carrier is in the majority, which counts. Thus, for $R_D \cong R_\infty$, it is necessary that $\mu_p p^* \gg \mu_n n^*$ when the positive charges discharge, and $\mu_n n^* \gg \mu_p p^*$ when negative ones do so. Note that when $\chi \gg 1$, $(n^*/p^*) \cong (2\chi)^2 \gg 1$ and when $\chi \ll -1$, $(n^*/p^*) \cong (2\chi)^{-2} \ll 1$.

The situation where $R_{DN} \cong 1$ and $R_{EN} \sim \infty$ is a limiting case of little interest, however. Then the equivalent circuit degenerates at all frequencies to the usual high-frequency limiting form of C_θ in parallel with R_∞ . Thus, such situations as $(0, \infty; 1, 1; \gg 10, M)$ and $(\infty, 0; 1, 1; \ll -10, M)$ need no further consideration, although a few curves pertaining to such cases will be presented. Likewise, such situations as $(0, \infty; \infty, 1; \chi, M)$ and $(\infty, 0; 0, 1; \chi, M)$ where the blocked carrier has zero mobility, are also of no particular interest.

As already mentioned, symmetry may be used to eliminate many duplicate cases from consideration. The transformation from $(r_p, r_n) = (0, \infty)$ to $(\infty, 0)$ reverses the values of G_{EN} and G_{DN} , but only for the cases $(0, \infty; \pi_m, 1; 0, M_i)$ and $(\infty, 0; \pi_m, 1; 0, M_i)$ do the corresponding values of R_{iN0} and C_{iN0} turn out to be the same. For $(0, B; C, 1; 0, F)$ and $(B, 0; C, 1; 0, F)$ the C_{iN0} values are the same but R_{iN0} , R_{DN} , and R_{EN} are all different.

Now let us first consider constant temperature conditions. Figure 2 shows how C_{iN0} and R_{iN0} depend on M for various fixed χ values for the $(\infty, 0; 1, 1; \chi, M)$ situation. In the $(0, 0; 1, 1; \chi, M)$ case (which is independent of the value of χ), the short-dashed curve shows how C_{iN0} differs from that for $(\infty, 0; 1, 1; 100, M)$ at large M . Similarly, the $(0, 0; 1, 1; \chi, M)$ R_{iN0} curve

is also essentially the same as that shown for $\chi = 100$ up to about $M = 10$, then it follows $(2M)^{-1}$ dependence for larger M .

Although the $\chi = \pm 100$ C_{iN0} and R_{iN0} curves approach each other for $M \gtrsim 10^6$, G_{DN} and G_{EN} are reversed for these cases. For $(\infty, 0; 1, 1; 100, M)$, the ratio R_{DN}/R_{iN0} approaches 5 for $M \gtrsim 10^6$ and is $\gg 10$ for $M < 10^4$. Since $R_{EN} \cong 1$ in this case, $R_{SN0} \cong R_{EN} + R_{iN0}$ will be appreciably smaller than R_{DN} for all M . Thus, the parallel branch of the equivalent circuit containing Z_{iN} will be important for all M values.

On the other hand, for $(\infty, 0; 1, 1; -100, M)$, $R_{DN} \cong 1$, $R_{EN} \cong 4 \times 10^4$, and $R_{iN0} \cong 8 \times 10^3$. In this situation, the parallel R_D resistive branch greatly dominates the branch containing Z_{iN} , and it will usually be impossible to measure C_{iN0} until χ has increased to a value considerably closer to zero. At $\chi = 0$, for example, $R_{DN} = R_{EN} = 2$, and R_{DN}/R_{iN0} is about 5.1 at $M = 1$ and approaches 2.5 for large M . Thus, the Z_{iN} branch is again important. Finally, note that at constant M , different $|\chi|$ values are associated with different values of M_i .

It is frequently of interest to hold M_i constant and vary χ . Such variation will then arise from changes in N_e alone. Figure 3 shows the results for $(\infty, 0; 1, 1; \chi, \underline{M}_i)$ for several values of M_i . Until now, the intrinsic-extrinsic case has been denoted as $(r_p, r_n; \pi_m, \pi_e; \chi, M)$, implying constant M . In those cases, such as the present one, where M_i is to be held constant, however, it or its value will be underlined in the case designation. Thus, a specific value shown in the M, M_i position will be of M when not underlined and of M_i when underlined.

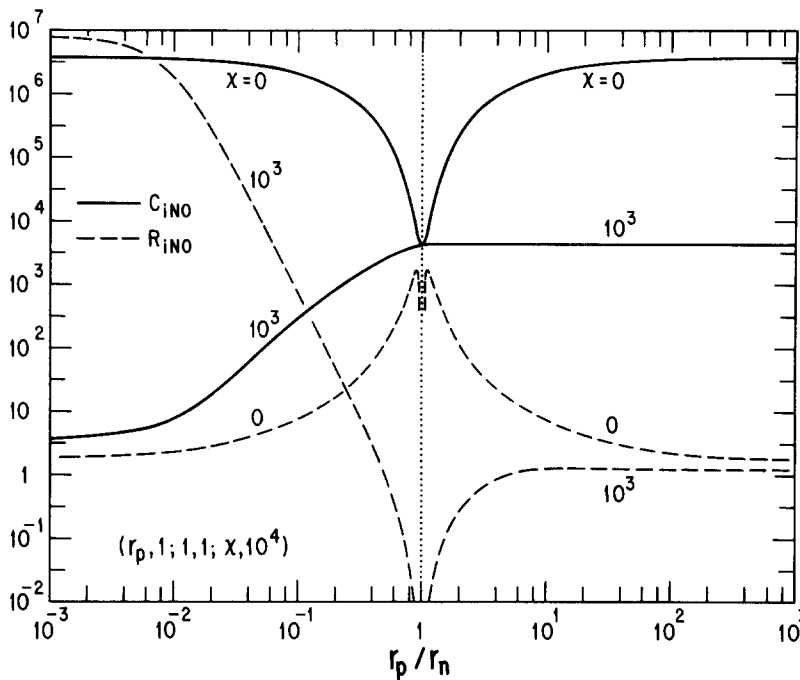


FIG. 4. Dependence of C_{iN0} and R_{iN0} on r_p/r_n for $(r_p, 1; 1, 1; \chi, 10^4)$ and $\chi = 0, 10^3$.

