

# Theory of small-signal ac response of solids and liquids with recombining mobile charge<sup>a)</sup>

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An exact, small-signal theory of the impedance of an electrode/material/electrode system under quite general conditions is presented. The system, assumed flat band, consists of a slab of material between two identical plane-parallel electrodes. The material may be a nondegenerate electronic semiconductor or an ionic conductor. Solid ionic conductors considered are Schottky and Frenkel defect materials, possibly containing neutral defect pairs and/or aliovalent impurities, and fast ion conductors such as Na- $\beta$ -alumina. Liquid ionic conductors treated include unsupported strong, weak or potential electrolytes, and possibly fused salts and oxides. Both intrinsic and extrinsic conduction conditions are included, with a single species of negative mobile charge of arbitrary valence and mobility and a single species of positive mobile charge of arbitrary valence and mobility assumed present. Intrinsic and extrinsic equilibrium and dynamic generation and recombination processes are taken into account. The boundary conditions employed permit the charge carriers to react directly at the electrode, to be adsorbed without reaction, or to react after the formation of an adsorbed intermediate. The general solution and various simplified special cases are discussed in detail. The general solution in the form presented here is sufficiently simple that it can be used without approximation as the fitting function in a newly developed weighted nonlinear least squares fitting procedure which treats simultaneously the real and imaginary parts of a complex function such as impedance. A discussion is presented showing how fitting parameter estimates thus derived from experimental data may be used to obtain a set of basic physical parameters characterizing the experimental electrode/material system. Finally, the physical interpretation and significance of many of the basic parameters is discussed in detail.

## I. INTRODUCTION

Since the early theoretical work of Jaffé on ac space-charge polarization in solids and liquids,<sup>1,2</sup> there has been considerable interest in the ac properties of such materials, both in the further development of theory and in the theoretical interpretation of experimental results (for recent reviews, see Refs. 3 and 4). Comparison of theory and experiment has sometimes allowed nearly unambiguous identification and interpretation of the physical processes operative in the experimental system, but too often has yielded only meagre agreement between prediction and observation and thus contributed little to our understanding of the system response. Two reasons may be given for such disappointing results: The theory may be too idealized and thus may not adequately include the effects of some important processes, and/or the procedures used in confronting theory and experiment may be too inflexible and limiting, especially when theoretical results are very complicated and may involve numerous parameters whose values need to be estimated. The present work should at least partly remedy these deficiencies in a number of cases.

Although the purpose of an experiment may sometimes only be to find how a given experimental system responds to a given stimulus, perhaps with the thought of eventually using the stimulus-response relationship in a particular application, one is often more concerned with deducing as many properties of the system as possible from the observed effects. In other words, we often wish to characterize the initially unknown (black box) system as completely as possible, thereby deducing something about its "color" and other structure. Here,

we shall be concerned with nondestructive electrical stimulus and response. A relevant block diagram is shown in Fig. 1. System characterization, as defined here, involves the estimation of values of all parameters entering the theory, thus making quantitative the specific model considered. Each distinct physical process may involve one or more parameters, and the theory becomes most transparent when each parameter can be associated with a single distinct physical process. Although the equivalent circuit step shown in the diagram is not essential to the electrical characterization process, it can often be helpful in showing the interconnection of the separate processes which may be present.

In selecting a model for extensive analysis, one must compromise between the desire to include the known or conjectured characteristics of the widest possible range of systems and the need to keep the mathematical formulation tractable and the results comprehensible. Among the factors which must be decided at the outset are: (i)

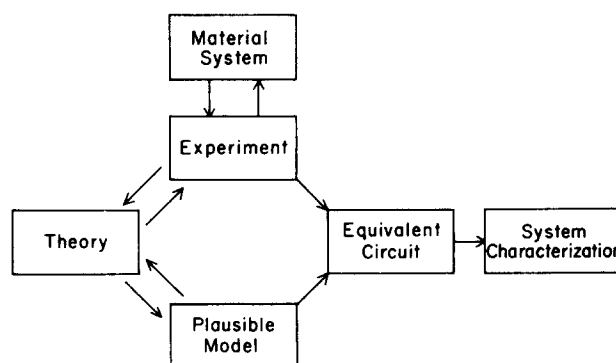


FIG. 1. Block diagram for characterization of a material system.

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the geometry of the system, (ii) the number of distinct species present, (iii) the charge and (iv) the mobility of each species, (v) the number of homogeneous chemical reactions which occur between the different species, (vi) the stoichiometry and kinetics of each such reaction, and (vii) the stoichiometry and kinetics of each electrode (heterogeneous) reaction.

Here, as in most of the earlier work on space-charge polarization, we consider solid or liquid materials between plane, parallel, identical electrodes separated by a distance  $l$ , and make the usual one-dimensional approximations.<sup>5</sup> Much of the earlier theoretical work dealt with a single species of possibly mobile negative charge and a single species of possibly mobile positive charge which were not allowed to combine with each other or with fixed centers. In many intrinsic-conduction situations, however, generation and recombination ( $G/R$ ) of charge carriers is known to occur and the neglect of such processes is undesirable. Even in cases of extrinsic conduction it is not always appropriate to assume full dissociation of neutral donor and acceptor centers. Although a treatment of an intrinsic-extrinsic space-charge problem has appeared,<sup>6</sup> it ignores dynamic  $G/R$  effects.

The model adopted in the present work is defined by the equations of Sec. II. Its principal novel feature is the inclusion of intrinsic and extrinsic  $G/R$  processes. The equations provide for one positive and one negative species, each of arbitrary mobility, which may combine with each other (reversibly) to form a neutral intrinsic center. In addition, neutral donor and acceptor centers may dissociate to form immobile impurity ions and mobile charged species identical to the positive and negative species arising from neutral center dissociation. In general, there are then four distinct charged species present: two immobile ones of valence numbers  $z_p = z_1$  and  $z_n = z_2$ , and two possibly mobile ones, also of valence numbers  $z_1$  and  $z_2$ . Although such a situation is limited and does not, for example, allow mixed electronic and ionic conduction with mobile electronic and ionic species of the same sign, it is still sufficiently broad to include many systems of experimental interest. There are also three distinct immobile neutral species possibly present: neutral intrinsic, donor, and acceptor centers. While provision for diffusion of neutral species is desirable for some applications, it results in a quantum jump in mathematical complexity and is not attempted here.

In Secs. III and IV we discuss respectively the exact equilibrium and small-signal ac solutions of the general model presented in Sec. II. While the equilibrium properties and small-signal response are essentially independent problems, their treatment in a single, consistent notation is clearly desirable. In Sec. V we discuss procedures for fitting the theoretical results obtained to experimental data and the physical significance of the model parameters in relation to different classes of materials. A very brief summary of this latter discussion is appropriate here as a preface to the formal development of the model.

The present treatment can be applied, either directly

or in one of its limiting forms, to solid materials such as single crystals showing intrinsic or extrinsic conduction, including conventional semiconductors and solid electrolytes, e.g., Si, AgCl, and  $\beta$ -alumina, to liquid materials such as unsupported electrolyte solutions, e.g., in the cell  $\text{Ag}|\text{AgNO}_3(\text{aq})|\text{Ag}$ , and perhaps to fused salts and oxides. The physical and chemical insights that one has concerning the material of interest should guide the processes of data fitting and parameter interpretation. In some cases all of the model parameters should correspond to physical properties of the material. In other cases it will be appropriate to use a limiting form of the general model with fewer parameters. Other materials may be well described if one assigns a single model parameter one value in the equilibrium treatment and another in small-signal response. In yet other cases, for which the generally accepted physical model does not completely agree with that adopted here, the equations governing small-signal response are, to good approximation, isomorphic to those of the present model. Finally, for some other systems the results presented here may provide a convenient means of parameterizing the data even though the physical significance of some or all of the parameters remains obscure.

Because the continuity and transport equations which govern the motion of charges in a solid or liquid are nonlinear, an exact analytic solution of the equations can only be obtained in the limiting case of small perturbation from the simplest equilibrium case, that where there are initially no electric fields present. Linearization of the equations then allows one to obtain an exact, small-signal solution for current as a function of applied potential difference or *vice versa*. All exact ac solutions of the equations obtained thus far are of this type. The solution is most conveniently expressed in terms of the total input impedance (or admittance) of the system,  $Z_T$ , as a function of frequency. Note that such solutions formally apply for ac signals of amplitude small compared to  $kT/e$  applied around equilibrium, here the point of zero electrode charge. The quality  $k$  is the Boltzmann constant,  $T$  the absolute temperature, and  $e$  the proton charge.

Thus far, all exact, small-signal ac solutions for the impedance have ignored the possible presence of a compact layer next to each electrode arising from the finite size of the charge carriers. This approximation is of no consequence for electronic conduction but may lead to significant inaccuracies under some conditions when the charge carriers are ions or lattice vacancies. Recently, however, a treatment has been given which shows how solutions which ignore this effect may be corrected for it.<sup>7</sup> Such correction has been explicitly considered for an intrinsic, no-recombination situation with charge of only one sign mobile. The existence of the general correction procedure makes it still worthwhile to be concerned with solutions which ignore inner layer effects and then to correct such solutions for these effects in cases where they become important. Thus, the present work will ignore finite size of carriers, take the reaction plane identical to the effective electrode surface plane, and employ the Chang-Jaffé boundary conditions<sup>2,6</sup> ap-

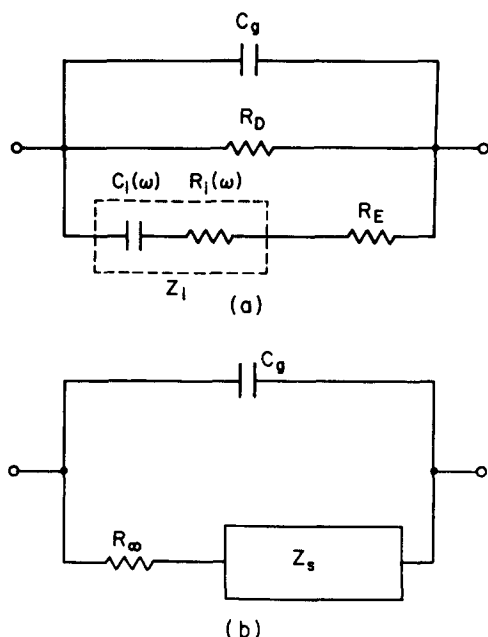


FIG. 2. Two general equivalent circuits used to represent the electrical response of a general linear system.

appropriate for small-signal response with no inner layer. Situations where full linearization is inapplicable will be investigated in future work using computer simulation techniques. Such situations include those in which intrinsic Frenkel diffuse double layers<sup>8</sup> are present near the electrodes, perhaps associated with surface states or specific ionic adsorption, and/or where a steady direct current passes through the material as well as a small-signal alternating current.

Although small-signal ac solutions of the present type are formally limited to small perturbations about flat-band equilibrium, a situation not often found experimentally, they are nevertheless valuable because they frequently seem to apply appreciably beyond these restrictions and because much more can be learned from their exact analytic forms, than from purely numerical solutions. They may also be used to obtain estimates, by comparison, of the accuracy of numerical solutions for those situations where such comparison can be made.

The present results differ from earlier ones in being both simpler and yet more general. They are more general because they include static and dynamic  $G/R$  effects for both intrinsic and extrinsic centers and because they may include as well incremental specific adsorption or surface state occupancy.

Most of the earlier work has been aimed at calculating the impedance  $Z_i$  which appears in the general equivalent circuit of Fig. 2(a). This circuit can represent any linear-system small-signal response because the circuit elements  $C_i(\omega)$  and  $R_i(\omega)$  are, in general, arbitrary functions of frequency. Here  $\omega$  is the radial frequency of the applied ac signal. The virtue of this circuit is that it explicitly separates out the limiting zero-frequency resistance  $R_D$  and the high-frequency limiting resistance  $R_\infty$ , the parallel combination of  $R_D$  and  $R_E$ . But this form of circuit requires that  $Z_i(\omega)$  involve no

$\omega \rightarrow 0$  dc path since all such paths are subsumed in  $R_D$ . This requirement leads to very appreciable complexity in the specific form of  $Z_i$  which follows from the exact solution of the pertinent differential equations of the problem even in the absence of dynamic  $G/R$  and adsorption effects. In particular, the resulting form of  $Z_i$  includes several difficult-to-eliminate differences between frequency-independent quantities which must formally cancel in order to ensure that all dc paths are accounted for by  $R_D$ . These differences occur at several levels in the hierarchy of equations which define  $Z_i(\omega)$  and must be completely eliminated in order to allow accurate computer evaluation of  $Z_i(\omega)$  to be carried out.

The above difficulty is not encountered when one calculates the  $Z_s$  of Fig. 2(b) instead of  $Z_i$ . Note that  $Z_s$  includes all the response of the system except that associated with bulk behavior, that which involves  $R_\infty$  and  $C_g \equiv \epsilon/4\pi l$ , the geometric capacitance of the system. Here  $\epsilon$  is the bulk dielectric constant of the material between electrodes separated by the distance  $l$ , and here and elsewhere all circuit impedances and circuit elements will always be given for unit electrode area. It is clear from the form of the Fig. 2(b) circuit that the zero-frequency limiting value of the real part of the total circuit impedance is  $\text{Re}(Z_{T0}) = R_\infty + \text{Re}(Z_{s0})$ , where a subscript zero denotes a  $\omega \rightarrow 0$  limit. It further turns out that  $\text{Re}(Z_{s0}) = Z_{s0}$  for situations of the present type. There are in this case no differences between large frequency-independent quantities which must be completely cancelled to obtain  $\text{Re}(Z_{s0})$  exactly; thus the explicit form of  $Z_s(\omega)$  is appreciably simpler than that of  $Z_i(\omega)$ . The present work is therefore concerned only with the calculation of  $Z_s(\omega)$ .

Finally, it has recently been found that several exact relations can be used to simplify very substantially the form of  $Z_s(\omega)$  which follows from the direct solution of the equations of the problem. The final resulting expression for  $Z_s(\omega)$  is much less hierarchal than the original one and is simple enough to be almost transparent in its implications. This simplicity is of great importance. A solution has now been found that includes the five main processes: Charge separation near an interface, adsorption-desorption, charge transfer at an electrode, mass transport (diffusion effects), and intrinsic-extrinsic  $G/R$ , and yet is simple enough that it may be economically used in a least squares comparison of theory and data.

A method of complex nonlinear least squares fitting has recently been developed which fits both real and imaginary parts of complex data simultaneously.<sup>9</sup> In addition, the resulting squared residuals may be arbitrarily weighted. Because of the availability of a simple enough solution to be used in such least squares fitting, one need be much less concerned with obtaining an exact or approximate equivalent circuit to represent the system response. Although approximate equivalent circuits will be employed where they are helpful in interpreting the response, one can now obtain parameter value estimates for the electrode-material system by direct fitting of the exact theoretical result for the total impedance,  $Z_T$ , to impedance data with no approximate

intermediate steps. The fitting procedure yields not only parameter-value estimates but estimates of their standard deviations and of that for the entire fit. The remainder of the present work is concerned with the applicable equations of the rather general model described above and their equilibrium and small-signal solutions. Most mathematical details appear in the appendices.

## II. GENERAL EQUATIONS

Consider a homogeneous material containing a concentration  $n$  of possibly mobile negative charge and a concentration  $p$  of possibly mobile positive charge. Notation will be considerably simplified if subscripts used to distinguish quantities associated with positive or negative species are taken as 1 or 2, respectively. Thus, e.g., the valence number and mobility of the positive species will be denoted by  $z_1$  and  $\mu_1$  rather than by  $z_p$  and  $\mu_p$  as in previous work. The material is also taken to contain, before any dissociation takes place, the immobile, neutral intrinsic, acceptor, and donor center concentrations,  $N_I^0$ ,  $N_A^0$ , and  $N_D^0$ , respectively. After arbitrary amounts of dissociation have occurred, the resulting neutral concentrations are  $N_I$ ,  $N_A$ , and  $N_D$ , and the immobile charged concentrations are  $N_A^+$  and  $N_D^+$ . The valence numbers of the latter quantities are  $z_1$  and  $z_2$ , respectively.

It will be assumed in the present work that recombination of charged entities to form either a neutral intrinsic center or a neutral acceptor or donor atom occurs by a simple bimolecular, mass action process. Many other recombination modes are of course possible; some have been described by Sah<sup>10</sup> for electrons and holes in semiconductors. The bimolecular rate law is employed here for simplicity; because it is usually an excellent approximation for donors and acceptors; and because one of us has shown<sup>11</sup> that for small deviations from equilibrium it can provide an adequate description of a wide variety of other recombination and trapping processes. Thus, this assumption often represents only a negligible or small specialization away from general recombination and trapping mechanisms. Whenever full dissociation occurs (i.e., no recombination), the form of the recombination rate law is of course immaterial, and the ratio  $\pi_e \equiv z_2/z_1$  will then be taken as arbitrary. On the other hand, when some recombination occurs,  $\pi_e$  will be taken as unity throughout this work, thus ensuring the applicability of the simple bimolecular rate law and consequently avoiding the need to consider combinations of sequential and/or instantaneous  $n$ -body recombinations with  $n > 2$ .

In the following work, we shall make the usual assumptions that dielectric constant, diffusion coefficients  $D_j$ , and mobilities are all position and field independent. In addition, the Einstein relation,  $D_j = (kT/e)(\mu_j/z_j)$  with  $j = 1, 2$ , will be assumed applicable. Let us consider a one-dimensional system and define the faradaic currents  $I_1$  and  $I_2$  and the total current (position-independent)  $I$ . In addition, take the average (or macro) potential as  $V$ , with  $\partial V/\partial x = -E$ , where  $E$  is the electric field at position  $x$ , measured from the left electrode.