Figure 3 is a log-log plot except that the values of C_{iN0} and R_{iN0} at $\chi=0$ are shown as points in the center. The curves with $\chi \lesssim -10$ are shown more for completeness than for possible experimental interest. Even at $\chi = -10$, $R_{DN} \cong 1$, $R_{EN} \cong 400$, and $R_{iN0} \cong 81$. As shown, there is very little dependence of R_{iN0} on M_i for $\chi < 0$. The minima in the C_{iN0} curves come from the competing effects of the M^2 term in Eq. (93), important for $|\chi|$ small and M large, and the $(r-1)$ term important under opposite conditions. Since $R_{EN} \cong 1$ here for $\chi \gg 1$, the $R_{iN0} \ll 1$ condition apparent for sufficiently large χ implies that R_{iN0} may be entirely neglected to good approximation. Then

$$\tau_{SN0} \cong \tau_{S0}/\tau_D \cong R_{SN0} C_{iN0} \cong R_{EN} C_{iN0} \cong C_{iN0}.$$

Thus under these conditions the time constant for charging C_{iN0} is generally very much longer than the dielectric relaxation time τ_D .

Next, the dependence of R_{iN0} and C_{iN0} on r_p/r_n is of interest. In Fig. 4 a fixed value of $r_n=1$ has been employed, but the curves would not have been much different had a smaller value been used. For $\chi=0$, the R_{iN0} and C_{iN0} curves are symmetric around $r_p=r_n$. At this point, R_{iN0} reaches a minimum value of about 10^{-4} , but it is clearly much larger unless r_p and r_n are very nearly equal.

When $\chi=10^3$, R_{iN0} again is about 10^{-4} at $r_p=r_n$, but it increases rapidly as r_p/r_n becomes less than unity and the minority carrier is more and more strongly blocked. The final limiting value approached is that for $(0, 1; 1, 1; 10^3, 10^4)$. Clearly, most of the interesting variation of R_{iN0} and C_{iN0} occurs in the range $10^{-2} \lesssim$

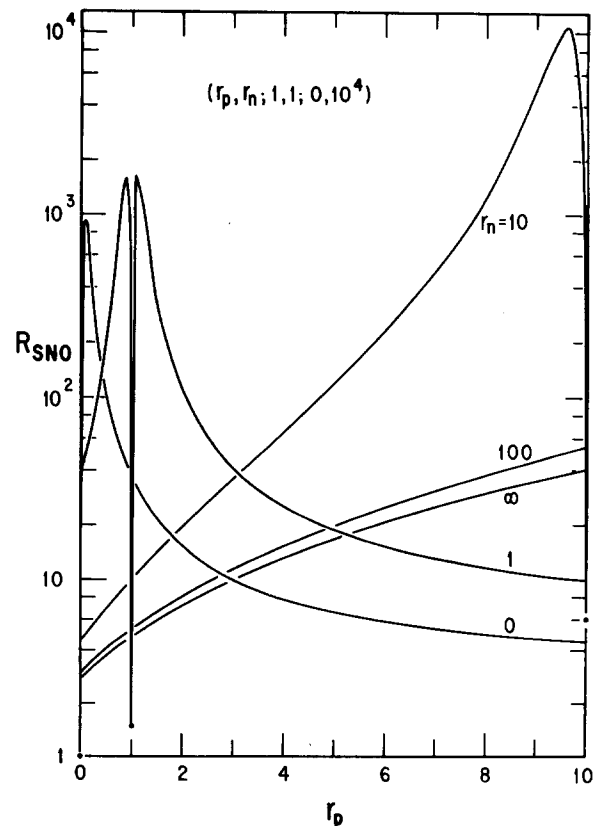


FIG. 5. The normalized quantity $R_{SN0} \equiv R_{iN0} + R_{EN}$ versus r_p for $(r_p, r_n; 1, 1; 0, 10^4)$ and several fixed values of r_n . The points indicate values of R_{SN0} when $r_p=r_n$.

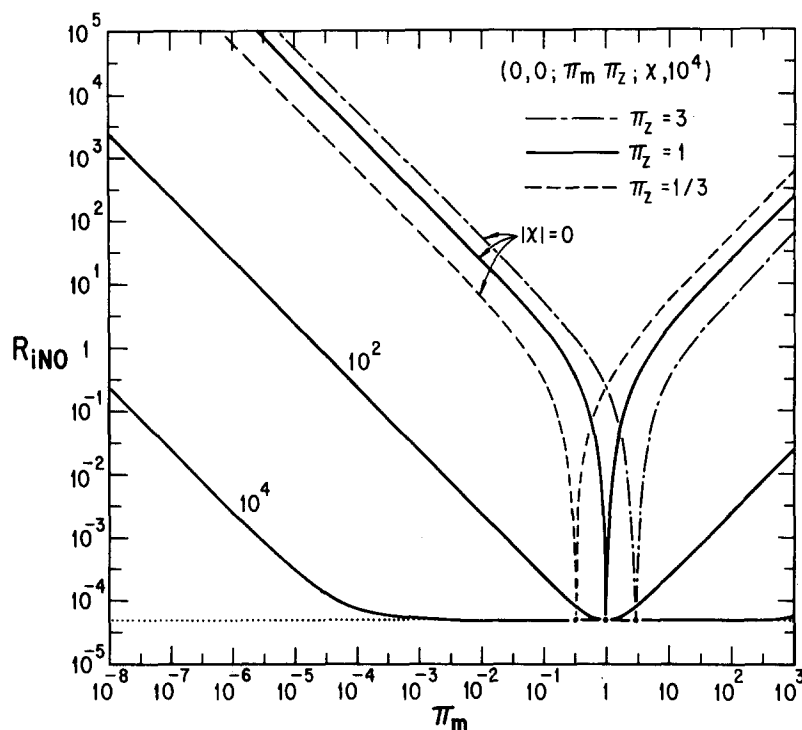


FIG. 6. Dependence of R_{iN0} on π_m for $(0, 0; \pi_m, \pi_z; \chi, 10^4)$ and several values of $|\chi|$ and π_z .