The current equations may now be written as<sup>6</sup>

$$I_1 = -(z_1 e \mu_1) \left[ p \frac{\partial V}{\partial x} + (kT/e z_1) \frac{\partial p}{\partial x} \right], \quad (1)$$

$$I_2 = (z_2 e \mu_2) \left[ -n \frac{\partial V}{\partial x} + (kT/e z_2) \frac{\partial n}{\partial x} \right], \quad (2)$$

and

$$I = I_1 + I_2 - \left( \frac{\epsilon}{4\pi} \right) \frac{\partial^2 V}{\partial t \partial x}. \quad (3)$$

The continuity equations are<sup>6, 7, 12</sup>

$$\frac{\partial N_I}{\partial t} = -k_{Ig} N_I + k_{Ir} n p, \quad (4)$$

$$\frac{\partial N_A}{\partial t} = -k_{Ag} N_A + k_{Ar} N_A^+ p, \quad (5)$$

$$\frac{\partial N_D}{\partial t} = -k_{Dg} N_D + k_{Dr} N_D^+ n, \quad (6)$$

$$\frac{\partial p}{\partial t} = -\frac{\partial N_I}{\partial t} - \frac{\partial N_A}{\partial t} - \left( \frac{1}{z_1 e} \right) \frac{\partial I_1}{\partial x}, \quad (7)$$

and

$$\frac{\partial n}{\partial t} = -\frac{\partial N_I}{\partial t} - \frac{\partial N_D}{\partial t} + \left( \frac{1}{z_2 e} \right) \frac{\partial I_2}{\partial x}. \quad (8)$$

Here the subscripts  $g$  and  $r$  stand for generation and recombination. Finally, Poisson's equation becomes

$$\frac{\partial^2 V}{\partial x^2} = - \left( \frac{4\pi e}{\epsilon} \right) (z_1 p - z_2 n + z_2 N_D^+ - z_1 N_A^+). \quad (9)$$

In the above equations, all concentrations are generally time and space dependent. A list of sub and superscript and symbol definitions is included at the end of this paper.

Boundary conditions are needed in order to solve the above set of equations. The generalized Chang-Jaffé boundary conditions<sup>2, 6</sup> which will be used here may be written as

$$I_{1L} = -z_1 e k_1 (p_L - p_e), \quad (10)$$

$$I_{1R} = z_1 e k_1 (p_R - p_e), \quad (11)$$

$$I_{2L} = z_2 e k_2 (n_L - n_e), \quad (12)$$

and

$$I_{2R} = -z_2 e k_2 (n_R - n_e), \quad (13)$$

where the subscripts  $L$ ,  $R$ , and  $e$  designate left, right, and bulk equilibrium values. Thus,  $I_{1R}$  is the instantaneous value of the component of faradaic current  $I_1$  at the right electrode, where the value of  $p$  is  $p_R$ . The quantities  $k_1$  and  $k_2$  are values of the effective heterogeneous reaction rates (evaluated at the point of zero electrode charge) associated with electrode reactions of the  $p$  and  $n$  carriers, respectively. In most previous work in this field they have been normalized to yield the dimensionless boundary parameters  $r_j \equiv (l/D_j)k_j$ ,  $j = 1, 2$ . Here, we shall employ the more convenient choices  $\rho_j \equiv r_j/2 \equiv (l/2)(k_j/D_j)$ . As we shall see later,  $k_j$  and  $\rho_j$  will be complex and frequency dependent when specific adsorption is present.<sup>7, 13-15</sup> For convenience take  $V_L = 0$  and  $V_R = V_a$ , the total potential difference applied to the system. It appears that an exact solution of the above

set of equations can only be obtained (for  $V_a \neq 0$ ) if they are linearized. Let  $V_a = V_{a0} + V_{at}e^{i\omega t}$ , and expand all potentials, currents, and concentrations in the general form  $Y = Y_0 + Y_t e^{i\omega t}$ , where higher-order terms are neglected in the expansions and in all products such as  $p(\partial V/\partial x)$ . Here the subscript  $i$  stands for incremental. The present small-signal ac solution around the point of zero charge for flat-band conditions requires that  $V_{a0} = 0$  and thus  $V_0(x) = 0$ . In addition, one must have  $|V_{at}| \ll kT/e$ , ensuring that  $|Y_t| \ll |Y_0|$  whenever  $Y_0 \neq 0$ .

### III. EQUILIBRIUM CONDITIONS

In the present flat-band solution, all static quantities, such as  $p_0$  and  $n_0$ , have their equilibrium values. Thus,  $p_0 = p_e$  and  $n_0 = n_e$ , independent of position. Even the solution of the system equations for equilibrium conditions yields rather complex results when three different  $G/R$  processes may be simultaneously operative. The calculation of the equilibrium values of  $p_0$  and  $n_0$  is carried out in Appendix A for various cases of interest. Note that in the most general extrinsic case, quintic equations in  $n_0$  and  $p_0$  appear, while simpler situations yield cubics or quadratics.

As mentioned in Appendix A, it is convenient to normalize extrinsic concentrations with intrinsic ones, yielding the normalized quantities  $\tilde{n}_0$  and  $\tilde{p}_0$ . Once  $\tilde{n}_0$  and  $\tilde{p}_0$  have been obtained using the equations of Appendix A, a number of further useful derived quantities may be defined. Let

$$G_\infty \equiv R_\infty^{-1} \equiv G_1 + G_2, \quad (14)$$

where

$$G_j \equiv (e/l)(z_j \mu_j y_{j0}), \quad (15)$$

and  $y_{10} \equiv p_0$ ,  $y_{20} \equiv n_0$ . Further define

$$\pi_m \equiv \mu_2/\mu_1, \quad \pi_e \equiv \pi_m(\tilde{n}_0/\tilde{p}_0), \quad (16)$$

$$\epsilon_j \equiv G_j/G_\infty = (1 + \pi_e^{3-2j})^{-1}, \quad (17)$$

$$\pi_e \equiv z_2/z_1, \quad \pi_f \equiv \pi_e(\tilde{n}_0/\tilde{p}_0), \quad (18)$$

$$\delta_j \equiv (1 + \pi_f^{3-2j})^{-1}, \quad (19)$$

$$\lambda_j \equiv \delta_j/\epsilon_j, \quad \phi \equiv 0.5(\tilde{n}_0 + \tilde{p}_0), \quad (20)$$

$$a \equiv \delta_1\lambda_1 + \delta_2\lambda_2, \quad b \equiv \lambda_1\lambda_2, \quad (21)$$

and

$$c \equiv \lambda_2 - \lambda_1, \quad d \equiv \lambda_2 + \lambda_1. \quad (22)$$

The general Debye length is

$$L_D \equiv [\epsilon kT/4\pi e^2(z_1^2 p_0 + z_2^2 n_0)]^{1/2}. \quad (23)$$

An important derived quantity is  $M \equiv (l/2)/L_D$ . When  $z_1 = z_2 = z_e$ ,  $L_D/L_I = \phi^{-1/2}$ , where  $L_I$  is the intrinsic Debye length for this case.

### IV. STEADY-STATE ac RESULTS

For maximum generality, the present solution will be given in normalized form. Let impedances and resistances be normalized with  $R_\infty$ , capacitances with  $C_g$ , and  $\omega$  with  $\tau_D \equiv R_\infty C_g$ , so that  $\Omega \equiv \omega \tau_D$ . Most of the processes of interest in the present work occur for  $\Omega \lesssim 1$ . Denote

the above normalization by a subscript "N." Then  $Z_{TN} \equiv Z_T/R_\infty$ . In normalized form, the relation between  $Z_T$  and  $Z_s$  consistent with the Fig. 2(b) circuit is

$$Z_{TN} = \frac{1 + Z_{sN}}{1 + i\Omega(1 + Z_{sN})}. \quad (24)$$

Since  $Re(Z_{sN0}) = Z_{sN0}$ , it follows that  $Z_{TN0} = 1 + Z_{sN0}$ . But this quantity, the normalized  $\Omega \rightarrow 0$  resistance, must equal  $R_{DN}$ , where  $R_D$  appears in Fig. 2(a). Earlier work<sup>4,6</sup> yields the following expression for  $R_{DN}$ ,

$$R_{DN} \equiv \left[ \frac{\epsilon_1}{1 + \rho_{10}^{-1}} + \frac{\epsilon_2}{1 + \rho_{20}^{-1}} \right]^{-1}, \quad (25)$$

where  $\rho_{10}$  and  $\rho_{20}$  are the  $\Omega \rightarrow 0$  values of the dimensionless boundary parameters  $\rho_1$  and  $\rho_2$ . These latter quantities are frequency independent in the absence of specific adsorption. Note that, unlike  $R_\infty$ ,  $R_D$  is not an equilibrium bulk property of the material but depends on the boundary conditions. It is independent of  $G/R$  parameters as it should be (but see discussion at the end of Appendix B). When  $\rho_{10} = 0$ , so that there is no  $\Omega \rightarrow 0$  Faradaic current of positive carriers, the result for  $Z_{sN0} \equiv R_{sN0} \equiv R_{DN} - 1$  simplifies appreciably and becomes

$$Z_{sN0} = \pi_e^{-1} + (\epsilon_2 \rho_{20})^{-1}, \quad (26)$$

$$(\rho_{10} = 0)$$

since  $\pi_e \equiv \epsilon_2/\epsilon_1$ .

The small-signal equations are obtained, as mentioned above, by separating all quantities into static and incremental terms as in  $Y = Y_0 + Y_t e^{i\omega t}$ , linearizing, separating out incremental terms, and cancelling  $e^{i\omega t}$  factors. Results are summarized in Appendix B. The cardinal result is the following irreducible expression (B34),

$$Y_{sN} \equiv Z_{sN}^{-1} \equiv \frac{h_s + Y_{MN}}{g_s + N_s}, \quad (27)$$

whose terms are given explicitly in Eqs. (B35), (B36), (B37'), and (B43)–(B48). The admittance has thus been found in terms of the basic  $[a_{jm}]$  elements (Appendix B.1), its eigenvalues  $\theta_j^2$ ,  $i\Omega$ , and a few other simple quantities such as  $\epsilon_j$ .

Although this  $Y_{sN}$  result, in its full generality, is still not trivially simple, it is, nevertheless, sufficiently uncomplicated that it can readily be employed as a fitting function in nonlinear, complex least squares data fitting.<sup>9</sup> In the most general case, the normalized expression for  $Y_{sN}$  involves the following parameters: (a)  $M$ ,  $\pi_e$ ,  $\pi_f$ , and  $\phi$  related to the specific species present; (b)  $\rho_{10}$ ,  $\rho_{1\infty}$ ,  $\xi_{1a}$  and  $\rho_{20}$ ,  $\rho_{2\infty}$ ,  $\xi_{2a}$  associated with the boundary conditions; and (c)  $N_A^0$ ,  $\tilde{N}_D^0$ ,  $\Lambda_I$ ,  $\Lambda_A$ ,  $\Lambda_D$ ,  $\xi_I$ ,  $\xi_A$ , and  $\xi_D$  associated with the three  $G/R$  processes possibly present in the bulk material (see Appendices A and B). In almost all practical cases, not all of these parameters must be determined from the fitting, however. Thus, for an intrinsic situation with the positively charged mobile species completely blocked, calculation of  $Y_{sN}$  involves  $M$ ,  $\pi_m$ ,  $\rho_{20}$ ,  $\rho_{2\infty}$ ,  $\xi_{2a}$ ,  $\Lambda_I$ , and  $\xi_I$  for incomplete dissociation and  $M$ ,  $\pi_m$ ,  $\pi_e$ ,  $\rho_{20}$ ,  $\rho_{2\infty}$ , and  $\xi_{2a}$  for complete dissociation. For a similar pure donor-type extrinsic conduction situation with full donor dis-

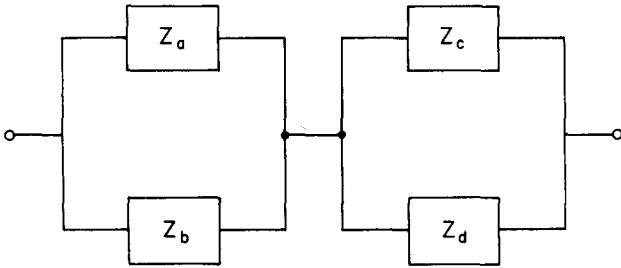


FIG. 3. General equivalent circuit used to represent the impedance  $Z_s$  of Fig. 2(b).

sociation and no specific adsorption, the parameters required are  $M$ ,  $\pi_e$ ,  $\pi_f$ ,  $\phi$ ,  $\rho_{20} = \rho_{2\infty}$ ,  $\bar{N}_D^0$ ,  $\Lambda_I$ , and  $\xi_I$ .

There are two important checks on the correctness of Eq. (27) which are worth mentioning. First, since the assignment of  $\theta_j^2$  indices is arbitrary, the solution should be invariant to the transformation  $\theta_1^2 \rightarrow \theta_2^2$ ,  $\theta_2^2 \rightarrow \theta_1^2$ ;  $\gamma_1 \rightarrow \gamma_2$ ,  $\gamma_2 \rightarrow \gamma_1$ ; and  $t_1 \rightarrow t_2$ ,  $t_2 \rightarrow t_1$ . It is indeed found to be invariant. Second, since the solution is normalized, it should be independently invariant to the interchange of positive and negative species. This translates to invariance against the 1-2, 2-1 index transformation for such quantities as  $\epsilon_j$ ,  $\rho_j$ , and  $a_{jm}$ . Again proper invariance is found.

The Eq. (27) admittance result leads to the general equivalent circuit of Fig. 3. Although there are infinitely many ways Eq. (27) may be analyzed to yield this general circuit, the choices

$$Z_{aN} \equiv g_s Z_{MN}, \quad (28)$$

$$Z_{bN} \equiv g_s / h_s, \quad (29)$$

$$Z_{cN} \equiv N_s Z_{MN}, \quad (30)$$

and

$$Z_{dN} \equiv N_s / h_s, \quad (31)$$

where  $Z_{MN} \equiv Y_{MN}^{-1}$ , seem appropriate and possibly simplest. In the following, specific expressions for these quantities and  $Y_{sN}$  will be considered for various illustrative, simplified cases. The following results do not, however, by any means exhaust the possibilities of the general Eq. (27) expression for system response. Further possibilities will be explored in later work.

### A. Ohmic conditions

Here  $\rho_j = \infty$  and the  $Z$ 's of Eqs. (28)–(31) all go to zero except  $Z_{aN}$  which is finite. Thus in this simplest case,  $Z_{sN} = 0$  and  $Z_{TN} = \psi^{-1} \equiv (1 + i\Omega)^{-1}$  from Eq. (24). As expected, only bulk circuit elements contribute to the impedance here.

### B. Completely blocking conditions

In this case  $\rho_j = 0$ ,  $h_s = 0$ , and  $g_s = 1$ . Therefore,  $Z_{bN} = Z_{dN} = \infty$  and  $Z_{sN} = Z_{sN}^0 \equiv (1 + N_s) Z_{MN}^0$ , which becomes, using (B37'), (which yields  $N_s = t_2$  here), and (B43),

$$Z_{sN}^0 = \frac{(\theta_1^2 - u_e \psi) \gamma_1 - (\theta_2^2 - u_e \psi) \gamma_2}{i\Omega \psi^{-1} [(\theta_1^2 - \theta_2^2) t_1 t_2 + (\theta_1^2 - u_e \psi) t_2 - (\theta_2^2 - u_e \psi) t_1]}. \quad (32)$$

This result cannot be further simplified in the general  $G/R$  case, and the necessary  $\theta_j^2$  values must be calculated from (B20) or (B23).

Further simplification is, however, easy in the special case  $h_j = 0$ ,  $\pi_e = \pi_m = \pi_f = \pi_z = 1$ . Then  $u_e = 1$ ,  $a_{jj} = 0.5 + i\Omega(1 + 0.5f_I)$ ,  $a_{jk} = -0.5 + 0.5i\Omega f_I$ , and it follows from (B20) that  $\theta_1^2 = \psi$  and  $\theta_2^2 = i\Omega(1 + f_I)$ . Equation (32) then yields just  $Y_{sN}^0 = i\Omega t_1 / \psi = (i\Omega / \psi) [(M\sqrt{\psi}) \coth(M\sqrt{\psi}) - 1]$ . Let  $r \equiv (M) \coth(M)$  and consider the series decomposition,  $Z_{sN}^0 \equiv R_{sN} + (i\Omega C_{sN})^{-1}$ . Then for  $\Omega \ll 1$ , one finds  $R_{sN} \rightarrow R_{sN0} = (r - 2)/2(r - 1)^2$  and  $C_{sN} \rightarrow C_{sN0} = r - 1$ , in agreement with earlier  $Z_{TN}$  results for the same case which did not include dynamic recombination.<sup>6,16,17</sup> Although intrinsic  $G/R$  effects appear in  $\theta_2^2$  here through the  $f_I$ , they cancel out of  $Y_{sN}^0$  in this case. This result is to be expected in this symmetrical, completely blocking, equal mobility and equal valence number situation. It is clear, however, that extrinsic and intrinsic  $G/R$  can strongly affect the general  $Z_{sN}^0$  of Eq. (32).