$r_p/r_n \lesssim 10^2$. In the actual computer calculations, infinite values for r_p or r_n have been approximated by 10^{20} . When $\chi \gg 1$, the results shown in Fig. 4 indicate that the situation where the minority carrier dominates in discharging [here $(r_p/r_n) \gg 1$] is again of much more physical interest (larger C_{iN0} , smaller R_{iN0}) than the opposite case.

In the intrinsic electrolyte case, a "discharge" resistance taken in series with a Warburg impedance is frequently of interest, especially in the case where an indifferent electrolyte is present.^{22,23,28,35} When the electrode reaction is taken to have an infinite rate, this discharge resistance is supposed to be zero, while it is greater than zero for finite rates. The present results indicate that the situation is somewhat different in the *unsupported* binary electrolyte situation since the present exact equivalent circuit doesn't lend itself entirely to such a conventional discharge-resistance interpretation. Here we have a true discharge resistance R_D as a separate parallel current path, not in series with any Warburg elements. Since R_E is, however, in series with Z_i , which shows Warburg frequency dependence in part of the frequency range, R_E might perhaps be considered as somewhat related to the conventional electrolyte discharge resistance. It is found, however, to *increase* as r_p increases at fixed r_n . For r_n fixed at zero, $R_E = 1$ at $r_p = 0$ and increases smoothly with increasing r_p , reaching 1.6 at $r_p = 6$ and 2 at $r_p = \infty$. On the other hand, the conventional discharge resistance would be expected to be zero for $r_p = \infty$ and to increase as r_p decreases at fixed r_n . Here this role is largely taken over by the true

discharge resistance R_D . For $r_n = 0$ it increases from 2 at $r_p = \infty$ to 3 at $r_p = 4$, reaches a much larger maximum near $r_p = 0$, then falls abruptly to zero at $r_p = r_n = 0$.

Since $R_S = R_E + R_i$ is the resistance through which C_i is charged, R_{SN0} itself is of some interest even though it is evidently not closely related to an electrolyte discharge resistance. Figure 5 shows how R_{SN0} depends on r_p for various fixed values of r_n in the $(r_p, r_n; 1, 1; 0, 10^4)$ situation. Here much of the dependence shown is dominated by that of R_{iN0} . A salient feature is the drop-off to a much lower value when $r_p = r_n$. The specific values of R_{SN0} for $r_p = r_n = 1, 3$, and 10 are shown as points on the graph. When $r_p \gg r_n$, R_{iN0} continuously decreases. Note that values of R_{SN0} of 10^3 or 10^4 greatly prolong the charge-discharge time of C_i and push the frequency response range of interest ($C_{iN} \gg 1$) to very low relative frequencies.

Figure 6 shows how R_{iN0} depends on π_m for the $(0, 0; \pi_m, \pi_z; \chi, 10^4)$ situation. $C_{iN0} = 9999$ for all the curves shown. For $\chi = 0$, curves with several values of π_z are plotted. As shown, they are symmetric around lines defined by $\pi_m = \pi_z$. In this figure M rather than M_i has been held constant as χ varies in order to demonstrate that R_{iN0} goes to the same value, $\sim 5 \times 10^{-5}$, for any χ when $\pi_m = \pi_z$. Clearly, the curves are much broadened when $|\chi| \gg 1$, and there is then a larger region where $R_{iN0} \ll 1$ and is thus unimportant.

Figure 7 shows corresponding curves for $(\infty, 0; \pi_m, 1; \chi, 10^3)$. Here C_{iN0} is not the same for all curves but goes from about 8.3×10^3 at $\chi = -10$ to 8.4×10^4 at $\chi = 0$ to 1.1×10^4 at $\chi = 10$. These results show directly

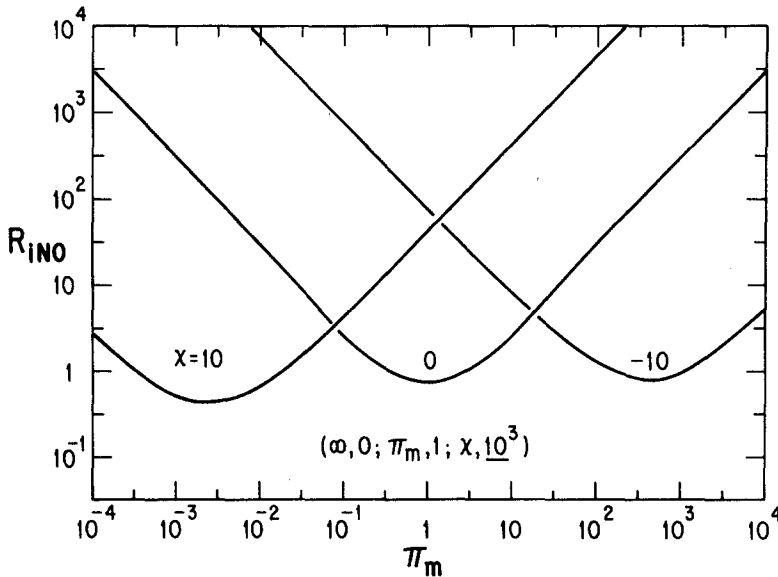


FIG. 7. Dependence of R_{iN0} on π_m for $(\infty, 0; \pi_m, 1; \chi, 10^3)$ and $\chi = -10, 0, 10$.

that it is π_e , not just π_m , which affects the shape and placement of the curves.

Finally, it is of interest to consider temperature dependence of R_{iN0} and C_{iN0} for a typical solid-state situation. Let us consider¹⁸ a KBr single crystal doped with 1.3×10^{-5} mole fraction of CaBr_2 . Using the results of Chandra and Rolfe,⁴⁶ one can calculate that for $\epsilon = 4.88$, $\pi_z = 1$, $l = 0.16$ cm, and $(10^3/T) = 1.59$ K⁻¹, $M_i \cong 3919$, $\chi \cong 517.7$, and $\pi_m \cong 165.4$. The corresponding value of M is about 8.92×10^4 . For these conditions, $n^* \cong 1.035 \times 10^8$ and $p^* \cong 9.658 \times 10^{-4}$. The much more mobile negative carriers are positive ion vacancies and the positive carriers are negative ion vacancies. Any electronic conduction present will be ignored. Because the experimental results show $\omega^{-3/2}$ behavior,¹⁸ the $(r_p, r_n) = (\infty, 0)$ boundary conditions seem more appropriate here than, say, $(0, 0)$. In general, both r_p and r_n are temperature dependent, and dependence of the form $\exp(-W/kT)$ has been suggested.^{2,7} No dependence should appear, however, for the present illustrative $(\infty, 0)$ limiting values.

Since the temperature dependence of such quantities as n_i , π_m , and χ will generally depend on the specific types of charge carriers present, I shall first consider some general relations, then specialize to the present ionic crystal case. Let temperature-dependent quantities evaluated at a given reference temperature T_r , such as that defined by $(10^3/T_r) = 1.59$ K⁻¹, be designated by the added subscript r . Further, take N_e , ω , z_p , and z_n temperature independent, and make the simplifying assumption that ϵ is also independent of temperature.

On using $z_p p_i = z_n n_i$, one immediately finds that

$$(n_i/n_{ir}) = (\chi_r/\chi). \quad (102)$$

It also follows that

$$(M_i/M_{ir}) = (L_{ir}/L_i) = [(T_r/T)(n_i/n_{ir})]^{1/2} \quad (103)$$

and

$$(M/M_r) = (M_i/M_{ir})[(p^* + \pi_z n^*)/(p_r^* + \pi_z n_r^*)]^{1/2}. \quad (104)$$

For $|\chi| \gg 1$ and $\pi_z \sim 1$, the quotient inside the square root approaches (χ/χ_r) . Thus (M/M_r) then goes to approximately $(T_r/T)^{1/2}$, much less temperature dependence than is usually found when $|\chi| \sim 0$ and $(M/M_r) \sim (M_i/M_{ir})$.

For future use it will be valuable to derive that temperature variation of Ω which is required to maintain constant ω (not necessarily zero) while T varies. Such Ω variation arises only from that of R_∞ when ϵ is temperature independent. Thus one finds

$$\begin{aligned} (\Omega/\Omega_r) &= (R_\infty/R_{\infty r}) \\ &= (z_p \mu_{pr} p_{efr} + z_n \mu_{nr} n_{efr}) / (z_p \mu_p p_{ef} + z_n \mu_n n_{ef}) \\ &= (n_{ir}/n_i) (\mu_{pr}/\mu_p) [(p_r^* + \pi_{mr} n_r^*) / (p^* + \pi_m n^*)]. \end{aligned} \quad (105)$$

Note that when $\chi \ll -1$ and $p^* \gg \pi_m n^*$, (Ω/Ω_r) is approximately equal to (μ_{pr}/μ_p) , while for $\chi \gg 1$ and $p^* \ll \pi_m n^*$, (Ω/Ω_r) approaches just (μ_{nr}/μ_n) . Although I shall here be concerned only with the temperature dependence of C_{iN0} and R_{iN0} , that of R_{i0} , the more directly measured quantity, may be obtained using Eq. (105) and the value of $R_{\infty r}$.

Now one may write

$$(n_i/n_{ir}) \cong (T/T_r)^m \exp[(h_s/2k)(T_r^{-1} - T^{-1})], \quad (106)$$

where h_s is the activation enthalpy for intrinsic carrier pair formation, and the value of m depends on the

nature of the intrinsic charge carriers. In the present KBr case, m is zero and h_s is the enthalpy associated with the formation of a pair of Schottky defects. Chandra and Rolfe⁴⁶ give $h_s = 2.53$ eV for KBr, the value I shall use here for illustrative purposes. Association into neutral complexes, such as positive and negative vacancy pairs, will be neglected but may be readily accounted for by reinterpreting n_i .

For Schottky vacancies in ionic crystals the usual expression for mobility⁴⁷ yields

$$(\mu_{ir}/\mu_i) = (T/T_r) \exp[(\Delta h_i/k)(T^{-1} - T_r^{-1})], \quad (107)$$

where $i = p$ or n . Let $h_m \equiv \Delta h_p - \Delta h_n$. I shall use the values⁴⁶ $\Delta h_p = 1.22$ eV and $\Delta h_n = 0.65$ eV. For this type of mobility temperature dependence it follows that

$$(\pi_m/\pi_{mr}) = \exp[(h_m/k)(T^{-1} - T_r^{-1})]. \quad (108)$$

We now have sufficient relations to allow the temperature dependence of R_{iN0} and C_{iN0} to be obtained for temperature-independent N_s . The assumption of constant N_s implies full dissociation of the dopant material at all temperatures of interest. Partial dissociation would add another source of temperature variation to χ .

Figure 8 shows how R_{iN0} and C_{iN0} vary over a significant range of temperature for the case $(\infty, 0; 165.4, 1; \chi_r, 3919)$ at $(10^3/T_r) = 1.59$ K⁻¹, using the KBr parameter values discussed above. In addition to

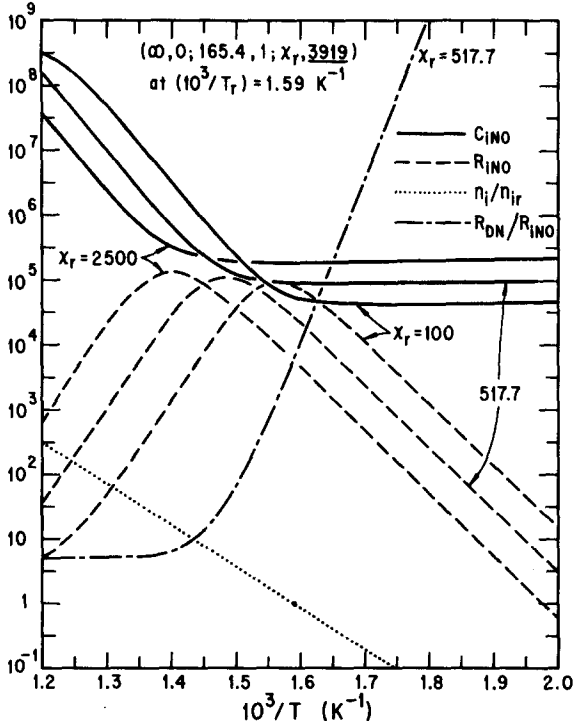


FIG. 8. Temperature dependence of C_{iN0} and R_{iN0} using parameters roughly pertaining to KBr which contains divalent cationic impurities. Positive mobile charges discharge, negative mobile charges in the majority.