### C. Equal boundary parameters

Here take  $\rho_1 = \rho_2 \equiv \rho_e$  and note that  $\rho_s \rightarrow \rho_e$ ,  $g_s \rightarrow g_e \equiv 1 + \rho_e$ , and  $h_s \rightarrow \rho_e(1 + \rho_e)$ . Then

$$Y_{sN} = \frac{\rho_e(1 + \rho_e) + Y_{MN}}{(1 + \rho_e) + N_s}. \quad (33)$$

Again in the  $h_j = 0$ ,  $\pi_e = \pi_m = \pi_f = \pi_z = 1$  case, this result simplifies greatly and becomes

$$Y_{sN} = \frac{\rho_e^2 + \psi^{-1} [i\Omega t_1 (\rho_e + \gamma_2) + \psi \rho_e \gamma_2]}{\rho_e + \gamma_2}, \quad (34)$$

where  $t_1$  and  $\gamma_2$  involve the specific  $\theta_j$ 's given in Sec. IV. B. It is clear that even in this  $\rho_1 = \rho_2$  case, explicit  $G/R$  effects will appear. Also, remember that if specific adsorption is present,  $\rho_e$  will be frequency dependent.

### D. No extrinsic effects and $\pi_m = \pi_z = 1$

In this case, the  $\theta_j^2$  and  $a_{jm}$  are again given by the results in Sec. IV. B. Thus,  $N_s = t_2$ ,  $Y_{MN}^0 = i\Omega t_1 \gamma_2 / \psi$ , and one finds  $Y_{MN}^1 = (\rho_a \psi^{-1}) [i\Omega t_1 + \psi t_2]$ , where  $\rho_a \equiv 0.5(\rho_1 + \rho_2)$ . Thus

$$Y_{sN} = \frac{\rho_1 \rho_2 + \psi^{-1} [i\Omega t_1 (\rho_e + \gamma_2) + \psi \rho_a \gamma_2]}{\rho_a + \gamma_2}, \quad (35)$$

which of course reduces to (34) when  $\rho_1 = \rho_2 \equiv \rho_e$ . In the  $\Omega \rightarrow 0$  limit,  $\gamma_2 \rightarrow 1$ ; so  $R_{sN0} = (\rho_{a0} + 1)/(\rho_{10}\rho_{20} + \rho_{a0})$ , where  $\rho_{a0} \equiv 0.5(\rho_{10} + \rho_{20})$ . The  $\rho_1 \rightarrow 0$  limit can be readily taken in (35); that for  $\rho_2 \rightarrow \infty$  yields  $Y_{sN} = 2\rho_1 + \gamma_2 + i\Omega \psi^{-1} t_1$ , a result, when  $\rho_1 = 0$  as well, of the same apparent form as one found earlier in the  $\rho_1 = 0$ ,  $\rho_2 = \infty$  case without any  $G/R$  effects.<sup>16,17</sup> Here, however, intrinsic  $G/R$  appears through the  $\gamma_2$  term which involves  $\theta_2$  and thus  $f_I$ . Only when  $\Lambda_I \rightarrow \infty$ , so that  $f_I = 0$  (the full dissociation case, which is particularly appropriate for solutions of strong electrolytes), is the  $Z_{TN}$  following from the present  $Y_{sN}$  result consistent with the earlier no-recombination one.

### E. One-mobile situation

Consider the situation where  $\pi_m \rightarrow \infty$ , i.e.,  $\mu_1 \rightarrow 0$ ,  $\mu_2 > 0$ . Then  $\pi_e \rightarrow \infty$ ,  $\epsilon_1 \rightarrow 0$ ,  $\epsilon_2 \rightarrow 1$ ,  $\lambda_1 \rightarrow \infty$ ,  $\lambda_2 \rightarrow \delta_2$ ,  $\lambda_{e1} \rightarrow \infty$ , and  $\lambda_{e2} \rightarrow \Delta_2$ . In addition,  $h_s \rightarrow \rho_2(1 + \rho_1)$ ,  $g_s \rightarrow (1 + \rho_1)$ ,  $a_{11} \rightarrow \infty$ ,  $a_{12} \rightarrow \infty$ ,  $A \rightarrow \infty$ , and  $B \rightarrow \infty$ . We shall assume that the  $\mu_1 \rightarrow 0$  limit dominates the  $\Omega \rightarrow 0$  one; that is, that one cannot reach frequencies so low that significant finite motion of positive charges is possible in a half cycle. Then it turns out that

$$\theta_1^2 \rightarrow \infty, \quad (36)$$

and

$$\theta_2^2 \rightarrow (A/4B) \rightarrow q\psi, \quad (37)$$

where the complex quantity  $q$  is

$$q \equiv \frac{\Delta_1 \Delta_2 + 2\phi u_e \delta_1 \delta_2 h_I}{\Delta_1 + 2\phi \delta_1 \delta_2 h_I}. \quad (38)$$

When  $\Lambda_I \rightarrow \infty$ ,  $h_I \rightarrow 0$  and  $q$  becomes just  $\Delta_2$ , involving extrinsic  $G/R$  only (see, however, Appendix A.II. 2b),

It follows from the above that in the general one-mobile case,  $\gamma_1 \rightarrow \infty$ ,  $N_s \rightarrow t_1 \rightarrow \infty$ , and  $Y_{MN} \rightarrow \infty$ . Thus,  $Z_{aN} \rightarrow 0$ ,  $Z_{bN} \rightarrow \rho_2^{-1}$ ,  $Z_{cN} \rightarrow N_s/Y_{MN}$ , and  $Z_{dN} \rightarrow \infty$ . Therefore,

$$Y_{sN} = Y_{cN} = \lim_{\tau_e \rightarrow \infty} (Y_{MN}/t_1). \quad (39)$$

The limit is readily evaluated and yields

$$Y_{sN} = i\Omega\psi^{-1}t_2 + \rho_2, \quad (40)$$

with intrinsic and extrinsic  $G/R$  processes being entirely expressed through the  $q$  in  $t_2$ . In the intrinsic case with  $\pi_e = 1$  and thus  $\delta_j = 0.5$ ,  $q$  reduces to

$$q = \frac{2 + \Lambda_I + i\Omega\xi_I}{2[1 + \Lambda_I + i\Omega\xi_I]}; \quad (41)$$

this  $q$  and the  $Y_{TN}$  following from (40) are in agreement with earlier work for this case.<sup>18</sup> In this work, which included no specific adsorption, approximate equivalent circuits and transient response results were also discussed but were only found useful for  $\rho_2 \ll M/\xi_I$ , a potentially serious limitation on  $\rho_2$ . In further work, an approximate solution nearly equivalent to Eq. (40) was presented which included intrinsic  $G/R$ , fully dissociated extrinsic behavior, and specific adsorption.<sup>4,7,15</sup> The use of the exact Eqs. (38) and (40) in complex least squares fitting eliminates the need for any approximations even in the most complicated case which includes extrinsic conduction, three kinds of dynamic  $G/R$  processes, and specific adsorption.

In the fully dissociated pure intrinsic situation, we need not assume  $\pi_e = 1$ , and  $q$  reduces to just  $\delta_2 \equiv (1 + \pi_e^{-1})^{-1}$  here. Then the  $M\theta_2$  term which appears in  $t_2$  becomes  $(M\sqrt{\delta_2})(1 + i\Omega)^{1/2}$ . But  $M\sqrt{\delta_2} = (l/2)[4\pi e^2 z_2^2 n_0 / \epsilon kT]^{1/2} \equiv (l/2L_{D2}) \equiv M_2$ , where  $L_{D2}$  is the appropriate Debye length when only negative charges are mobile. In this case we see that the  $i\Omega\psi^{-1}t_2$  term of (40) is the same as the  $i\Omega\psi^{-1}t_1$  equal mobility, completely blocking result of Sec. IV. B except for the appearance of  $M\theta_2 = M_2\psi^{1/2}$  here and  $M\theta_1 = M\psi^{1/2}$  there. The mobility difference thus only appears through the change in  $M$ .

It is now of interest to see how  $Y_{sN}$  and  $Y_{TN}$  may be expressed and interpreted in the specific adsorption situation in which  $\rho_2$  is given by Eq. (B38) and may be complex. Equation (40) may be rewritten as

$$Z_{sN} = \frac{1}{i\Omega\psi^{-1}t_2 + \frac{1}{\rho_2^{-1}}}, \quad (40')$$

and  $\rho_2^{-1}$  developed in a continued fraction as well. One obtains

$$Z_{sN} = \frac{1}{Y_{2N} + \frac{1}{R_{2N} + \frac{1}{Y_{3N} + \frac{1}{R_{3N}}}}}, \quad (40'')$$

where

$$Y_{2N} \equiv i\Omega(t_2/\psi), \quad (42)$$

$$R_{2N} \equiv \rho_{2\infty}^{-1}, \quad (43)$$

$$Y_{3N} \equiv i\Omega C_{3N} \equiv i\Omega(\xi_{2a}\rho_{2\infty}^2/\rho_{2m}), \quad (44)$$

$$R_{3N} \equiv \rho_{2m}/\rho_{20}\rho_{2\infty}, \quad (45)$$

and

$$\rho_{2m} \equiv \rho_{2\infty} - \rho_{20}. \quad (46)$$

It follows from the above that  $Z_{sN0} \equiv R_{sN0} = R_{2N} + R_{3N} = \rho_{20}^{-1}$ , in agreement with (B49) in this case. Note that  $\rho_{2m}$  may be positive or negative, leading to possible negative resistances and capacitances.<sup>4,7</sup>

The equation connecting  $Z_{TN}$  and  $Z_{sN}$  may also be written in continued fraction form as follows

$$Z_{TN} = \frac{1}{Y_{1N} + \frac{1}{R_{1N} + Z_{sN}}}, \quad (24')$$

where

$$Y_{1N} \equiv i\omega C_1/G_\infty \equiv i\omega C_g/G_\infty \equiv i\Omega C_{gN} \equiv i\Omega, \quad (47)$$

and

$$R_{1N} \equiv R_1/R_\infty \equiv R_{\infty N} \equiv 1. \quad (48)$$

Thus when Eqs. (24') and (40'') are combined, one obtains a six-section continued fraction form of  $Z_{TN}$ . Although the general  $Z_{sN}$  expression of Eq. (27) may also be developed into a continued fraction, insufficient simplification occurs to make this approach worthwhile in the general case.

It will be noted that the full continued fraction obtained in the present case involves only frequency-independent circuit elements, except for that which is associated with  $Y_{2N}$ . We have

$$(Y_{2N}/i\Omega) \equiv C_{2N}(\Omega) \\ = \frac{M[q(1+i\Omega)]^{1/2} \coth\{M[q(1+i\Omega)]^{1/2}\} - 1}{1+i\Omega}. \quad (40)$$

In the general case when  $\tilde{N}_j^0 \neq 0$ ,  $q$  will be essentially frequency independent ( $q \approx q_0$ ) when  $\Omega \ll \xi_I^{-1}\Lambda_I$ ,  $\xi_1^{-1}(\Lambda_1 + \tilde{p}_0)$ , and  $\xi_2^{-1}(\Lambda_2 + \tilde{n}_0)$ . The most stringent condition is likely to be the first, since though  $\xi_I$  is usually of the

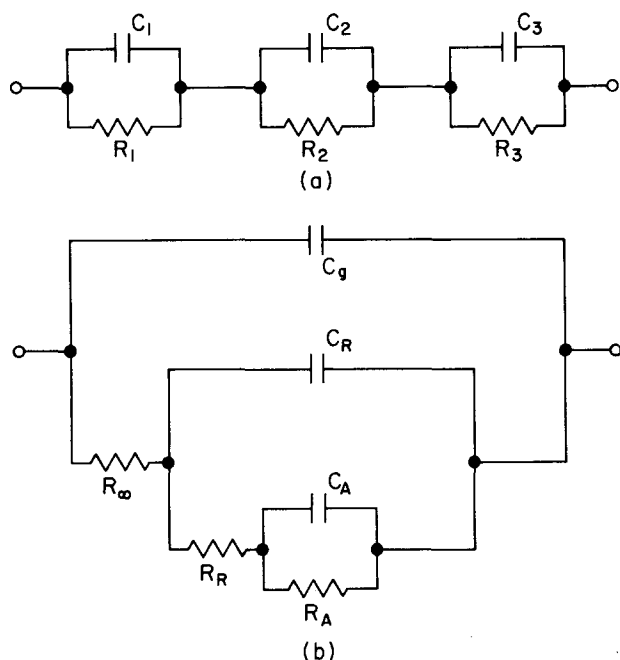


FIG. 4. Two approximate equivalent circuits for  $Z_T$  when  $\pi_m = \infty$ . (a) Voigt-type equivalent circuit representing  $Z_T$  when time constants are all well separated; (b) Ladder network representation of  $Z_T$  appropriate for any time constant separation.

order of unity for ionic charge carriers, it may be as large as  $10^4$  in some electronic situations,<sup>18</sup> and for solids  $\Lambda_I$  may be even smaller than  $10^{-6}$  at room temperature. Certainly these conditions will usually also imply  $\Omega \ll 1$ . Let  $r_0 \equiv (M\sqrt{q_0}) \coth(M\sqrt{q_0})$ . Then for sufficiently small  $\Omega$ ,  $(Y_{2N}/i\Omega) \cong r_0 - 1 \equiv C_{2N0}$ . In this low-frequency region,  $Z_{TN}$  may be entirely expressed by an equivalent circuit of frequency-independent elements. This circuit is of the form of a finite ladder network.

In earlier work for the present case with extrinsic centers fully dissociated or absent,<sup>4</sup> the Voigt-type equivalent circuit of Fig. 4(a) was found applicable for  $\Omega < 1$ , but the relations between its elements and quantities such as  $M$ ,  $\rho_{20}$ , and  $\rho_{2\infty}$  were not found invariant to the magnitude of these quantities except when all time constants differed by a factor of  $10^2$  or more from each other. The circuit of Fig. 4(b), which is a ladder network, was then found heuristically<sup>7</sup> and for  $\Omega \ll 1$  is properly invariant when we identify the present  $C_1 \equiv C_g$ ,  $R_1 \equiv R_\infty$ ,  $C_{20} \equiv (r_0 - 1)C_g \equiv C_R$ ,  $R_2 \equiv R_\infty/\rho_{2\infty} \equiv R_R$ ,  $C_3 \equiv (\xi_{2a}\rho_{2\infty}^2/\rho_{2m})C_g \equiv C_A$  and  $R_3 \equiv (\rho_{2m}/\rho_{20}\rho_{2\infty})R_\infty \equiv R_A$ . Here the subscripts "R" and "A" stand for reaction and adsorption. The present work shows explicitly under what conditions the Fig. 4(b) circuit is a good approximation with the frequency-independent element values defined above. The exact equivalent circuit is just that of Fig. 4(b) with  $C_R$  replaced by the frequency-dependent element  $C_2(\omega) \equiv (Y_{2N}/i\Omega)C_g \equiv (Y_2/i\omega)$ . Note that in the fully dissociated intrinsic case when  $\Lambda_I = \infty$  and  $h_j = 0$ ,  $q_0 = \delta_2$  and  $C_{RN} = (M_2) \coth(M_2) - 1$ .

We can write  $Y_{TN} \equiv Z_{TN}^{-1} \equiv G_{PN} + i\Omega C_{PN}$ , where  $G_{PN} \equiv R_{PN}^{-1}$ . It follows from the exact, hierarchical ladder network circuit that for  $\Omega \rightarrow 0$ ,

$$R_{PN0} \equiv R_{TN0} = 1 + R_{2N} + R_{3N} = 1 + \rho_{20}^{-1}, \quad (49)$$

and

$$C_{PN0} = 1 + \left( \frac{R_{2N} + R_{3N}}{1 + R_{2N} + R_{3N}} \right)^2 C_{2N0} + \left( \frac{R_{3N}}{1 + R_{2N} + R_{3N}} \right)^2 C_{3N}, \\ = 1 + (1 + \rho_{20})^{-2} [(\gamma_0 - 1) + \xi_{2a}\rho_{2m}]. \quad (50)$$

In the intrinsic case Eq. (41) leads to  $r_0 = M_2 [(\Lambda_I + 2)/(\Lambda_I + 1)]^{1/2} \coth\{M_2 [(\Lambda_I + 2)/(\Lambda_I + 1)]^{1/2}\}$ . For  $\Lambda_I \ll 1$ ,  $r_0$  becomes just  $r \equiv (M) \coth(M)$  since  $M_2\sqrt{2} = M$  here; thus, the immobile charges have been effectively mobilized as far as the low frequency capacitance is concerned. When  $\Lambda_I \gg 1$ , on the other hand,  $r_0 = (M_2) \coth(M_2)$  and only the mobile negative charges play a role in the capacitance.

An expression equivalent to Eq. (50) has been presented earlier for the fully dissociated intrinsic case without adsorption<sup>6,19</sup> and a slightly less general equation for the same situation appeared even earlier.<sup>20</sup> In the intrinsic, completely blocking situation,  $C_{PN0} = C_{RN} + 1 = r_0$ , exactly the appropriate normalized diffuse double layer capacitance.<sup>21</sup> Comparisons have already been published of the present reaction resistance  $R_2 \equiv R_R$  with that found in supported electrolyte cases<sup>19,22</sup> and with that to be expected when the compact layer is accounted for.<sup>7</sup> Since complex impedance plane plots and discussion have already been presented of the response of the system for intrinsic, fully dissociated conditions with adsorption,<sup>4,7,15</sup> no further such results will be given here. The detailed effects of both intrinsic and extrinsic  $G/R$  processes on the impedance-plane semicircles found in the absence of these processes will be presented in later work.