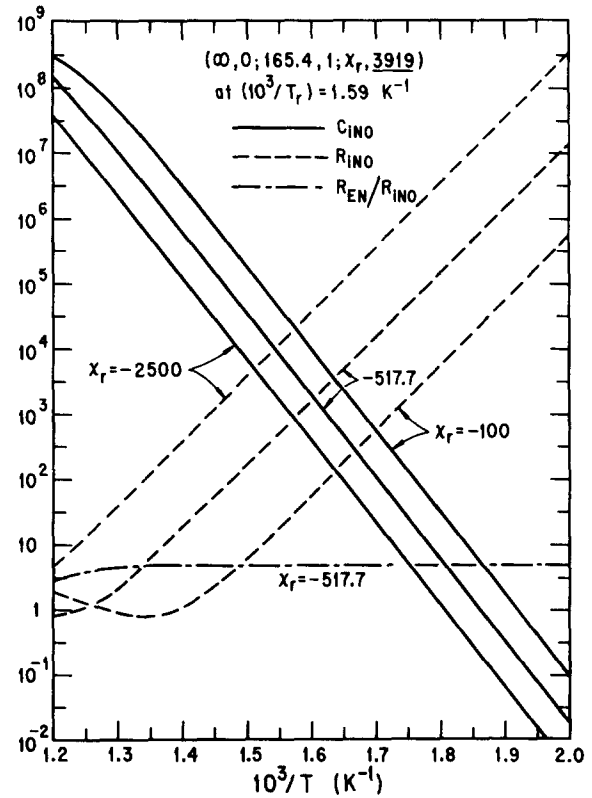


FIG. 9. Temperature dependence of C_{iN0} and R_{iN0} for the same parameters as in Fig. 8 except doping with divalent anionic impurities. Positive mobile charges discharge, positive mobile charges also in the majority.

curves with $\chi_r = 517.7$, I have included ones having χ_r about a factor of 5 larger and smaller.

The material is virtually intrinsic at $(10^3/T) = 1.2$ K⁻¹. The three χ 's are about 1.1, 2.0, and 8.2 at this high end of the temperature range. On the other hand, at 2.0 K⁻¹ the material is strongly extrinsic with χ values of about 4×10^4 , 2×10^6 , and 10^6 . The quantity π_m varies from about 12.5 at the high temperature end to 2.5×10^3 at the low end. For the situation with $\chi_r = 517.7$, $R_{DN} \approx 168$ at $(10^3/T) = 1.2$ K⁻¹ and has reached about 7×10^6 by 1.5 K⁻¹. Thus R_{EN} remains essentially unity over the whole range shown. Note that curves for (n_i/n_{ir}) and (R_{DN}/R_{iN0}) are also shown on this graph. For $\chi_r = 517.7$, M and C_{iN0} are, respectively, about 1.1×10^5 and 2.7×10^8 at $(10^3/T) = 1.2$ K⁻¹ and thus $C_{aN} \gg C_{bN}$. On the other hand, at 2.0 K⁻¹, $M \approx C_{iN0} \approx 8 \times 10^4$ and $C_{bN} \gg C_{aN}$. The slow $(T_r/T)^{1/2}$ dependence of C_{iN0} for $(10^3/T) \gtrsim 1.7$ K⁻¹ is scarcely apparent on the present scale.

For the conditions of Fig. 8 the majority carriers are blocked. For comparison, in Fig. 9 I have shown the opposite case, all χ 's negative. Although the curve shows that (R_{EN}/R_{iN0}) remains very near 5 over the entire temperature range, (R_{SN0}/R_{DN}) increases so rapidly, as $(10^3/T)$ increases from 1.2 K⁻¹, that there

is soon no hope of measuring the large C_{iN0} values apparent in the figure. What counts here is not so much the absolute magnitude of R_{SN0} as the degree to which the R_s , C_i branch is shorted out by the parallel R_D branch. For $\chi_r = -517.7$, $R_{DN} \cong 1.9$ and $R_{SN0} \cong 2.9$ at 1.2 K^{-1} . By 1.5 K^{-1} , however, $R_{DN} \cong 1$ and $R_{SN0} \cong 10^3$, making meaningful measurement of C_{iN0} very difficult. By 1.7 K^{-1} , R_{SN0} has reached about 9.5×10^4 .

Thus, when the majority carriers discharge, experimentally interesting results are only possible under the present conditions in the range where the material is intrinsic to weakly extrinsic. As we have seen, the limitation does not apply when the majority carriers are blocked. On the other hand, the likely strong exponential temperature dependence of r_p and r_n , when they are not taken exactly ($\infty, 0$) at $T = T_r$ [say (200, 0.01) instead, for example] will lead to great reduction in both quantities as T decreases below T_r . Then, for T appreciably below T_r , r_p may even be $\ll 1$, greatly reducing the discharge of the majority carriers for the $\chi \ll -1$ case. Under such conditions, the C_{iN0} curves of Fig. 9 will tend to saturate at their completely blocking values as $10^3/T$ increases, and these curves will then look much more like those of Fig. 8.

Finally, comparison of Figs. 8 and 9 shows that in the high-temperature regions near the left sides C_{iN0} values are the same for both figures and are thus independent of the sign of χ . Actual deviations begin to occur between the $\chi_r = 517.7$ and $\chi_r = -517.7$ results, for example, at about $(10^3/T) = 1.4 \text{ K}^{-1}$. At this point, $|\chi| \cong 31.8$, indicating that deviation only occurs when $2n_i$ is appreciably less than N_s . Deviations also appear for the $\chi_r = 100$ and 2500 curves at temperatures where χ is about 30. Let us define such a temperature as T_d , that where C_{iN0} begins to depend appreciably on the sign of χ ; that is, it depends on whether minority or majority carriers discharge. Let the corresponding χ value be denoted by χ_d .