#### F. Partially ohmic conditions $|\rho_1| < \infty$ , $\rho_2 \rightarrow \infty$

For these conditions, one finds

$$Z_{aN} = \epsilon_1 \psi / I_{12} (P_{12} t_1 + P_{22} t_2), \quad (51)$$

$$Z_{bN} = \epsilon_1 / (\epsilon_2 + \rho_1) = [\pi_e + \epsilon_1^{-1} \rho_1]^{-1}, \quad (52)$$

and  $Z_{cN} = Z_{dN} = 0$ . Here  $I_{12} \equiv (\theta_1^2 - \theta_2^2)^{-1}$ . We can now write

$$Y_{sN} = \pi_e + \epsilon_1^{-1} \rho_1 + (\epsilon_1 \psi)^{-1} I_{12} (P_{12} t_1 + P_{22} t_2) \\ = \pi_e \gamma_2 + \epsilon_1^{-1} \rho_1 + (\epsilon_1 \psi)^{-1} I_{12} [P_{12} t_1 + (P_{22} - \epsilon_2 \psi I_{12}^{-1}) t_2] \\ = \pi_e \gamma_2 + \epsilon_1^{-1} \rho_1 + \left[ \frac{A_b t_1 + B_b t_2}{\psi (\theta_1^2 - \theta_2^2)} \right], \quad (53)$$

where

$$A_b \equiv \epsilon_1^{-1} P_{12} = \pi_e (\theta_1^2 + a_{21} - a_{22}) + i\Omega \epsilon_1^{-1} (\theta_1^2 - a_{22}) \\ = \pi_e (\theta_1^2 - u_e - i\Omega \lambda_{e2}) + i\Omega \epsilon_1^{-1} (\theta_1^2 - a_{22}), \quad (54)$$

and

$$B_b \equiv \epsilon_1^{-1} [P_{22} - \epsilon_2 \psi (\theta_1^2 - \theta_2^2)] \\ = \pi_e \psi \theta_2^2 + i\Omega [\theta_1^2 - \pi_e \psi f_I - \epsilon_1^{-1} \{\Delta_1 + (\epsilon_2 + i\Omega) \lambda_{e1}\}]. \quad (55)$$

The term  $\pi_e \gamma_2$  has been introduced in (53) because it does not disappear as  $\Omega \rightarrow 0$  and, in fact, corresponds closely to a similar term appearing in  $Y_{sN}$  for supported-electrolyte conditions without recombination.<sup>17</sup> Since the term in square brackets in Eq. (53) approaches zero as  $\Omega \rightarrow 0$ ,  $\pi_e \gamma_2$  is evidently a first approximation to the pres-



ent more complicated *unsupported* response in the  $\rho_1 = 0$  situation.<sup>3,4,7</sup>

Further simplification of the present form of  $Y_{sN}$  is possible if one restricts  $\Omega$  to small enough values that  $\theta_2^2$  is well approximated by only the first term of Eq. (B23). Then  $|A| \ll |2B|^2$ , leading to  $0 \leq \Omega \ll [|u_e^2|/b_e + u_e f_I]$  and  $\theta_2^2 \cong i\Omega[(b_e/u_e) + f_I]$ , usually much less than unity. Retaining terms to first order in  $\Omega$  only (see Appendix C), one finds that the expressions for  $A_b$  and  $B_b$  simplify appreciably to  $A_b \cong i\Omega u_{e0}^{-1} \lambda_{e10}^2$  and  $B_b \cong i\Omega \pi_e (c_{e0} + u_{e0}^{-1} b_{e0} - 1) \cong i\Omega [1 + \epsilon_1^{-1}(u_{e0} - 1) - u_{e0}^{-1} \lambda_{e10}^2]$ , where  $c_e \equiv \lambda_{e2} - \lambda_{e1}$ . To the same order in  $\Omega$ ,  $\rho_1 \cong \rho_{10} + i\Omega \xi_{1a} \rho_{1m}$ , and  $\theta_1^2 - \theta_2^2 \cong u_{e0} + i\Omega(u_{ef} + d_{e0} - 2u_{e0}^{-1} b_{e0} - f_{I0})$ , where  $u_{ef}$  is defined in Appendix C. These results allow Eq. (53) to be rewritten in approximate form for the present  $\Omega$  range.

In the fully dissociated intrinsic regime, where  $\pi_e = \pi_m$ , the above results simplify even more. Let us consider the  $\rho_1 = 0$ ,  $\rho_2 \rightarrow \infty$ , or  $(0, \infty)$  situation only here. Then  $\theta_2^2 \cong i\Omega b$ ,  $A_b \cong i\Omega \lambda_1^2$ , and  $B_b \cong i\Omega \pi_e (c + b - 1) \cong i\Omega (1 - \lambda_1^2)$ . In order to retain only first-order  $\Omega$  terms in (53), we take  $\theta_1^2 - \theta_2^2 \cong u_{e0}$ , which becomes unity in the present case. Thus (53) reduces to

$$Y_{sN} \cong \pi_e \gamma_2 + i\Omega [\lambda_1^2 t_1 + (1 - \lambda_1^2) t_2]. \quad (53')$$

Now to first order,  $\theta_1^2 \cong 1 + i\Omega a$  here,  $\Omega t_1 \cong \Omega(\gamma - 1)$ , equal to  $\Omega C_{RN}$  in the present two-mobile case, and  $\Omega t_2 = 0(\Omega^2) - 0$ . Thus,

$$Y_{sN} \cong \pi_e \gamma_2 + i\Omega \gamma_1^2 (\gamma - 1) \\ \cong (\pi_e M \sqrt{i\Omega b}) \coth(M \sqrt{i\Omega b}) + i\Omega \lambda_1^2 [(M) \coth(M) - 1], \quad (53'')$$

where we have approximated  $\gamma_1$  by  $(M) \coth(M)$ , adequate for  $\Omega \ll a^{-1}$ , which is consistent with the  $|A| \ll |2B|^2$  condition in this case.

The above results show that the approximate equivalent circuit of the  $Z_s$  part of the system in the present low frequency range is just a finite-length Warburg impedance,  $Z_W \cong R_\infty / \pi_e \gamma_2$ , in parallel with a frequency-independent capacitance,  $C_{PW} \cong \lambda_1^2 C_{RN} C_g = [(1 + \pi_e)/(1 + \pi_f)]^2 (\gamma - 1) C_g$ , equal to  $[(1 + \pi_m)/(1 + \pi_e)]^2 (\gamma - 1) C_g$  in the present fully-dissociated intrinsic situation. When  $\pi_m = \pi_e = 1$ ,  $(C_{PW} + C_g)$  is thus just the usual diffuse double layer capacitance. On the other hand, when  $\pi_m \gg 1$ , so that the species which is not blocked at the electrode is far more mobile than the other,  $C_{PW} \gg C_R$ . But note that in this case,  $|Z_s|$  will be small and may even be negligible (unmeasurable) compared to  $R_\infty$ .

The normalized impedance  $Z_{WN}$  leads to a typical finite-length Warburg arc when plotted parametrically as a function of  $\Omega$  in the complex (normalized) impedance plane.<sup>4,19,22</sup> Its peak, of normalized height  $0.417\pi_m^{-1}$ , occurs at  $\Omega = \Omega_p \cong 2.53(bM^2)^{-1}$ . Our present results are formally restricted to  $\Omega \ll b^{-1}$ , where here  $b = (\pi_m + 2 + \pi_m^{-1})/4$  and will thus be large when  $\pi_m \ll 1$ , the case where  $Z_s$  dominates the total impedance. Actually, one finds that the present approximation for  $Y_{sN}$  is reasonably good even for  $\Omega \gtrsim b^{-1}$ . The reason is that  $\theta_2^2 = i\Omega$  exactly when  $\pi_m = \pi_e = 1$  and thus  $b = 1$ . It is therefore of interest to ask how much  $-\text{Im}(Z_{WN})$  has declined from its peak when  $\Omega$  has increased from  $\Omega_p$  to say  $2.53/b$ .

When  $\Omega$  increases by a factor of  $M^2$ ,  $-\text{Im}(Z_{WN})$  decreases by approximately  $M$  to roughly  $0.4/\pi_m M$ . If  $\pi_m \ll M^{-1}$ , this can still be appreciably greater than unity. Thus, we see that when  $\pi_m \ll 1$ , so Warburg effects are dominant, even the present simple approximate solution will apply for  $0 \leq \Omega \leq \Omega_p$  and, in addition, over the potentially wide range of  $\Omega_p \leq \Omega \lesssim b^{-1}$  when  $M \gg 1$ , the usual situation.

In summary, the unsupported case, because of its Poisson-equation coupling between positive and negative charges, leads to modified finite Warburg response, including a parallel capacitance which is nearly equal to the diffuse double layer capacitance,  $rC_g$ , for  $\pi_m = \pi_e = 1$  and is as small as  $(r - 1)C_g/4$  for  $\pi_e = 1$ ,  $\pi_m \ll 1$ .

## G. Low frequency limiting quantities

The general results can be appreciably simplified in the very low frequency region. Expand all quantities of interest to first order in  $\Omega$  so that for the general quantity  $Y$ ,  $Y(\Omega) = Y_0 + i\Omega Y_f + \dots$ . Expressions for the  $\Omega \rightarrow 0$  and first-order parts of all quantities of interest are summarized in Appendix C. From Eq. (27) we may write

$$Y_{sN} - Y_{sN0} + i\Omega Y_{sNf} \cong G_{sN0} + i\Omega C_{sN0} \\ = \frac{h_{s0} + i\Omega(h_{sf} + Y_{MNf})}{g_{s0} + i\Omega(g_{sf} + N_{sf})}. \quad (56)$$

It follows that  $G_{sN0} \cong R_{sN0}^{-1} = h_{s0}/g_{s0}$  and

$$C_{sN0} \cong g_{s0}^{-1} [g_{s0}(h_{sf} + Y_{MNf}) - h_{s0}(g_{sf} + N_{sf})]. \quad (57)$$

Since  $R_{TN0} \cong R_{DN} = 1 + R_{sN0} = (g_{s0} + h_{s0})/h_{s0}$  and  $(g_{s0} + h_{s0}) \cong g_{10}g_{20}$ , it follows that  $R_{TN0} \cong g_{10}g_{20}/h_{s0} = [(\epsilon_1 \rho_{10}/g_{10}) + (\epsilon_2 \rho_{20}/g_{20})]^{-1}$ , in agreement with Eq. (25). It is worth noting that the physical requirement that  $R_{TN0}$  must not involve dynamic  $G/R$  effects is satisfied by this result.

The simplification of Eq. (57) using the results of Appendix C is much more complicated. First, let us form the final desired  $C_{PN0}$ . Figure 2b and/or the first part of Eq. (50) with  $R_{2N} = R_{sN0}$ ,  $C_{2N} = C_{sN0}$ ,  $R_{3N} = 0$ , and  $C_{3N} = 0$  yields

$$C_{PN0} = 1 + \frac{C_{sN0}}{[1 + G_{sN0}]^2} \\ = 1 + \frac{g_{s0}^2 C_{sN0}}{(g_{s0} + h_{s0})^2} = 1 + \frac{g_{s0}^2 C_{sN0}}{(g_{10}g_{20})^2} \\ \cong 1 + C_{\alpha N0} + C_{\beta N0} + C_{\gamma N0}. \quad (58)$$

The contribution from specific adsorption,  $C_{\alpha N0}$ , turns out to be

$$C_{\alpha N0} \cong (g_{10}g_{20})^{-2} (g_{s0} h_{sf} - h_{s0} g_{sf}) \\ \cong (g_{10}g_{20})^{-2} [\epsilon_1 g_{20}^2 \xi_{1a} \rho_{1m} + \epsilon_2 g_{10}^2 \xi_{2a} \rho_{2m}]. \quad (59)$$

This reduces in the  $\rho_{10} = \rho_{1\infty} = 0$  case to just

$$C_{\alpha N0} = g_{20}^{-2} [\epsilon_2 \xi_{2a} \rho_{2m}]. \quad (60)$$

Note that  $C_{\alpha N0}$  may be very much larger than unity for  $\xi_{2a} \gg 1$ , i.e., slow adsorption.

It follows from Eqs. (57) and (58) that we may write

$$C_{\beta N0} \cong (g_{10}g_{20})^{-2} A_1 t_{10}, \quad (61)$$

and

$$C_{\gamma N0} \equiv (g_{10}g_{20})^{-2} A_2 t_{2f}, \quad (62)$$

where

$$A_1 \equiv g_{s0} [1 + u_{e0}^{-2} (\rho_{10} \Delta_{20} \lambda_{e20} + \rho_{20} \Delta_{10} \lambda_{e10}) - h_{s0} [u_{e0}^{-2} (\Delta_{10} \lambda_{e10} + \Delta_{20} \lambda_{e20}) - 1]], \quad (63)$$

and

$$A_2 \equiv g_{s0} (h_{s0} - \rho_{10} \rho_{20}) - h_{s0} = \epsilon_1 \epsilon_2 (\rho_{20} - \rho_{10})^2. \quad (64)$$

After considerable tedious algebra,  $A_1$  may be rewritten in simplified form as

$$A_1 = g_{10}g_{20} + u_{e0}^{-2} (\rho_{20} - \rho_{10}) (g_{20} \Delta_{10}^2 - g_{10} \Delta_{20}^2). \quad (63')$$

Thus, finally one has

$$C_{\beta N0} = (g_{10}g_{20})^{-2} (A_1) [r_e - 1], \quad (61')$$

where

$$r_e \equiv (M\theta_{10}) \coth(M\theta_{10}), \quad (65)$$

and  $\theta_{10} \equiv (u_{e0})^{1/2}$ . In addition, one finds

$$C_{\gamma N0} = (g_{10}g_{20})^{-2} (\epsilon_1 \epsilon_2 M^2/3) (\rho_{20} - \rho_{10})^2 (u_{e0}^{-1} b_{e0} + f_{I0}). \quad (62')$$

Since  $\epsilon_1 \epsilon_2 b \equiv \delta_1 \delta_2$ , the expressions for  $C_{\beta N0}$  and  $C_{\alpha N0}$  do not depend on  $\epsilon_j$  and thus are also independent of the  $\mu_j$ 's.

The above results do not apply in the one-mobile ( $\pi_m \rightarrow \infty$ ) situation, which has been treated separately in Sec. IV. E. On the other hand, if  $\pi_m$  (and thus  $\pi_e$ ) is very large but not infinite, then the Sec. IV. E results will apply for  $\Omega\pi_e \gg 1$  and the present ones for  $\Omega\pi_e \ll 1$ . For very large  $\pi_e$ , the latter condition may be difficult to achieve experimentally. Let us now consider expressions for  $C_{PN0}$  in various simplifying cases.

### 1. $M \rightarrow 0$

Here  $C_{\alpha N0}$  remains unchanged and  $C_{\beta N0}$  and  $C_{\gamma N0}$  both become proportional to  $M^2$  and thus go to zero. Only the geometric and adsorption contributions to  $C_{PN0}$  remain.

### 2. $\rho_{10} = \rho_{20} \equiv \rho_{e0}$ and $\rho_{1\infty} = \rho_{2\infty} \equiv \rho_{e\infty}$

In this case  $C_{\alpha N0}$  reduces to

$$C_{\alpha N0} = g_{e0}^{-2} \rho_{em} [\epsilon_1 \xi_{1a} + \epsilon_2 \xi_{2a}], \quad (66)$$

where  $\rho_{em} \equiv \rho_{e\infty} - \rho_{e0}$  and  $g_{10} = g_{20} \equiv g_{e0}$ . Note that  $C_{\alpha N0} \rightarrow 0$  when  $\rho_{em} \rightarrow 0$ , but it is not zero when  $\rho_{e0} = 0, \rho_{e\infty} \neq 0$ . We also obtain for the present situation

$$C_{\beta N0} = g_{e0}^{-2} (r_e - 1), \quad (67)$$

and

$$C_{\gamma N0} = 0. \quad (68)$$

### 3. $\rho_{20} \rightarrow \infty$

For this condition, one finds

$$C_{\alpha N0} \rightarrow \epsilon_1 g_{10}^{-2} \xi_{1a} \rho_{1m}. \quad (69)$$

The other contributions reduce to

$$C_{\beta N0} \rightarrow g_{10}^{-2} (u_{e0}^{-2} \Delta_{10}^2) (r_e - 1), \quad (70)$$

and

$$C_{\gamma N0} \rightarrow g_{10}^{-2} (\epsilon_1 \epsilon_2 M^2/3) (u_{e0}^{-1} b_{e0} + f_{I0}). \quad (71)$$

These expressions are consistent with those that follow for  $C_{sN0}$  from the results of Sec. IV. F.

### 4. No adsorption, no dynamic G/R

In this case,  $C_{\alpha N0} = 0$ , and one need only set  $\Delta_{j0}$  to  $\delta_j$  and  $u_{e0} = 1$  in Eqs. (63') and (61') to obtain  $C_{\beta N0}$ , and  $u_{e0} = 1, b_{e0} = b$  in Eq. (62') to obtain  $C_{\gamma N0}$ . Further, here  $\rho_{j0} \equiv \rho_j$  and  $r_e$  reduces to  $r$ . The results agree with those found earlier for this situation.<sup>6</sup>

### 5. G/R effects

To what degree can the presence of dynamic G/R affect  $C_{PN0}$ ? First, we see that  $C_{\alpha N0}$  is independent of dynamic G/R parameters. It does depend, however, on equilibrium G/R through its dependence on  $\epsilon_j$  and thus on  $\tilde{n}_0/\tilde{p}_0$ .

Second,  $C_{\beta N0}$  is independent of the intrinsic G/R parameter  $f_{I0}$  but does depend on  $\Delta_{j0}^2/u_{e0}^2$ , ratios which cannot exceed unity even in the extreme extrinsic situation where  $h_{10}$  and/or  $h_{20}$  may themselves exceed unity. The main effect of extrinsic G/R on  $C_{\beta N0}$  will thus be in  $r_e$ , where  $(u_{e0})^{1/2}$  may itself possibly be considerably larger than unity.

The  $C_{\gamma N0}$  contribution depends on both extrinsic and intrinsic G/R processes, but  $u_{e0}^{-1} b_{e0} \equiv [\Delta_{10} \Delta_{20} / (\Delta_{10} + \Delta_{20})] (b/\delta_1 \delta_2)$  cannot exceed  $(b/\delta_1 \delta_2) \equiv (\epsilon_1 \epsilon_2)^{-1}$  times the smaller of  $\Delta_{10}$  and  $\Delta_{20}$ , since the  $h_{j0}$  are always  $\geq 0$ . Since, however,  $\Delta_{10}$  and  $\Delta_{20}$  will generally be less than two,  $u_{e0}^{-1} b_{e0}$  will not usually be much larger than  $b$ , its limit in the absence of extrinsic G/R processes. For example, for the numerical values mentioned in Appendix A. II. 2,  $b \approx 8.167$  and  $u_{e0} b_{e0} \approx 9.154$ . On the other hand, the  $f_{I0} = 2\phi b/\Lambda_I$  term may greatly exceed  $b$  in the usual  $\Lambda_I \ll 1$  case.<sup>3</sup> Then for intrinsic conduction,  $\phi = 1, \delta_j = 0.5$ , and  $C_{\gamma N0} = [(\rho_{20} - \rho_{10})/g_{10}g_{20}]^2 [(M^2/12)(1 + 2\Lambda_I^{-1})]$ . This result can be rewritten, with  $M = M_I$ , as

$$C_{\gamma N0} = [(\rho_{20} - \rho_{10})/g_{10}g_{20}]^2 (l^2/48) \times (8\pi e^2 z_e^2 C_{I0}/\epsilon kT) (1 + 2\Lambda_I^{-1}). \quad (72)$$

But, on introducing the relation  $\Lambda_I^{-1} \equiv \tilde{N}_I^0 - 1$ , one finds that the quantity  $c_{I0}(1 + 2\Lambda_I^{-1})$  becomes just  $(2N_I^0 - c_{I0})$ . For full dissociation this quantity reduces to just  $N_I^0$ , as it should. For  $\Lambda_I \ll 1$ , however, it becomes  $2N_I^0$ , twice as large!

Now  $f_I \sim 0$  when  $(\Omega \xi_I)^2 + \Lambda_I^2 \gg b^2$ . In this frequency region, where  $\Omega \ll 1$  may still be possible, the effective  $L_I$  and  $M_I$  will involve just  $c_{I0}$  since there will be insufficient time in a half cycle for intrinsic G/R to contribute to the capacitance. In this region, the effective  $C_{\gamma N}$  capacitance may be expected to be proportional to just  $c_{I0}$ , as in Eq. (72) with  $\Lambda_I \rightarrow \infty$ . But as  $\Omega \rightarrow 0, C_{\gamma N0}$  involves  $(2N_I^0 - c_{I0})$ , larger than  $c_{I0}$  by the factor  $2\Lambda_I^{-1} + 1$ , usually  $\gg 1$ . The increase arises because as  $\Omega \rightarrow 0$  there is time near the peak of a half cycle for virtually all neutral intrinsic centers to dissociate and for the resulting charges to move appreciably and contribute

to  $C_{\gamma N0}$ . Thus, the presence of intrinsic  $G/R$ , almost always to be expected in solids, can greatly increase  $C_{PN0}$  over the value one might calculate using the equilibrium  $C_{I0}$  but not properly accounting for the dynamic effects of  $G/R$ .<sup>3</sup> A somewhat similar enhancement effect was later noted in a trapping- $G/R$  situation.<sup>23</sup> Here, however, we have shown how extrinsic and extrinsic  $G/R$  effects can together lead to very appreciable enhancement.

It is finally worth noting that when  $M \gg 1$ , the usual situation,  $C_{\gamma N0}$  will be much larger than  $C_{BN0}$  provided  $\rho_{20}$  and  $\rho_{10}$  are not zero or nearly equal. When these conditions don't apply,  $C_{\gamma N0}$  will also usually be much larger than  $C_{\alpha N0}$  as well, but it should be noted that  $C_{\alpha N0}$  can be the larger, even for  $M \gg 1$ , for a sufficiently slow adsorption process (which, of course, forces one to extend  $\Omega$  measurements to the very small  $\Omega$  region in order to achieve capacitance results independent of  $\Omega$ ). It is evident that in general  $C_{PN0}$  can exceed the diffuse double layer value of  $\tau$  primarily because of possible contributions from  $C_{\alpha N0}$  and  $C_{\gamma N0}$ .

The effects of dynamic  $G/R$  are of particular interest in the one-mobile case where  $G/R$  can effectively mobilize immobile charges as far as capacitance is concerned. Equation (40) shows that when adsorption is absent  $C_{sN0} = t_{20} = \tau_0 - 1$  in this case. Here  $\tau_0$  involves  $M\sqrt{q_0}$  [see Eq. (38)], where

$$q_0 \equiv \frac{\Delta_{10}\Delta_{20} + 2\phi\delta_1\delta_2\mu_{e0}h_{I0}}{\Delta_{10} + 2\phi\delta_1\delta_2h_{I0}}. \quad (73)$$

The pure intrinsic limit results have already been discussed in Sec. IV. E.

For simplicity let us consider a donor-type extrinsic case for which  $\Delta_{10} \ll \Delta_{20}$ . Then  $u_{e0} \approx \Delta_{20}$  and Eq. (73) reduces to  $q_0 \approx \Delta_{20}$ . [For the specific illustrative situation mentioned in Appendix A. II. 2,  $\Delta_{10} \approx 0.1542$ ,  $\Delta_{20} \approx 1.483$ , and  $q_0$  turns out to be about 1.599, essentially equal to  $u_{e0}$  in this case where the  $h_{I0}$  terms in  $q_0$  dominate.] For  $M \gg 1$ ,  $C_{sN0} \approx \tau_0 \approx M\sqrt{q_0} \approx M\sqrt{\Delta_{20}}$ , a quantity which may be written as

$$\begin{aligned} M\sqrt{\Delta_{20}} &= [4\pi(ez_e)^2(n_0 + p_0)\{n_0/(n_0 + p_0)\}(1 + h_{20})/\epsilon kT]^{1/2} \\ &= \{[4\pi(ez_e)^2/\epsilon kT]\{n_0\}[1 + [\Lambda_2\tilde{N}_2^0/(\Lambda_2 + \tilde{n}_0)^2]]\}^{1/2} \\ &\approx M_2[1 + \{\Lambda_2\tilde{N}_2^0/(\Lambda_2 + \tilde{n}_0)^2\}]^{1/2}. \end{aligned} \quad (74)$$

Thus, we may write

$$(M\sqrt{\Delta_{20}}/M_I) = [(\tilde{n}_0/2)\{1 + [\Lambda_2\tilde{N}_2^0/(\Lambda_2 + \tilde{n}_0)^2]\}]^{1/2}. \quad (75)$$

Now when  $\Lambda_2 \rightarrow \infty$ ,  $\tilde{n}_0 \rightarrow \tilde{N}_2^0$ , provided  $\tilde{N}_2^0 \gg 1$ . Then Eq. (75) yields just  $[\tilde{N}_2^0/2]^{1/2}$  and the concentration which appears in the capacitance for this fully dissociated situation is  $n_0 \approx N_2^0$ , as it should be in the one-mobile case. On the other hand, when  $\tilde{n}_0 \gg \Lambda_2$  and thus  $\tilde{n}_0 < \tilde{N}_2^0$ , the concentration appearing in the Debye length and in  $C_{sN0}$  becomes  $n_0[1 + (\Lambda_2\tilde{N}_2^0/\tilde{n}_0^2)]$ , again showing some extrinsic  $G/R$  enhancement. For the numerical case mentioned above, the situation is intermediate since there  $\Lambda_2 = 1$  and  $n_0 \approx 2.889$ . Using the value  $\tilde{N}_2^0 = 10$ , one finds that the factor  $\Lambda_2\tilde{N}_2^0/(\Lambda_2 + \tilde{n}_0)^2$  is about 0.661, by no means negligible compared to unity.

## V. DATA FITTING AND PARAMETER INTERPRETATION

If one wishes to test the applicability of the present theory of small-signal ac response to available  $Z_T(\omega)$  or  $Y_T(\omega)$  data, the first most appropriate step is to fit the theory to the data using a nonlinear least squares fitting procedure for complex data.<sup>9</sup> This procedure allows independent weighting of the individual real and imaginary squared residuals; such weighting can take account of the varying estimated uncertainties of real and imaginary measured values. Fitting of both  $Z_T$  and corresponding  $Y_T$  data will usually yield somewhat different parameter value estimates and estimates of the uncertainties of these quantities when the data contain errors. With adequate weighting, any such differences should be within statistical error (two or three standard deviations), however, provided the theory is indeed applicable. Since not all processes included in the theory may occur in the material under investigation, and since the available frequency range may not yield data influenced by all of the processes actually present, the fitting procedure allows any of the parameters of the theory to be held fixed. Thus, for an intrinsic material, one would set the  $\tilde{N}_j^0$  to zero and could set the  $\Lambda_j$  and  $\xi_j$  to any nonzero values.

In the first part of this section, the transformations from the complete fitting parameters of the theory to more basic ones characterizing the material-electrode system will be summarized, while the second part will deal with the interpretation and applicability of the latter set for various situations. Although all transformations will be given, one should remember that in all but the most general case, not all of them will be used for a single fitting.

It is assumed that the separation length,  $l$ , and effective area,  $A$ , of plane-parallel, identical electrodes are known from independent measurements. Using a least squares set of parameter values derived from the fit of  $Z_T$  or  $Y_T$  data, one may then calculate the following quantities. First convert the fitting results for  $R_\infty$  and  $C_g$  to their present unit area forms. One can immediately obtain  $\tau_D \equiv R_\infty C_g$  and  $\epsilon = (4\pi l)C_g$ . If  $C_g$  is in  $\mu F/cm^2$  and  $l$  in cm, then  $\epsilon \approx 11.294/C_g$ . When the highest available  $\omega$  is  $\ll \tau_D^{-1}$ , so  $C_g$  cannot be well estimated, it will often be sufficient to calculate it if an independent value for  $\epsilon$  is known. Then an estimate of  $\tau_D$  can be obtained.

The quantities  $\pi_z$ ,  $z_1$ , and  $z_2$  are not fitting parameters of the theory, although  $\pi_e$  and  $\pi_f$  are. If the fitting yields any significant  $G/R$  parameters, we automatically set  $\pi_e = 1$ , and complete analysis of the results then requires independent knowledge (or an estimate) of  $z_e \approx z_1 = z_2$ . In the complete dissociation case, on the other hand, one needs to know  $z_1$  and  $z_2$  in the general situation but only  $z_1$  or  $z_2$  in the fully dissociated pure intrinsic case since then  $\pi_f = \pi_e$  and a value of  $\pi_f$  will be available from the fitting. These are not usually serious restrictions since one will often know the valence numbers of the mobile charges in a material of interest.

Let us write  $G_\infty \equiv R_\infty^{-1} \equiv (e/l)D_a$ , where  $D_a \equiv (z_1\mu_1 p_0$

+  $z_2 \mu_2 n_0$ ). When  $R_\infty$  is in the ohm  $\text{cm}^2$  and concentrations and mobilities are in units of  $\text{cm}^{-3}$  CGS units, one has  $D_a \approx 6.242 \times 10^{18} (lG_\infty)$ . Next, from the fitting value of  $M$ , we can form  $L_D^2 = (l/2M)^2 = (\epsilon kT/4\pi e^2 D_b)$ , where  $D_b \equiv (z_1^2 p_0 + z_2^2 n_0)$ . It follows that  $D_b \approx 5.715 \times 10^4 \epsilon (T/300)(M/l)^2$ . But  $D_b$  may be rewritten as  $z_1^2 p_0 (1 + \pi_f) \equiv z_2^2 n_0 [1 + \pi_f^{-1}]$ . If we now calculate  $\epsilon_j$ ,  $\delta_j$ , and  $\lambda_j$  from the fitting values of  $\pi_e$  and  $\pi_f$ , we can write  $p_0 = \delta_1 z_1^{-2} D_b$ ,  $n_0 = \delta_2 z_2^{-2} D_b$ , and  $(p_0/n_0) = \pi_f^{-1} \pi_e^2$ . When these results are used in the expression for  $D_a$ , one finds  $(D_a/D_b) = (z_2^{-1} \mu_2 \delta_2 + z_1^{-1} \mu_1 \delta_1)$ . Since  $\pi_m \pi_f = \pi_e \pi_e$ , it follows that  $\mu_j = z_j \lambda_j^{-1} (D_a/D_b)$ . Note also that  $(n_0 + p_0) = z_e^{-2} D_b$  when  $\pi_e = 1$ . From these results we may immediately form  $\pi_m = \mu_2/\mu_1$  and  $D_j = (kT/e)(\mu_j/z_j)$ . Now since  $\rho_{j0}$ ,  $\rho_{j\infty}$ , and  $\xi_{ja}$  are fitting parameters associated with electrode adsorption/reaction processes, one can form the following more basic quantities from their estimates:  $k_{j0} = (2D_j/l)\rho_{j0}$ ,  $k_{j\infty} = (2D_j/l)\rho_{j\infty}$ , and  $\tau_{ja} = \tau_D \xi_{ja}$ . These quantities are, of course, independent of homogeneous  $G/R$  conditions.

When intrinsic dissociation is incomplete, one cannot use the three quantities  $\phi$ ,  $\Lambda_I$ , and  $\xi_I$  which appear in  $f_I$  as separate fitting parameters because to do so would overparametrize the model.<sup>24</sup> These quantities enter the fitting equations directly only through  $f_I$  [see Eq. (B16)] and thus cannot all be taken as independent. Instead, rewrite  $(f_I/2b)$  in terms of two separate fitting parameters as  $(G_I + i\Omega S_I)^{-1}$ , where  $G_I \equiv (\Lambda_I/\phi) \equiv (2k_{Ie}/k_{Ir})(n_0 + p_0)^{-1}$  and  $S_I \equiv (\xi_I/\phi) \equiv 2/[\tau_D k_{Ir}(n_0 + p_0)]$ . These new parameters thus differ from  $\Lambda_I$  and  $\xi_I$  only in extrinsic situations. The above results now allow us to form the estimates  $k_{Ie} = G_I/\tau_D S_I$  and  $k_{Ir} = 2z_e^2/(\tau_D S_I D_b)$ .

Now in the general intrinsic-extrinsic case, what other free fitting parameters must be used in addition to those already discussed above? In order to evaluate the  $h_j$  we need the parameters  $\Lambda_j$ ,  $\xi_j$ ,  $\tilde{N}_j^0$ , and  $\tilde{n}_0$  and  $\tilde{p}_0$ , as shown by Eq. (B6). Again we must be careful to use no more parameters than absolutely necessary. First, since  $\tilde{p}_0 = \pi_e \pi_f^{-1} \tilde{n}_0$ , which becomes  $\tilde{p}_0 = \pi_f^{-1} \tilde{n}_0$  in the present  $\pi_e = 1$  situation, one may eliminate  $\tilde{p}_0$ . Now the electroneutrality condition [Eq. (A8)] may be written in normalized form as  $\tilde{n}_0 - \tilde{p}_0 = (1 - \pi_f^{-1}) \tilde{n}_0 = \tilde{N}_{D0}^+ - \tilde{N}_{A0}^- = [\Lambda_2 \tilde{N}_2^0 / (\Lambda_2 + \tilde{n}_0)] - [\Lambda_1 \tilde{N}_1^0 / (\Lambda_1 + \pi_f^{-1} \tilde{n}_0)]$ , an implicit relation for  $\tilde{n}_0$ . When values of  $\Lambda_j$ ,  $\tilde{N}_j^0$ , and  $\pi_f$  are available (either initial, local, or final values associated with the least squares fitting), the above equation may be readily solved for  $\tilde{n}_0$  by Newton-Raphson iteration. Values of  $\tilde{n}_0$  obtained in this fashion may then be used in each step of the separate iterative least squares procedure, which requires evaluation of the  $h_j$  for each step. From the final fitting values of  $\Lambda_j$ ,  $\xi_j$ ,  $\tilde{N}_j^0$  and the final calculated value of  $\tilde{n}_0$ , which has been constrained to be consistent with the electroneutrality relation, one may then obtain the estimated values:  $c_{I0} = n_0/\tilde{n}_0$ ,  $\Lambda_I = k_{Ie}/k_{Ir} c_{I0}$ ,  $\xi_I = (\tau_D k_{Ir} c_{I0})^{-1}$ ,  $\tau_I = \tau_D \xi_I$ ,  $N_{I0}^0 = c_{I0} (1 + \Lambda_I^{-1})$ ,  $N_{I0} = k_{Ir} n_0 p_0 / k_{Ie}$ ,  $\tau_j = \tau_D \xi_j$ ,  $k_{jr} = (\tau_j c_{I0})^{-1}$ ,  $k_{jg} = \Lambda_j / \tau_j$ , and  $N_j^0 = c_{I0} \tilde{N}_j^0$ . In addition, one may form  $\tilde{n}_0 \tilde{p}_0 = \pi_f^{-1} \tilde{n}_0^2$  and compare the estimate thus obtained with unity (see later discussion in this section). Note that in the incompletely dissociated, pure intrinsic case  $\tilde{N}_j^0 = 0$  and  $\pi_f$  is fixed at unity and is thus not a free fitting parameter. In this situa-

tion, no iteration is required to obtain  $\tilde{n}_0$  since  $\tilde{n}_0 = \tilde{p}_0 = 1$ . None is required in the complete compensation situation either, where again  $\pi_f \approx 1$  and for  $0 \leq \Lambda_I \ll 1$  (equilibrium conditions), the situation cannot be distinguished from pure intrinsic conduction.