For a material such as KBr,

$$n_i = N \exp[(S_s/2k) - (h_s/2kT)],$$

where N is the number of anion or cation sites/unit volume and S_s is the entropy for Schottky vacancy formation. One can now readily derive an expression for T_d . The result may be written

$$T_d = \frac{h_s}{S_s + 2k \ln[2\chi_d(N_s/N)^{-1}]}. \quad (109)$$

Here, $|N_s/N|$ is just the mole fraction of charged impurities, and the argument of the logarithm may be written alternatively as (N/n_{id}) , where $n_{id} \equiv N_s/2\chi_d$. Thus, in comparing theory and experiment, one must reach $T \lesssim T_d$ before it is possible to distinguish between positive or negative χ values on the basis of C_{iN0} values alone.

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APPENDIX

I. Eigenvalues

Take the a_{ij} elements defined in Eqs. (75)–(77) as the elements of a matrix \mathbf{A} . The symmetry of the problem allows one to write

$$P_1 = c_{11}S_1 + c_{12}S_2 \quad (A1)$$

and

$$N_1 = c_{21}S_1 + c_{22}S_2, \quad (A2)$$

where $S_k \equiv \sinh(\theta_k Y)$ and $k = 1, 2$. Here the θ_k^2 are the eigenvalues of \mathbf{A} , determined from $|\mathbf{A} - I\theta^2| = 0$, where I is the identity matrix.

The eigenvalue equation leads to

$$\theta_{\pm}^2 = 0.5\{1 + i\Omega d \pm [1 + 2i\Omega(a-b) - \Omega^2 c^2]^{1/2}\}, \quad (A3)$$

where

$$a \equiv (\delta_p^2/\epsilon_p) + (\delta_n^2/\epsilon_n), \quad (A4)$$

$$b \equiv (\delta_n \delta_p / \epsilon_n \epsilon_p) \equiv \delta_n \delta_p (\epsilon_n^{-1} + \epsilon_p^{-1}), \quad (A5)$$

$$c \equiv (\delta_n / \epsilon_n) - (\delta_p / \epsilon_p), \quad (A6)$$

and

$$d \equiv a + b \equiv (\delta_n / \epsilon_n) + (\delta_p / \epsilon_p). \quad (A7)$$

Note that $(a-b) \equiv (\delta_n - \delta_p)c$. Now define $\theta_1^2 \equiv \theta_+^2$ and $\theta_2^2 \equiv \theta_-^2$. Two exact relations between θ_1^2 and θ_2^2 are

$$\theta_1^2 \theta_2^2 = b(i\Omega - \Omega^2) \quad (A8)$$

and

$$\theta_1^2 + \theta_2^2 = 1 + i\Omega d. \quad (A9)$$

Further, define

$$e \equiv b(1-a) \equiv -\delta_n \delta_p c^2. \quad (A10)$$

Then as $\Omega \rightarrow 0$ we find

$$\theta_1^2 \rightarrow 1 + i\Omega a + \Omega^2 e + \dots \quad (A11)$$

and

$$\theta_2^2 \rightarrow i\Omega b - \Omega^2 e + \dots \quad (A12)$$

We shall later need the quantities

$$\eta_1 \equiv M\theta_1, \quad \eta_2 \equiv M\theta_2, \quad (A13)$$

and

$$\gamma_1 \equiv \eta_1 \coth \eta_1, \quad \gamma_2 \equiv \eta_2 \coth \eta_2. \quad (A14)$$

Note that when $\pi_m = \pi_s = C$: $a = b = 1$, $c = 0$, $d = 2$, and $e = 0$ for any values of C and χ when n^* and p^* are calculated from Eqs. (70) and (71). When $\pi_s = 1$, a is given by $1 + (2\xi)^{-2}[(\pi_m + \pi_m^{-1}) - 2]$.

II. Calculation of Y_{2N}

Let $Y = M$. Then $S_k \equiv \sinh \eta_k \equiv S_{kM}$. Similarly, define $C_k \equiv \cosh(\theta_k Y)$ and $C_{kM} \equiv \cosh \eta_k$. Next subtract Eq.

(80) from Eq. (81) and use in the result expressions for P_{1M}' and N_{1M}' derived from (A1) and (A2) after differentiation and evaluation at $Y=M$. After simplification, one obtains

$$c_{2211} \equiv c_{22}/c_{11} = -(S_{1M}J_1/S_{2M}J_2), \quad (\text{A15})$$

where

$$J_1 \equiv r_p + r_n c_2 + 2f_2 \gamma_1, \quad (\text{A16})$$

$$J_2 \equiv r_n + r_p c_1 + 2f_1 \gamma_2, \quad (\text{A17})$$

$$c_1 \equiv c_{12}/c_{22}, \quad c_2 \equiv c_{21}/c_{11}, \quad (\text{A18})$$

and

$$f_1 \equiv 1 + c_1, \quad f_2 \equiv 1 + c_2. \quad (\text{A19})$$

If we now use (A1) and (A2) in (73) and (74) and set the coefficients of S_1 and S_2 individually to zero, we obtain

$$c_1 \equiv (\theta_2^2 - a_{22})/a_{21} = \delta_p^{-1} [\delta_n + i\Omega(\delta_n/\epsilon_n) - \theta_2^2] \quad (\text{A20})$$

and

$$\begin{aligned} c_2 &\equiv (\theta_1^2 - a_{11})/a_{12} = \delta_n^{-1} [\delta_p + i\Omega(\delta_p/\epsilon_p) - \theta_1^2] \\ &= -1 + (\epsilon_n \delta_n)^{-1} (\epsilon_n \theta_2^2 - i\Omega \delta_n), \end{aligned} \quad (\text{A21})$$

where the last equation is obtained on using (A9). It also follows from (A9) that

$$\delta_n c_2 = -\delta_p c_1. \quad (\text{A22})$$

Now we may rewrite (A1) and (A2) as

$$P_1 = c_{11}(S_1 + c_{2211}c_1 S_2) \quad (\text{A23})$$

and

$$N_1 = c_{11}(c_2 S_1 + c_{2211} S_2), \quad (\text{A24})$$

where c_{11} is undetermined. It remains to obtain V_1^* . When (A23) and (A24) are substituted in Eq. (60) and the result integrated, one obtains

$$E_1^*(Y) = C + c_{11}(\delta_p \theta_1^{-1} f_1 C_1 - c_{2211} \delta_n \theta_2^{-1} f_2 C_2), \quad (\text{A25})$$

where C is an integration constant and (A22) has been used. The constant C can be evaluated by taking $Y=M$ in (A25) and equating the result to the E_{1M}^* obtained by adding Eqs. (80) and (81). The complete expression for $E_1^*(Y)$ then becomes

$$\begin{aligned} E_1^*(Y) &\equiv (c_{11} S_{1M}/2M J_2) \\ &\times (\gamma_1 J_2 \{1 - c_2 + 2\delta_p f_1 \theta_1^{-2} [(C_1/C_{1M}) - 1]\} \\ &+ \gamma_2 J_1 \{1 - c_1 + 2\delta_n f_2 \theta_2^{-2} [(C_2/C_{2M}) - 1]\} \\ &+ \frac{1}{2} [J_2(r_p - r_n c_2) - J_1(r_p c_1 - r_n)]). \end{aligned} \quad (\text{A26})$$