When either  $h_1$  or  $h_2$  is nonzero,  $\tilde{n}_0$  may still be obtained from data fitting as above, but it is no longer needed when  $h_j = 0$ , either because  $\tilde{N}_j^0 = 0$  or because  $\Lambda_j \rightarrow \infty$ . Now when  $h_j = 0$  and  $f_I \neq 0$ , one can still obtain  $k_{Ie}$ ,  $k_{Ir}$ ,  $n_0$ ,  $p_0$ , and  $\mu_j$  from the fitting as above. But the  $\tilde{N}_j^0$ 's are now no longer free fitting parameters. To proceed, one may first obtain an estimate of  $(N_D^0 - N_A^0)$  from the calculated values of  $n_0$  and  $p_0$  using Eq. (A8') with tilde normalization removed. This estimate will approximate zero in the  $N_j = 0$  intrinsic case where  $n_0 = p_0 = c_{I0}$ . Then this result may be substituted into (A29) or (A29') in unnormalized form to obtain an equation connecting  $c_{I0}$  and  $N_A^0$  or  $c_{I0}$  and  $N_D^0$ . If either  $N_A^0$  or  $N_D^0$  is zero, often a good approximation in a strong extrinsic case, an estimate of  $c_{I0}$  may then be calculated together with the estimate of whichever of  $N_A^0$  or  $N_D^0$  is nonzero. Finally, estimates of  $\Lambda_I$ ,  $\xi_I$ ,  $\tau_I$ ,  $N_I^0$ , and  $N_{I0}$  may be calculated as above. If  $N_A^0$  and  $N_D^0$  are simultaneously nonzero and significant, independent knowledge of one of them or of  $c_{I0}$  will be required to complete the calculation of the more basic parameters in this case.

Finally, when  $f_I = 0$  as well as  $h_j = 0$ , fitting yields estimates of  $n_0$ ,  $p_0$ , and  $\mu_j$  if  $z_1$  and  $z_2$  are known. The electroneutrality condition here yields  $(z_2 N_D^0 - z_1 N_A^0) = (z_2 n_0 - z_1 p_0)$ , so that if again one of  $N_D^0$  or  $N_A^0$  is zero, an estimate of the other may be obtained. One may then use Eq. (A12) or (A13) to obtain an estimate of  $N_I^0$ . In the more realistic fully dissociated, pure intrinsic case, the free fitting parameter  $\pi_f = \pi_e$  may be used to eliminate either  $z_1$  or  $z_2$  when the other is known. In this case,  $n_0 = \pi_e^{-1} p_0 = n_I = \pi_e^{-1} p_I$  and (A12) and (A13) yield  $N_I^0 = (mz_1)^{-1} n_0 = (mz_2)^{-1} p_0$ .

The above results show that when the necessary valence numbers are known, one can usually obtain values of all remaining basic characterization parameters from fitting results. They fall into three groups: first  $\epsilon$ ,  $\tau_D$ ,  $\mu_j$ ,  $D_j$ ,  $c_{I0}$ ,  $n_0$ ,  $p_0$ ,  $N_{I0}^0$ , and  $N_{I0}$  for the basic material; second, the heterogeneous electrode-reaction rate constants  $k_{j0}$ ,  $k_{j\infty}$ , and  $\tau_{ja}$ ; and finally the intrinsic-extrinsic conduction  $G/R$  homogeneous rate constants  $\tau_I$ ,  $k_{Ie}$ ,  $k_{Ir}$ ,  $\tau_j$ ,  $k_{jr}$ , and  $k_{jg}$ .

It is now appropriate to comment on the physical significance of the basic parameters in general and in relation to particular electrode/material systems. The complex, frequency-dependent, electrode reaction rate constant  $k_j^*(\omega) = (k_{j0} + i\omega \tau_{ja} k_{j\infty}) / (1 + i\omega \tau_{ja})$  was introduced<sup>13-15</sup> in order to generalize the Chang-Jaffé boundary conditions (10)-(13) to cases in which the electrode reaction of the charged species  $Y_j$  involves the formation of an adsorbed intermediate species  $\Gamma_j$  with the possible transfer of electrons ( $e^-$ ) to the electrode in the adsorption step. The introduction of  $k_j^*(\omega)$  in the form given above allows one to treat the first-order adsorption-reaction sequence:



$$\Gamma_j \rightleftharpoons C_j + z_{j2} e^-, \quad (77)$$

where the concentration of  $C_j$  is held constant and  $C_j$  does not pass into the electrolyte unless it is a neutral species. The sequence is then characterized by the relaxation time  $\tau_{ja}$  given by

$$\tau_{ja}^{-1} \equiv \left[ \frac{\partial (v_{j2} - v_{j1})}{\partial [\Gamma_j]} \right]_0, \quad (78)$$

where  $v_{j1}$  is the rate of formation of  $\Gamma_j$  from  $Y_j$  and  $v_{j2}$  is the rate of formation of  $C_j$  from  $\Gamma_j$ . For the important special case of simple (pure) specific adsorption in which  $\Gamma_j$  does not react further to form  $C_j$ , one sets  $v_{j2} = 0$ .

On replacing real  $k_j$ 's in Eqs. (10)–(13) by  $k_j^*(\omega)$ , one ensures the proper relationship between the small-signal current and the concentration of each charge carrier when adsorption occurs. A derivation of the Chang–Jaffé boundary conditions with complex rate constants was given by us in a recent paper<sup>7</sup> which also considered the case in which the concentration of  $C_j$  was allowed to vary. In that work we also discussed compact layer effects on the rate of adsorption/reaction and indicated how the results obtained for Chang–Jaffé boundary conditions could be corrected for overpotential effects.

The complex rate constant formalism also offers an approach to the trapping of electrons or holes in surface states at an electrode/semiconductor junction. To treat this case one must set  $z_{j1} = z_{j2} = 0$  and regard  $\Gamma_j$  as the (electronic) charge carrier trapped in the surface state and  $C_j$  as the charge carrier in the electrode.

Taken at face value, the  $G/R$  equations (4)–(6) describe the unimolecular dissociation of neutral entities and the bimolecular association of charged species. Introducing the equilibrium constants  $K_I \equiv k_{Ig}/k_{Ir} \equiv \Lambda_I c_{I0}$ ,  $K_A \equiv k_{Ag}/k_{Ar} \equiv \Lambda_A c_{A0}$ , and  $K_D \equiv k_{Dg}/k_{Dr} \equiv \Lambda_D c_{D0}$ , we may write the equilibrium expressions (see Appendix A),

$$n_0 p_0 = K_I N_{I0}, \quad (79)$$

$$N_{A0} p_0 = K_A N_{A0}, \quad (80)$$

and

$$N_{D0}^+ n_0 = K_D N_{D0}. \quad (81)$$

In some materials it may be more appropriate to use the solubility product expression

$$n_0 p_0 = c_{I0}^2 \quad (82)$$

(also treated in Appendix A) which may be viewed as a limiting case of Eq. (79). The fact that the equilibrium expressions (79)–(81) apply in a particular material does not, however, guarantee that the original rate equations (4)–(6) are valid. One of us has found,<sup>11</sup> nevertheless, that when the equilibrium concentrations are governed by (79)–(81) or (82), (80), and (81), and  $G/R$  kinetics are governed by one of several different sets of rate laws, the simple expressions (4)–(6) provide an adequate description of  $G/R$  under small-signal conditions provided proper interpretation is made of the rate constants  $k_{Ig}$ ,  $k_{Ir}$ ,  $k_{Ag}$ ,  $k_{Ar}$ ,  $k_{Dg}$ , and  $k_{Dr}$  and of quantities derived from them appearing in the system response function.

When the rate equations (4)–(6) apply, the times  $\tau_I$  and  $\tau_j$  admit of direct physical interpretation. In intrinsic material at equilibrium both generalization and recombination processes occur continuously at the rate  $k_{Ir} c_{I0}^2$ . The average lifetime of a charge carrier is thus the concentration  $c_{I0}$  divided by this rate, or  $\tau_I \equiv (k_{Ir} c_{I0})^{-1}$ . In weakly extrinsic material ( $N_j^0 \ll c_{I0}$ ) formation and dissociation of the neutral impurities occur at the rate  $k_{jr} N_{j0}^+ c_{I0}$ . Thus  $\tau_j \equiv (k_{jr} c_{I0})^{-1}$  is the average lifetime of an ionized impurity center in the limit  $N_j^0 \rightarrow 0$ . The results we have obtained for systems with arbitrary extrinsic character are concisely expressed in terms of the carrier and ionized impurity lifetimes of the intrinsic or weakly extrinsic material. The relationship of these lifetimes to other definitions of charge carrier lifetime has recently been discussed by one of us.<sup>11</sup>

We now consider the equilibrium and dynamic  $G/R$  properties of different classes of materials and examine first the case of electronic semiconductors. It is well known that in semiconductors the equilibrium concentrations of charge carriers and of neutral and ionized impurities are governed by the Fermi level, which is itself determined by the properties of the intrinsic material and the concentration and properties of the impurities. In terms of the Fermi level  $E_F$  one has<sup>25</sup>

$$n_0 = N_c \mathcal{F}_{1/2}[(E_F - E_c)/kT], \quad (83)$$

$$p_0 = N_v \mathcal{F}_{1/2}[(E_v - E_F)/kT], \quad (84)$$

$$N_{D0}^+ = N_{D0} g_D^{-1} \exp[(E_c - E_F - E_d)/kT], \quad (85)$$

and

$$N_{A0}^- = N_{A0} g_A^{-1} \exp[(E_v + E_F - E_a)/kT], \quad (86)$$

where  $E_c$  and  $E_v$  are the energies of the conduction band bottom and valence band maximum;  $N_c$  and  $N_v$  are the corresponding effective densities of electron and hole states;  $g_D$  and  $g_A$  are the degeneracies of the donor and acceptor levels; and  $E_d$  and  $E_a$  are the donor and acceptor energies. Here

$$\mathcal{F}_{1/2}(x) \equiv 2\pi^{-1/2} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{1 + \exp(\epsilon - x)} \quad (87)$$

is a Fermi integral.

Since the current equations (1) and (2), and thus the treatment of this paper, are only valid for nondegenerate semiconductors, in which the Fermi level lies in the band gap several  $kT$  away from the valence and conduction bands, we restrict our consideration to this case. In the approximation  $\mathcal{F}_{1/2}(x) \sim \exp(x)$ , valid for nondegenerate materials, one has

$$n_0 p_0 = N_c N_v \exp[(E_v - E_c)/kT] = c_{I0}^2 \quad (88)$$

$$N_{A0}^- p_0 = [N_v g_A^{-1} \exp(-E_a/kT)] N_{A0}, \quad (89)$$

and

$$N_{D0}^+ n_0 = [N_c g_D^{-1} \exp(-E_d/kT)] N_{D0}. \quad (90)$$

Numerical computations using (83)–(86) for representative systems suggest that (88)–(90) are valid to within a few percent as long as  $E_F$  is at least  $3kT$  away from the valence and conduction bands. Equations (89) and (90) correspond directly to (80) and (81) and permit direct identification of  $K_A$  and  $K_D$ .

One of us has recently found<sup>26</sup> that somewhat better approximations to the exact results (83)–(86) under non-degenerate conditions are given by the expressions

$$n_0 p_0 = 2^{-3} \exp[(E_v - E_c)/kT] [\hat{N} - n_0] [\hat{N}_v - p_0], \quad (91)$$

$$N_{A0} p_0 = 2^{-3/2} g_A^{-1} \exp(-E_a/kT) N_{A0} [\hat{N}_v - p_0], \quad (92)$$

$$N_{D0} n_0 = 2^{-3/2} g_D^{-1} \exp(-E_d/kT) N_{D0} [\hat{N}_c - n_0], \quad (93)$$

where  $\hat{N}_v \equiv 2^{3/2} N_v$  and  $\hat{N}_c \equiv 2^{3/2} N_c$ . These expressions all correspond to charge transfer reactions of the form



Although the expressions (91)–(93) offer some theoretical insight into equilibrium in semiconductors, the simpler expressions (88)–(90) should suffice for many experimental situations.

In semiconductors, intrinsic and extrinsic  $G/R$  may occur by photon-assisted, phonon-assisted, or Auger-like mechanisms.<sup>10,25</sup> In addition, intrinsic  $G/R$  may occur by the sequential trapping of electrons and holes (Shockley–Read<sup>27</sup> mechanism). One of us has recently shown<sup>11</sup> that under small-signal conditions intrinsic  $G/R$  in semiconductors may often be described by a limiting form of Eq. (14) while extrinsic  $G/R$  may frequently be described by Eqs. (5) and (6), even though the rate laws applicable under more general conditions are of a different form. In that work it was concluded that  $\Lambda_I = 0$  and  $\Lambda_I > 0$  were appropriate assumptions in the semiconductor case. It is plausible, however, that a small finite value of  $\Lambda_I$  might sometimes provide a better fit to the data over the accessible frequency range and that a more detailed theoretical treatment might provide a meaningful physical interpretation for a non-zero value of  $\Lambda_I$ .  $G/R$  phenomena in semiconductors have been the subject of numerous studies, and it has been found that electron and hole lifetimes vary considerably from one material to another.<sup>28</sup> These results indicate that  $\xi_I$  may take on values ranging from much smaller than unity to much larger than unity in various semiconductors.<sup>11,18</sup>

It is often possible to characterize solid ionic conductors as materials with Schottky disorder, materials with Frenkel disorder, or disordered-sublattice materials (fast ionic conductors).<sup>29</sup> We first consider materials with Schottky disorder, of which the alkali halides are the most prominent and well studied examples. For concreteness we assume the material to have chemical formula  $MX$  and to consider of singly charged cations and anions. Schottky disorder is the presence of cation and anion vacancies ( $V_M^+$  and  $V_X^-$  in the notation of Kröger and Vink<sup>30</sup>) which function as the charge carriers  $N^-$  and  $P^+$ , respectively. The equilibrium concentrations of free charge carriers are governed by an expression of the solubility product form<sup>31,32</sup>:

$$n_0 p_0 = K_s. \quad (95)$$

Here, and throughout the discussion below, we neglect those effects of interaction among the charged species which would require the introduction of activity coefficients<sup>32</sup> in expressions such as (95). This idealization is often well justified and simplifies the present discussion considerably.

In general, at thermal equilibrium there will also be present bound complexes of oppositely charged carriers which may be denoted  $(NP)^i$ , with  $i = 1, 2, \dots$  indicating the different possible geometrical arrangements of the vacancy pairs.<sup>31,32</sup> Here we shall assume that all such bound complexes may be well approximated as neutral and immobile. We neglect the relaxation of their multipolar response to the electric field; an effect seldom significant in the  $\Omega \lesssim 1$  region of greatest interest in the present work. One may, of course, relate the equilibrium concentration of each type of bound complex to that of the free carriers as

$$[(NP)^i]_0 = K_i^{-1} n_0 p_0, \quad (96)$$

thus formally expressing the equilibrium between the bound complexes and the free carriers. Summing over  $i$ , one obtains the expression

$$[(NP)]_0 = K_I^{-1} n_0 p_0, \quad (97)$$

which permits us to identify  $N_{I0}$  as  $[(NP)]_0$ .

Schottky defect materials,  $MX$ , often contain aliovalent impurities  $R^{2+}$  or  $Y^{2-}$  which can take the place of the  $M^+$  and  $X^-$  ions in the crystal lattice to form  $R_M^+$  and  $Y_X^-$  centers which we may treat as ionized donor and acceptor centers,  $D^+$  and  $A^-$ , respectively. These centers may also form bound complexes  $(DN)^i$  and  $(AP)^i$  whose concentrations at equilibrium are governed by the mass action expressions

$$[(DN)^i] = K_{Di}^{-1} N_D^+ n_0, \quad (98)$$

and

$$[(AP)^i] = K_{Ai}^{-1} N_A^- p_0. \quad (99)$$

Summing over  $i$ , one obtains the expressions

$$[(DN)] = K_D^{-1} N_D^+ n_0, \quad (100)$$

and

$$[(AP)] = K_A^{-1} N_A^- p_0, \quad (101)$$

where  $[(DN)]$  and  $[(AP)]$  denote the total concentration of  $(DN)$  and  $(AP)$  complexes. Identifying  $[(DN)]$  and  $[(AP)]$  as  $N_{D0}$  and  $N_{A0}$ , we see that the position of equilibrium in Schottky defect materials is determined by expressions of the familiar forms (82), (80), and (81).

The nonequilibrium kinetics of a Schottky defect material with aliovalent impurities can in principle be quite complicated if any of the neutral complexes,  $(NP)$ ,  $(DN)$ , or  $(AP)$  exist in more than one form (structure). One might then have to consider not only the rates of association and dissociation of the neutral centers but also the rates at which their structures change from one form to another. In the foregoing treatment it has been assumed in effect that only one form of each neutral species is of significance in dynamic space charge phenomena—a logical first approximation to the more complicated case. In Appendix B we indicate how the present treatment may be generalized to include more than one form of each neutral center and identify some conditions under which only a single form of each complex need be considered.

An apparently paradoxical aspect of the Schottky defect

case is that while the concentration of neutral centers  $[(NP)]$  does not enter into the equilibrium condition, it does enter into the treatment of dynamical  $G/R$ . Since a cation and an anion vacancy may be created by transporting a cation and an anion to the macroscopic crystal surface (or to a grain boundary or line imperfection),  $n_0$  and  $p_0$  are determined by the requirement of thermodynamic equilibrium between the crystal interior and its surface. For a single crystal of moderate size and negligibly low dislocation density, diffusion of vacancies to and from the surface will be exceedingly slow compared to the longest experimentally practical period of the ac measurements. One is then justified in using the solubility product expression (82) in the equilibrium case and using Eq. (4) in the dynamic treatment with  $N_I$  identified as  $[(NP)]$ . (One sets  $\Lambda_I = 0$  in the treatment of Appendix A but not in the expressions of Appendix B.) An innovation which might prove useful for Schottky defect materials, particularly those with a significant number of grain boundaries or dislocation loops, is to consider  $k_{I_g}$  in Eq. (4) to be a complex frequency-dependent quantity of the form  $k_{I_g}^* = i\Omega \xi_{I_g} k_{I_g\infty} / (1 + i\Omega \xi_{I_g})$ , where the parameter  $\xi_{I_g}$  reflects the geometry and state of imperfection of the crystal.