Finally, we may use Eq. (68) to obtain V_1^* . The result may be written

$$V_1^* = -(c_{11} S_{1M}/J_2) (g_p Q_1 + g_n Q_2 + e_1 J_2 t_1 + e_2 J_1 t_2), \quad (\text{A27})$$

where

$$g_p \equiv 1 + (r_p/2), \quad g_n \equiv 1 + (r_n/2), \quad (\text{A28})$$

$$Q_1 \equiv J_2 - J_1 c_1, \quad Q_2 \equiv J_1 - J_2 c_2, \quad (\text{A29})$$

$$t_1 \equiv \gamma_1 - 1, \quad t_2 \equiv \gamma_2 - 1, \quad (\text{A30})$$

$$e_1 \equiv 1 - c_2 - 2\delta_p f_1 \theta_1^{-2}, \quad (\text{A31})$$

and

$$e_2 \equiv 1 - c_1 - 2\delta_n f_2 \theta_2^{-2}. \quad (\text{A32})$$

When the preceding results are used in Eq. (84), one obtains

$$Y_{2N} = -2Q_s / [(g_p Q_1 + g_n Q_2) + (e_1 J_2 t_1 + e_2 J_1 t_2)], \quad (\text{A33})$$

where

$$Q_s \equiv \epsilon_p Q_1 + \epsilon_n Q_2. \quad (\text{A34})$$

Much reduction to basic quantities is still possible in (A33). Expansion of the elements in (A29) leads to

$$Q_1 = 2[g_n f_3 + (f_1 t_2 - f_2 c_1 t_1)] \quad (\text{A35})$$

and

$$Q_2 = 2[g_p f_3 + (f_2 t_1 - f_1 c_2 t_2)], \quad (\text{A36})$$

where

$$f_3 \equiv 1 - c_1 c_2 = f_1 - c_1 f_2 = f_2 - c_2 f_1. \quad (\text{A37})$$

The quantity Q_s may now be expanded to yield

$$Q_s = 2[g_s f_3 + f_1 t_2 (1 - f_2 \epsilon_n) + f_2 t_1 (1 - f_1 \epsilon_p)], \quad (\text{A38})$$

where

$$g_s \equiv g_p \epsilon_n + g_n \epsilon_p. \quad (\text{A39})$$

Next, define the denominator of Eq. (A33) as D_2 , a quantity which can be put in the form

$$D_2 = 4g_p g_n f_3 + h_2 t_1 + h_1 t_2, \quad (\text{A40})$$

where

$$\begin{aligned} h_1 &\equiv e_2 J_1 + 2f_1 (g_p - c_2 g_n) \\ &= 4[(g_p - c_1 c_2 g_n) - \delta_n f_2 \theta_2^{-2} (g_p + c_2 g_n) + (e_2 f_2 t_1/2)] \end{aligned} \quad (\text{A41})$$

and

$$\begin{aligned} h_2 &\equiv e_1 J_2 + 2f_2 (g_n - c_1 g_p) \\ &= 4[(g_n - c_1 c_2 g_p) - \delta_p f_1 \theta_1^{-2} (g_n + c_1 g_p) + (e_1 f_1 t_2/2)]. \end{aligned} \quad (\text{A42})$$

Since as $\Omega \rightarrow 0$, e_1 , f_2 , h_2 , and t_2 all go to zero,

$$Y_{2N0} = -(g_s/g_p g_n) \equiv -G_{EN}, \quad (\text{A43})$$

a result which leads to Eq. (85).

III. Calculation of Z_{iN}

First define

$$Y_{3N} \equiv Z_{3N}^{-1} \equiv Y_{2N} + G_{EN}. \quad (\text{A44})$$

Then from Eq. (88) we may write

$$Z_{iN} = Z_{3N} - R_{EN}, \quad (\text{A45})$$

where $R_{EN} \equiv G_{EN}^{-1}$. Next let

$$S_0 \equiv e_1 J_2 t_1 + e_2 J_1 t_2 \quad (\text{A46})$$

and

$$g_d \equiv g_p \epsilon_n - g_n \epsilon_p. \quad (\text{A47})$$

Then on using (A33), (A43), and (A44)-(A47), one finds

$$Z_{iN} = [2(g_n g_p)^2/g_s] \{Q_s/[g_s S_0 + g_d (g_p Q_1 - g_n Q_2)]\}. \quad (\text{A48})$$

The above expression for Z_{iN} , although more appropriate for calculation than Eq. (88), can still be greatly reduced to yield a much more transparent and useful form. After a great deal of algebra, (A48) may be re-

expressed in terms of more basic quantities as

$$Z_{iN} = (g_p g_n)^2 \left(\frac{(Q_s/2g_s)}{D_i} \right), \quad (\text{A49})$$

where

$$D_i \equiv D_a + D_b + D_c, \quad (\text{A50})$$

$$D_a \equiv t_1(g_n + c_1 g_p) m_a, \quad (\text{A51})$$

$$D_b \equiv t_1 t_2 g_s m_b, \quad (\text{A52})$$

$$D_c \equiv t_2(g_p + c_2 g_n) m_c, \quad (\text{A53})$$

$$m_a \equiv i\Omega g_s \delta_p \epsilon_p^{-1} \theta_1^{-2} - f_2 \epsilon_n g_p, \quad (\text{A54})$$

$$m_b \equiv i\Omega f_1 \delta_p \epsilon_p^{-1} \theta_1^{-2} - f_2(c_1 + \delta_n f_2 \theta_2^{-2}), \quad (\text{A55})$$

and

$$m_c \equiv i\Omega g_s \delta_n \epsilon_n^{-1} \theta_2^{-2} - f_1 \epsilon_p g_n. \quad (\text{A56})$$

These equations form the final computational expression for Z_{iN} . A Fortran program listing for Z_{TN} , Z_{iN} , etc., calculations in the general $(r_p, r_n; \pi_m, \pi_z; \chi, M)$ case is available.