Estimates of the recombination rate constants can be obtained from the Langevin<sup>33</sup> theory of recombination which applies when the charge carrier mean free paths are much smaller than  $e^2/\epsilon kT$ .<sup>11,34</sup> From this theory one has

$$k_{Ir} = 4\pi(\mu_n + \mu_p)z_e e/\epsilon, \quad (102)$$

$$k_{Ar} = 4\pi\mu_p z_e e/\epsilon, \quad (103)$$

and

$$k_{Dr} = 4\pi\mu_n z_e e/\epsilon; \quad (104)$$

and thus  $\xi_A = \pi_m \tilde{n}_0 + \tilde{p}_0$ ,  $\xi_D = \tilde{n}_0 + \pi_m^{-1} \tilde{p}_0$ , and  $\xi_I^{-1} = \xi_A^{-1} + \xi_D^{-1} = \epsilon_2 \tilde{n}_0^{-1} (1 + \pi_m^{-1})$ . Determination of these parameters by the fitting of experimental data provides a test of the applicability of the Langevin theory to such materials.

In materials with Frenkel disorder, cation vacancies ( $V_M^+$ ) function as  $N^*$  while cation interstitials ( $M_i^+$ ) function as  $P^*$ . The mass action law for the concentrations of free charge carriers is<sup>35</sup>

$$n_0 p_0 = K_F [M_M^+][V_i^+], \quad (105)$$

where  $[M_M^+]$  is the concentration of cations on normal cation sites and  $[V_i^+]$  is the concentration of unoccupied interstitial sites. There will also be bound complexes  $(NP)^{\dagger}$  present at equilibrium with each type of complex satisfying an equilibrium law

$$[(NP)^{\dagger}]_0 = (K_I')^{-1} [M_M^+][V_i^+]_0. \quad (106)$$

Combination of the two expressions yields a relation of the form of Eq. (96) where, in the present case,  $K_I = K_I' K_F$ . Summing over the various types of bound complexes then again leads to Eq. (97), an expression of the equilibrium constant form (79).

Frenkel defect materials may also contain aliovalent impurities  $R^{2+}$  or  $Y^{2-}$  occupying lattice sites which we may identify as  $D^+$  and  $A^-$ . Bound complexes  $(DN)^{\dagger}$  and

$(AP)^{\dagger}$  will also in general be present and will obey the same mass action laws (98)–(101) as in the Schottky case. For the usual situation of small defect concentrations, it is reasonable to replace (105) by the simpler solubility product form

$$n_0 p_0 = K_F \quad (107)$$

and to solve (107), (100), and (101) simultaneously to determine the equilibrium concentration.

The nonequilibrium kinetics of Frenkel defect materials may, as in the Schottky defect case, be complicated by the existence of different structural forms of the neutral complexes. An additional complication in the Frenkel case is that a pair of defects may be created spontaneously by the displacement of a cation from its normal lattice position. If it is assumed that this process effectively results in the generation of free charge carriers, one would replace the term  $\partial N_I / \partial t$  in Eqs. (7) and (8) by

$$\left( \frac{\partial N_I}{\partial t} \right)_{\text{eff}} = k_{Ir}(np - n_0 p_0), \quad (108)$$

which is consistent with the approximation of Eq. (107) and requires  $\Lambda_I = 0$  in expressions for the dynamic system response. Neutral acceptor and donor complexes would be treated as in Eqs. (5) and (6). A more general treatment, which allows for changes in the structure of neutral complexes and formation and dissociation of the unperturbed lattice, is illustrated in the latter part of Appendix B.

Disordered-sublattice materials such as  $\alpha\text{AgI}$ ,  $\text{RbAg}_4\text{I}_5$ , and  $\text{Na-}\beta\text{-alumina}$  are characterized by the existence of one or more mobile cations per unit cell. Although it would thus seem that the electrical response of such systems is intrinsically a many-body problem, it is sometimes<sup>9,36</sup> assumed that the current equation (1) may be applied in such materials, and it is then not unreasonable to hope that the present treatment may be applicable, at the least as a convenient means of parameterizing the data. We shall not discuss these materials in detail here, but will point out that in nonstoichiometric materials such as the  $\beta\text{-aluminas}$  the presence of charge centers compensating the excess or deficit of mobile cations requires some thought to be given to the possible existence of  $G/R$  effects.

We now briefly consider conducting liquid materials. The present treatment is directly applicable to fully dissociated intrinsic materials such as unsupported solutions of strong electrolytes. It should also be useful for solutions of weak electrolytes, especially when ion pairs diffuse slowly compared to the free ions.  $G/R$  in solutions of potential electrolytes (e.g., aqueous acetic acid) may be described by the neutral-center dissociation/association expression (4). Saturated solutions of nearly insoluble salts [e.g.,  $\text{AgCl(aq)}$ ] would be treated in a manner analogous to Schottky defect materials. Finally, the present results may prove useful in parameterizing measurements made on fused salts and oxides, and if so, may aid in the development of physical models for these materials. In Table I we summarize the  $\Lambda_I$  values appropriate to equilibrium and

TABLE I. Summary of  $\Lambda_I$  values appropriate for intrinsic  $G/R$  from structureless neutral centers. See Appendix B for discussion of  $G/R$  involving "structured" neutral centers.

Conduction type	Equilibrium conditions	Dynamic conditions
Electronic	$\Lambda_I = 0$	$\Lambda_I \approx 0$
Schottky Defect	$\Lambda_I = 0$	$\Lambda_I > 0$
Frenkel Defect		$\Lambda_I \approx 0$
Fast Ion		$\Lambda_I \gg 1$
Ionic (strong electrolyte)		$\Delta_I \rightarrow \infty$
Ionic (saturated solution of nearly insoluble salt)	$\Delta_I = 0$	$\Lambda_I > 0$
Ionic (solution of potential electrolyte)		$\Lambda_I > 0$
Ionic (fused salt or oxide)		$\Lambda_I > 0$

dynamic conditions based on the discussion of this section.

## LIST OF SYMBOLS

### A. Major subscripts

- $a$  Applied; average; adsorption
- $c$  Compensation
- $e$  Equilibrium; extrinsic; equality
- $f$  First order in  $\Omega$ . See Appendix C.
- $g$  Generation
- $i$  Incremental; index for different configurations of a neutral complex
- $j$   $j = 1, 2$
- $k$   $k = 1, 2$ , and  $k \neq j$
- $n$  Negative
- $p$  Positive
- $r$  Recombination
- $s$  Series;  $1 \rightarrow 2, 2 \rightarrow 1$  symmetry
- $A$  Acceptor; adsorption
- $D$  Donor
- $I$  Intrinsic
- $L$  Left
- $N$  Normalization:  $R_N \equiv R/R_\infty$ ,  $C_N \equiv C/C_\infty$
- $P$  Parallel
- $R$  Right; reaction
- $T$  Total
- $W$  Warburg

0 Bulk equilibrium; static;  $\omega \rightarrow 0$  limit

1  $p$  or  $A$

2  $n$  or  $D$

$\infty$   $\omega \rightarrow \infty$  limit

### B. Major superscripts

- 0 Limit of a quantity when  $\rho_j = 0$ ; limit of concentration before any dissociation
- + Indicates an ionized donor
- Indicates an ionized acceptor
- $\sim$  Normalization with  $n_I$ ,  $p_I$ , or  $c_I$

### C. Major symbols in text

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

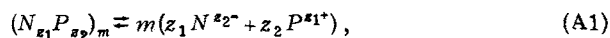
- $a$   $\delta_1 \lambda_1 + \delta_2 \lambda_2$ , (21)
- $a_{jm}$  (B10)–(B13)
- $b, b_e$   $\lambda_1 \lambda_2$ , (21);  $\lambda_{e1} \lambda_{e2}$ , (B26)
- $c, c_e$   $\lambda_2 - \lambda_1$ , (22);  $\lambda_{e2} - \lambda_{e1}$
- $d, d_e$   $\lambda_2 + \lambda_1$ , (22);  $\lambda_{e2} + \lambda_{e1}$ , (B27)
- $e$  Protonic charge
- $f_I$   $2\phi b h_I$ , (B16)
- $f_s$   $(\theta_j^2 - \theta_k^2)/(\theta_j^2 - a_{kk})$ , (B33)
- $g_j$   $1 + \rho_j$
- $g_s$   $1 + \rho_s$ , (B36)
- $h_j$  (B6)
- $h_s$   $\rho_1 \rho_2 + \epsilon_1 \rho_1 + \epsilon_2 \rho_2$ , (B35)
- $h_I$   $(\Lambda_I + i\Omega \xi_I)^{-1}$ , (B5)
- $k$  Boltzmann constant; rate constant
- $k_j$  Electrode reaction rate constants, (10)–(13)
- $k_{jg}, k_{jr}$  Acceptor and donor generation and recombination rate constants.  $k_{1g} \equiv k_{Ag}$ ,  $k_{2g} \equiv k_{Dg}$ , etc.
- $k_{Ig}, k_{Ir}$  Intrinsic center generation and recombination rate constants.
- $l$  Separation distance of plane, parallel electrodes
- $n$  Concentration of mobile negative charges
- $p$  Concentration of mobile positive charges
- $q$  (38)
- $r$   $(M) \coth(M)$ ; Previous  $r_p \equiv r_1 \equiv 2\rho_1$ ,  $r_n \equiv r_2 \equiv 2\rho_2$
- $r_e$   $(M\sqrt{u_{e0}}) \coth(M\sqrt{u_{e0}})$ , (65)
- $r_0$   $(M\sqrt{q_0}) \coth(M\sqrt{q_0})$
- $t_j$   $\gamma_j - 1$ , (B29)
- $u_e$   $\Delta_1 + \Delta_2$ , (B27)
- $v$   $1 + \Lambda_I^{-1}(1 - \tilde{n}_0 \tilde{p}_0)$
- $x$  Distance measured from left electrode



$y_{j0}$ $y_{10} \equiv p_0$ ; $y_{20} \equiv n_0$	$Z_s$ $Y_s^{-1}$
$z_j$ $z_1 \equiv z_p$ ; $z_2 \equiv z_n$ . Valence numbers of mobile charges	$Z_M$ $Y_M^{-1}$
$A$ $4(a_{11}a_{22} - a_{12}a_{21})$ , (B19), (B24)	$Z_T$ $Y_T^{-1}$ . Total input impedance
$A_b$ (54)	$Z_w$ $R_\infty / \pi_e \gamma_2$
$A_j$ (63), (64)	$\gamma_j$ $(M\theta_j) \coth(M\theta_j)$ , ((B28)
$B$ $(a_{11} + a_{22})$ , (B18), (B25)	$\delta_j$ $(1 + \pi_f^{3-2j})^{-1}$ , (19)
$B_b$ (55)	$\epsilon$ Bulk dielectric constant
$C_g$ $\epsilon / 4\pi l$ . Geometric capacitance for unit electrode area	$\epsilon_j$ $(1 + \pi_e^{3-2j})^{-1}$ , (17)
$C_A$ $(\xi_{2a} \rho_{2\infty}^2 / \rho_{2m}) C_g$ . Adsorption capacitance for $\pi_m \rightarrow \infty$	$\theta_j^2$ (B20)
$C_{PW}$ $\lambda_1^2 (\gamma - 1) C_g$	$\lambda_j$ $\delta_j / \epsilon_j$
$C_R$ $(\gamma_0 - 1) C_g$ . Reaction capacitance for $\pi_m \rightarrow \infty$	$\lambda_{ej}$ $\Delta_j / \epsilon_j$
$D_a$ $(z_1 \mu_1 p_0 + z_2 \mu_2 n_0)$	$\mu_j$ $\mu_1 \equiv \mu_p$ ; $\mu_2 \equiv \mu_n$ . Mobilities
$D_b$ $(z_1^2 p_0 + z_2^2 n_0)$	$\xi_j$ $\tau_j / \tau_D$ , (B8)
$D_j$ $(kT/e)(\mu_j / z_j)$ . Diffusion coefficients	$\xi_{ja}$ $\tau_{ja} / \tau_D$ , (B38)
$G_\infty$ $(e/l)(z_1 \mu_1 p_0 + z_2 \mu_2 n_0)$ , (14)	$\xi_I$ $\tau_I / \tau_D$ , (B7)
$I_{12}$ $(\theta_1^2 - \theta_2^2)^{-1}$	$\pi_e$ $\pi_m (\tilde{n}_0 / \tilde{p}_0)$ , (16)
$L_D$ (23). Debye length	$\pi_f$ $\pi_e (\tilde{n}_0 / \tilde{p}_0)$ , (18)
$L_{D2}$ $(\epsilon kT / 4\pi (ez_2)^2 n_0)^{1/2}$	$\pi_m$ $\mu_2 / \mu_1$
$L_I$ Intrinsic-conduction Debye length for $z_1 = z_2 \equiv z_e$	$\pi_e$ $z_2 / z_1$
$M$ $(l/2) L_D^{-1}$	$\rho_j$ $(l/2)(k_j / D_j)$ , (B38). Complex electrode reaction parameters
$M_I$ $(l/2) L_I^{-1}$	$\rho_{j0}$ $(l/2)(k_{j0} / D_j)$
$M_2$ $(l/2) L_{D2}^{-1}$	$\rho_{j\infty}$ $(l/2)(k_{j\infty} / D_j)$
$N$ Intrinsic, donor, or acceptor concentration	$\rho_s$ $(\epsilon_1 \rho_2 + \epsilon_2 \rho_1)$ , (B36)
$N_s$ (B37), (B37')	$\tau_j$ $(k_{jr} c_{I0})^{-1}$ . Acceptor and donor relaxation times
$N_A$ $N_1$ . Acceptor concentration	$\tau_{ja}$ Adsorption relaxation times
$N_D$ $N_2$ . Donor concentration	$\tau_D$ $R_\infty C_g$ . Dielectric relaxation time
$P_{j1}$ (B47)	$\tau_I$ $(k_{Ir} c_{I0})^{-1}$ . Intrinsic center relaxation time
$P_{j2}$ (B48)	$\phi$ $0.5(\tilde{n}_0 + \tilde{p}_0)$
$R_A$ $(\rho_{2m} / \rho_{20} \rho_{2\infty}) R_\infty$ . Adsorption resistance for $\pi_m \rightarrow \infty$	$\psi$ $1 + i\Omega$
$R_D$ $Z_{T0} \equiv R_\infty + Z_{s0}$ , (25). Low frequency limiting resistance	$\omega$ Radial frequency
$R_R$ $\rho_{2\infty}^{-1} R_\infty$ . Reaction resistance for $\pi_m \rightarrow \infty$	$\Delta_j$ $\delta_j (1 + h_j)$ , (B14)
$R_\infty$ $G_\infty^{-1}$ . High frequency limiting bulk resistance	$\Lambda_j$ $k_{jg} / k_{jr} c_{I0}$
$T$ Absolute temperature	$\Lambda_I$ $k_{Ig} / k_{Ir} c_{I0}$
$W_j$ (B46)	$\Omega$ $\omega \tau_D$ . Normalized frequency
$Y_{sN}$ $Z_{sN}^{-1}$ , (27), (B34)	
$Y_{MN}$ $Y_{MN}^0 + Y_{MN}^1$ , (B43)	
$Y_{TN}$ $Z_{TN}^{-1}$ , (24). Total normalized input admittance	
$Z_{aN}$ $g_s Z_{MN}$ , (28)	
$Z_{bN}$ $g_s / h_s$ , (29)	
$Z_{cN}$ $N_s Z_{MN}$ , (30)	
$Z_{dN}$ $N_s / h_s$ , (31)	

## APPENDIX A: EQUILIBRIUM SOLUTIONS

We consider, for concreteness, chemical species  $N$  and  $P$  which combine to form an intrinsic neutral center. Let  $n_0 \equiv [N^{*2-}]$  and  $p_0 \equiv [P^{*1+}]$ . To retain maximum generality in the limiting fully dissociated case we do not at first require  $\pi_e \equiv z_2 / z_1$  to be unity. In general, the dissociation of an intrinsic center may be written



where  $z_1 m$  and  $z_2 m$  must be integers. Thus  $m$  is constrained to be an integer divided by the greatest common factor of  $z_1$  and  $z_2$ . Similarly, if we set  $N_{D0}^+ = [D^{z_2+}]$  and  $N_{A0}^- = [A^{z_1-}]$ , where  $D$  and  $A$  are donor and acceptor species, we have

$$(DN) \rightleftharpoons D^{z_2+} + N^{z_1-}, \quad (A2)$$

and

$$(AP) \rightleftharpoons A^{z_1-} + P^{z_2+}. \quad (A3)$$

Conservation of particle number and charge then lead to

$$N_{A0}^- = N_A^0 - N_{A0}, \quad (A4)$$

$$N_{D0}^+ = N_D^0 - N_{D0}, \quad (A5)$$

$$n_0 = m z_1 (N_I^0 - N_{I0}) + N_{D0}^+, \quad (A6)$$

and

$$p_0 = m z_2 (N_I^0 - N_{I0}) + N_{A0}^-. \quad (A7)$$

In addition, the electroneutrality condition following from Eq. (9) of the text is

$$z_1 (p_0 - N_{A0}^-) = z_2 (n_0 - N_{D0}^+), \quad (A8)$$

consistent with the above relations. Although Eq. (A1) deals with a more general situation than does Eq. (4), the latter will only be used when  $\pi_g = 1$ . In this case of incomplete dissociation and simple bimolecular recombination, it is physically reasonable to take  $m z_1 = m z_2$  as unity. In addition, Eqs. (4)–(6) of the text become, for equilibrium conditions,

$$k_{I\bar{g}} N_{I0} = k_{I\bar{r}} n_0 p_0, \quad (A9)$$

$$k_{A\bar{g}} N_{A0} = k_{A\bar{r}} N_{A0} p_0, \quad (A10)$$

and

$$k_{D\bar{g}} N_{D0} = k_{D\bar{r}} N_{D0}^+ n_0. \quad (A11)$$

### I. Full dissociation of all centers

Here,  $N_{I0} = N_{D0} = N_{A0} = 0$ . Equations (A6) and (A7) reduce to

$$n_0 = m z_1 N_I^0 + N_D^0, \quad (A12)$$

and

$$p_0 = m z_2 N_I^0 + N_A^0, \quad (A13)$$

where  $m$  must be determined from the stoichiometry of intrinsic-center dissociation (Eq. A1).