IV. Calculation of C_{iN0} and R_{iN0}

In the $\Omega \rightarrow 0$ limit, it turns out from (A49) that Z_{iN} reduces to the form

$$Z_{iN} \cong (g_p g_n)^2 [(a_0 + i\Omega b_0)/(i\Omega)(c_0 + i\Omega d_0)]. \quad (\text{A57})$$

In terms of these quantities

$$R_{iN0} = (g_p g_n)^2 [(b_0 c_0 - a_0 d_0)/c_0^2] \quad (\text{A58})$$

and

$$C_{iN0} = (g_p g_n)^{-2} (c_0/a_0). \quad (\text{A59})$$

It is thus clear that to obtain all $\Omega \rightarrow 0$ contributions to R_{iN0} one must expand D_i to second order in Ω . The normalized time constant $\tau_{iN0} \equiv \tau_{i0}/\tau_D$ is just

$$\tau_{iN0} \equiv R_{iN0} C_{iN0} \equiv (b_0/a_0) - (d_0/c_0). \quad (\text{A60})$$

Next, as $\Omega \rightarrow 0$ we need

$$c_1 \rightarrow \delta_n \delta_p^{-1} + i\Omega c \delta_n \delta_p^{-1} + \dots, \quad (\text{A61})$$

$$c_2 \rightarrow -1 - i\Omega c - \Omega^2 e \delta_n^{-1} + \dots, \quad (\text{A62})$$

$$t_1 \rightarrow (r-1) - i\Omega(a/2)(M^2 \text{csch}^2 M - r) + \dots, \quad (\text{A63})$$

$$t_2 \rightarrow i\Omega(M^2/3) \{b - i\Omega[(b^2 M^2/15) - e]\} + \dots, \quad (\text{A64})$$

$$f_3 \rightarrow \delta_p^{-1} + 2i\Omega c \delta_n \delta_p^{-1} + \dots, \quad (\text{A65})$$

$$(g_n + c_1 g_p) \rightarrow (g_n + \delta_n \delta_p^{-1} g_p) + i\Omega c \delta_n \delta_p^{-1} g_p + \dots, \quad (\text{A66})$$

$$(g_p + c_2 g_n) \rightarrow (g_p - g_n) - i\Omega c g_n + \dots, \quad (\text{A67})$$

and

$$(Q_s/2g_s) \rightarrow \delta_p^{-1} + i\Omega \delta_p^{-1} \{2c \delta_n + g_s^{-1} \times [(M^2 b/3) + (r-1)(a-1)]\} + \dots. \quad (\text{A68})$$

Now let

$$g_s \equiv g_p \delta_n + g_n \delta_p. \quad (\text{A69})$$

Then, after extensive further algebra, one finds

$$m_a \rightarrow i\Omega \{g_s - i\Omega \delta_p [a(g_n - g_p) + \epsilon_p^{-1} g_p]\} + \dots, \quad (\text{A70})$$

$$m_b \rightarrow i\Omega \delta_p^{-1} + \dots, \quad (\text{A71})$$

$$m_c \rightarrow (\delta_p^{-1} \epsilon_p \epsilon_n)$$

$$\times \{(g_p - g_n) - i\Omega[(1-a)(g_p - g_n) + g_n c]\} + \dots, \quad (\text{A72})$$

$$D_a \rightarrow (i\Omega \delta_p^{-1}) [(r-1)g_s^2 + i\Omega g_s \{(r-1) \times \{[a(1+\delta_p) - 2\delta_p \epsilon_p^{-1}]g_p - a\delta_p g_n\} - (g_s a/2)(M^2 \text{csch}^2 M - r)\}] + \dots, \quad (\text{A73})$$

$$D_b \rightarrow (i\Omega \delta_p^{-1}) [i\Omega(r-1)(M^2 b g_s/3)] + \dots, \quad (\text{A74})$$

and

$$D_c \rightarrow (i\Omega \delta_p^{-1}) (\delta_n \delta_p M^2/3) \{ (g_p - g_n)^2 - i\Omega[(bM^2/15) \times (g_p - g_n)^2 + 2c g_n (g_p - g_n)] \} + \dots. \quad (\text{A75})$$

It follows that

$$a_0 \equiv \delta_p^{-1}, \quad (\text{A76})$$

$$b_0 \equiv \delta_p^{-1} \{2c \delta_n + g_s^{-1} [(M^2 b/3) + (r-1)(a-1)]\}, \quad (\text{A77})$$

$$c_0 \equiv \delta_p^{-1} [(r-1)g_s^2 + (\delta_n \delta_p M^2/3)(g_p - g_n)^2], \quad (\text{A78})$$

and

$$d_0 \equiv \delta_p^{-1} [(r-1)((M^2 b g_s/3) + g_s \{[a(1+\delta_p) - 2\delta_p \epsilon_p^{-1}]g_p - a\delta_p g_n\}) - (g_s^2 a/2)(M^2 \text{csch}^2 M - r) - (g_p - g_n) \times (\delta_n \delta_p M^2/3) [(M^2/15)(g_p - g_n) + 2c g_n]]. \quad (\text{A79})$$

Equations (A59), (A76), and (A78) lead to

$$C_{iN0} = (g_p g_n)^{-2} [(\delta_p \delta_n M^2/3)(g_p - g_n)^2 + (r-1)g_s^2]. \quad (\text{A80})$$

Similarly, exact expressions for R_{iN0} and τ_{iN0} may be formed using Eqs. (A58)–(A60) and (A76)–(A79). Although the general results are too long to write out conveniently, they readily lead to simpler expressions in such cases as $(r_p, r_n) = (0, 0)$, $(\infty, 0)$, and $(0, \infty)$.

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