### II. Partial dissociation

#### 1. Intrinsic conduction

Designate the intrinsic concentrations  $n_0$  and  $p_0$  as  $n_{I0}$  and  $p_{I0}$ . Then Eq. (A8) yields  $z_1 p_{I0} = z_2 n_{I0}$ . When  $\pi_g = 1$ ,  $n_{I0} = p_{I0} \equiv c_{I0}$ , where this common value then satisfies

$$c_{I0} = N_I^0 - N_{I0}. \quad (A14)$$

Let us now define

$$\Lambda_I \equiv k_{I\bar{g}} / k_{I\bar{r}} c_{I0}, \quad (A15)$$

a quantity determining the amount of equilibrium dissociation. In addition, define the recombination parameter

$$R_I \equiv k_{I\bar{r}} N_I^0 / k_{I\bar{g}} \quad (A16)$$

and the dissociation ratio

$$D_I \equiv c_{I0} / N_I^0 = (1 + \Lambda_I^{-1})^{-1}. \quad (A17)$$

As  $D_I \rightarrow 0$ ,  $\Lambda_I \rightarrow 0$ , and  $R_I \rightarrow \infty$ . Similarly, as full dissociation is approached,  $D_I \rightarrow 1$ ,  $\Lambda_I \rightarrow \infty$ , and  $R_I \rightarrow 0$ . We shall use  $\Lambda_I$  as a main parameter of the solution.

It will now be convenient in the general case to introduce the following normalization. Let  $\tilde{n}_0 \equiv n_0 / n_{I0}$  and  $\tilde{p}_0 \equiv p_0 / p_{I0}$ . Since this is equivalent to normalizing with  $c_{I0}$  in the  $\pi_g = 1$  situation, normalize  $G/R$ -related quantities with  $c_{I0}$ . Thus, for example,  $\tilde{N}_{I0} \equiv N_{I0} / c_{I0}$ . For the pure intrinsic situation,  $\tilde{n}_0 = \tilde{p}_0 = 1$ . In general,  $\tilde{n}_0 / \tilde{p}_0 = (p_{I0} / n_{I0})(n_0 / p_0) = \pi_g (n_0 / p_0)$ . Now Eqs. (A9) and (A14) lead for intrinsic conditions to  $\Lambda_I^{-1} = \tilde{N}_{I0} = (R_I + 0.25)^{1/2} - 0.5$ , and  $\Lambda_I = (\tilde{N}_{I0}^0 - 1)^{-1}$ . Thus  $\tilde{N}_{I0}^0$  can be obtained from knowledge of  $\Lambda_I$ . In the above, the ratio  $(c_{I0}^2 / n_{I0} p_{I0})$  has been set to its  $\pi_g = 1$  value of unity. Finally, one also obtains  $R_I = \tilde{N}_{I0}^0 / \Lambda_I$  and  $D_I = (\tilde{N}_{I0}^0)^{-1}$ .

#### 2. Extrinsic conduction-general

We shall first consider the most general situation. To save space, replace "A" subscripts by 1 and "D" subscripts by 2 and denote either by  $j$  ( $j=1, 2$ ). Whenever an equation involving  $j$  appears, it should be understood unless otherwise stated that it represents both the  $j=1$  and the  $j=2$  equations. Further, take  $N_{j0}^+$  as signifying  $N_{10}^+$  for  $j=1$  and  $N_{20}^+$  for  $j=2$ . Let

$$\Lambda_j \equiv k_{j\bar{g}} / k_{j\bar{r}} c_{I0}. \quad (A18)$$

We select  $\Lambda_I$ ,  $\Lambda_1 \equiv \Lambda_A$ ,  $\Lambda_2 \equiv \Lambda_D$ ,  $\tilde{N}_1^0 \equiv \tilde{N}_A^0$ , and  $\tilde{N}_2^0 \equiv \tilde{N}_D^0$  as the main parameters of the present treatment. Quantities such as  $R_j$  and  $D_j$  may be defined analogously to  $R_I$  and  $D_I$  as needed. The use of  $R_j$  in the description of extrinsic  $G/R$  in semiconductors is examined in earlier work by one of us.<sup>37</sup> With the above definitions, Eqs. (A9)–(A11) become, for  $\pi_g = 1$ ,

$$\Lambda_I \tilde{N}_{I0} = \tilde{n}_0 \tilde{p}_0, \quad (A9')$$

$$\Lambda_j \tilde{N}_{j0} = \tilde{N}_{j0}^+ \tilde{y}_{j0}, \quad (A19)$$

where  $\tilde{y}_{10} \equiv \tilde{p}_0$  and  $\tilde{y}_{20} \equiv \tilde{n}_0$ . On using (A4), (A5), and (A19), one finds

$$\tilde{N}_{j0}^+ = \Lambda_j \tilde{N}_j^0 / (\Lambda_j + \tilde{y}_{j0}). \quad (A20)$$

Because of the presence of extrinsic  $G/R$ , Eq. (A9') shows that  $\Lambda_I$  no longer equals  $\tilde{N}_{I0}^{-1}$ ; it is defined by Eq. (A15). On the other hand,  $N_I^0$  and  $\tilde{N}_I^0$  are the same in both intrinsic and extrinsic situations. Thus even for extrinsic conduction we can still write  $\tilde{N}_I^0 = 1 + \Lambda_I^{-1}$ .

Now Eqs. (A6), (A7), (A9'), and (A20) yield

$$\tilde{y}_{j0} = 1 + \Lambda_I^{-1} (1 - \tilde{y}_{j0} \tilde{y}_{k0}) + [\Lambda_j \tilde{N}_j^0 / (\Lambda_j + \tilde{y}_{j0})], \quad (A21)$$

where  $k=2$  when  $j=1$  and 1 when  $j=2$ . These results for  $\tilde{n}_0$  and  $\tilde{p}_0$  satisfy Eq. (A8) in normalized form when  $\pi_g = 1$ . In order to obtain specific values for  $\tilde{n}_0$  and  $\tilde{p}_0$  when  $\Lambda_I$ ,  $\Lambda_j$ , and  $\tilde{N}_j^0$  values are given, the coupled set (A21) may be solved by iteration in the general case. Unfortunately, one finds that convergence is extremely slow, especially for  $\Lambda_I \ll 1$ , the usual case for solids. An alternative is to transform these equations into

separate quintic equations in  $\tilde{n}_0$  and  $\tilde{p}_0$  and solve them. But there is a further and much preferable alternative. Let us introduce the new variable  $v \equiv 1 + \Lambda_I^{-1}(1 - \tilde{n}_0 \tilde{p}_0)$ , not necessarily equal to unity. Then, Eq. (A21) becomes a quadratic in  $\tilde{y}_{j0}$  involving  $v$  as an unknown parameter. Its formal solution is

$$\tilde{y}_{j0} = \left( \frac{v - \Lambda_j}{2} \right) + \left[ \left( \frac{v - \Lambda_j}{2} \right)^2 + \Lambda_j(v + \tilde{N}_j^0) \right]^{1/2}, \quad (\text{A22})$$

particularly useful when  $\Lambda_j \leq v$ . To avoid the possibility of the appearance of small differences between large numbers, a condition which reduces calculation accuracy, one may apply the general formula

$$\mp \sqrt{a} + \sqrt{a+b} \equiv b / (\pm \sqrt{a} + \sqrt{a+b}) \quad (\text{A23})$$

to (A22), yielding

$$\tilde{y}_{j0} = \frac{\Lambda_j(v + \tilde{N}_j^0)}{\left( \frac{\Lambda_j - v}{2} \right) + \left[ \left( \frac{\Lambda_j - v}{2} \right)^2 + \Lambda_j(v + \tilde{N}_j^0) \right]^{1/2}}, \quad (\text{A22}')$$

a result to be used in place of (A22) when  $\Lambda_j > v$ . Now using (A22) or (A22'), one may form  $v \equiv 1 + \Lambda_I^{-1}(1 - \tilde{y}_{j0} \tilde{y}_{k0})$ , with  $j = 1$  or  $2$ , yielding an implicit equation for  $v$  itself. Let

$$f(v) = v - 1 + \Lambda_I^{-1}(\tilde{y}_{j0} \tilde{y}_{k0} - 1). \quad (\text{A24})$$

We now need only solve  $f(v) = 0$  for  $v \equiv v_s$  by an iterative procedure such as the Newton-Raphson method, with the epsilon algorithm<sup>38</sup> used to speed convergence if necessary. Then to obtain the appropriate values of  $\tilde{n}_0$  and  $\tilde{p}_0$ , one need only substitute the converged value of  $v$ ,  $v_s$ , into (A22) or (A22'). As an example, for  $\Lambda_I = 10^{-4}$ ,  $\Lambda_1 = 10^{-2}$ ,  $\Lambda_2 = 1$ ,  $\tilde{N}_1^0 = 1$ , and  $\tilde{N}_2^0 = 10$ , one finds  $v_s \equiv 0.318055264$ , yielding  $\tilde{n}_0 \approx 2.88924704$  and  $\tilde{p}_0 \approx 0.3461345398$ . Thus, here  $(\tilde{n}_0 \tilde{p}_0 - 1) \approx 6.819 \times 10^{-5}$ . Let us now consider simpler special cases.

*a. Intrinsic limit of extrinsic conduction.* When  $\tilde{N}_j^0 = 0$  and/or  $\Lambda_j = 0$ , (A22) yields  $\tilde{y}_{j0} = v$ . Then the condition  $f(v) = 0$  becomes  $(v - 1) + \Lambda_I^{-1}(v^2 - 1) = 0$ , whose solution is  $v = v_s = 1$ . The alternate solution  $v = -(1 + \Lambda_I)$  leads to nonphysical (i.e., negative) values of  $\tilde{y}_{j0}$ . Thus, the extrinsic-intrinsic expressions reduce properly to the correct  $\tilde{n}_0 = \tilde{p}_0 = 1$  result in the intrinsic limit.

*b. Extrinsic conduction—full intrinsic dissociation.* This case involves  $\Lambda_I \rightarrow \infty$ , a condition usually associated with liquids (e.g., molten salts or strong electrolyte solutions) since a crystal composed largely of neutral centers would melt if full intrinsic dissociation occurred, unless one of the charge carrier species were effectively immobile. Except in the latter special case, it would be unphysical to set  $\tilde{N}_j^0 \neq 0$  in the present treatment since we have assumed the extrinsic centers to be immobile. In general, when  $\Lambda_I \rightarrow \infty$ ,  $f(v) = 0$  becomes  $v - 1 = 0$ . Then  $\tilde{n}_0$  and  $\tilde{p}_0$  values may be obtained from (A22) or (A22') with  $v = v_s = 1$ .

*c. Extrinsic conduction—donors or acceptors present.* Here either  $\tilde{N}_A^0 = 0$  and  $\tilde{N}_D^0 > 0$  or  $\tilde{N}_A^0 > 0$  and  $\tilde{N}_D^0 = 0$ . Equations (A21) may then be combined to yield the cubic (involving the particular  $j$  value for which  $\tilde{N}_j^0 > 0$ )

$$\begin{aligned} \tilde{y}_{j0}^3 + (\Lambda_I + \Lambda_j) \tilde{y}_{j0}^2 - [1 + \Lambda_I + \Lambda_j \tilde{N}_j^0 - \Lambda_I \Lambda_j] \tilde{y}_{j0} \\ = \Lambda_j [1 + \Lambda_I(1 + \tilde{N}_j^0)]. \end{aligned} \quad (\text{A25})$$

Note that if, for example,  $\tilde{N}_D^0 > 0$ ,  $\tilde{n}_0$  may be obtained from the solution of (A25) and  $\tilde{p}_0$  from  $(1 + \Lambda_I)/(\Lambda_I + \tilde{n}_0)$ , following from (A21). It usually turns out to be simpler, however, to use the general solution of Sec. A. II. 2 in these cases.

*d. Extrinsic conduction—full extrinsic dissociation.* Here,  $\Lambda_j \rightarrow \infty$  and  $\tilde{N}_{j0}^+ = \tilde{N}_j^0$ . Again a quadratic must be solved and Eq. (A23) may again be used. Let

$$\eta_F \equiv (\tilde{N}_D^0 + \tilde{N}_A^0)/2, \quad (\text{A26})$$

$$\chi_F \equiv (\tilde{N}_D^0 - \tilde{N}_A^0)/2, \quad (\text{A27})$$

and

$$\phi_F \equiv [(1 + 0.5\Lambda_I)^2 + \Lambda_I\eta_F + \chi_F^2]^{1/2}. \quad (\text{A28})$$

Then one obtains from (A21),

$$\tilde{p}_0 = 1 - \chi_F + \frac{\Lambda_I\eta_F + \chi_F^2}{1 + 0.5\Lambda_I + \phi_F} \quad (\text{A29})$$

for  $\chi_F < 0$ , and

$$\tilde{p}_0 = \frac{1 + \Lambda_I(1 + \tilde{N}_A^0)}{\chi_F + 0.5\Lambda_I + \phi_F} \quad (\text{A29}')$$

for  $\chi_F \geq 0$ . Finally,  $\tilde{n}_0$  may be found from the electro-neutrality condition [Eq. (A8)] in the form

$$\tilde{n}_0 = \tilde{p}_0 + 2\chi_F. \quad (\text{A8}')$$

*e. Complete compensation.* The compensation condition is  $\tilde{N}_{10}^+ = \tilde{N}_{20}^+$ , leading to  $\tilde{y}_{10} = \tilde{y}_{20} \equiv \tilde{y}_{c0}$  from Eq. (A8) with  $\pi_\pm = 1$ , and to  $[\Lambda_1 \tilde{N}_1^0 / (\Lambda_1 + \tilde{y}_{c0})] = [\Lambda_2 \tilde{N}_2^0 / (\Lambda_2 + \tilde{y}_{c0})]$  from (A20). The solution of this equation for full extrinsic dissociation is  $\tilde{N}_1^0 = \tilde{N}_2^0 \equiv \tilde{N}_c^0$ . Equation (A21) then leads to

$$\tilde{y}_{c0} \equiv \tilde{n}_0 \equiv \tilde{p}_0 = - \left( \frac{\Lambda_I}{2} \right) + \left[ \left( \frac{\Lambda_I}{2} \right)^2 + 1 + \Lambda_I(1 + \tilde{N}_c^0) \right]^{1/2}, \quad (\text{A30})$$

appropriate for  $\Lambda_I < 1$ , and

$$\tilde{y}_{c0} = \frac{1 + \Lambda_I(1 + \tilde{N}_c^0)}{\left( \frac{\Lambda_I}{2} \right) + \left[ \left( \frac{\Lambda_I}{2} \right)^2 + 1 + \Lambda_I(1 + \tilde{N}_c^0) \right]^{1/2}}, \quad (\text{A30}')$$

appropriate for  $\Lambda_I \geq 1$ . Thus we see that, surprisingly, only when  $\Lambda_I(1 + \tilde{N}_c^0) \ll 1$  does a perfectly compensated material in which donors and acceptors are fully dissociated exhibit the pure intrinsic concentrations  $n_0 = p_0 = c_{j0}$ . In fact, for  $[1 + \Lambda_I(1 + \tilde{N}_c^0)] \gg (\Lambda_I/2)^2$ ,  $\tilde{y}_{c0} \approx [1 + \Lambda_I(1 + \tilde{N}_c^0)]^{1/2}$ , which will be much larger than unity for large enough  $\tilde{N}_c^0$ .

When the extrinsic charges are not fully dissociated, it turns out that exact compensation requires both  $\tilde{N}_1^0 = \tilde{N}_2^0 \equiv \tilde{N}_c^0$  and  $\Lambda_1 = \Lambda_2 \equiv \Lambda_c$ . Then  $\tilde{y}_{c0}$  can be obtained directly by solving the cubic following from Eq. (A21) or, more simply, by solving for  $v$  in  $f(v) = 0$ . Again  $\tilde{y}_{c0}$  will generally not be unity even with perfect compensation. If  $\tilde{N}_{10}^+$  is set equal to  $\tilde{N}_{20}^+$  without requiring that both  $\tilde{N}_1^0 = \tilde{N}_2^0$  and  $\Lambda_1 = \Lambda_2$  hold, one obtains a simple expression

for  $\tilde{y}_{c0}$ . But this expression, which is independent of  $\Lambda_I$ , is inconsistent with that following from Eq. (A21) in the present case. Thus both  $\tilde{N}_{j0}$  and  $\Lambda_j$  equations must hold simultaneously for compensation to be exact. One may therefore conclude that when either donors or acceptors or both are not fully dissociated, as a practical matter it will be impossible to achieve perfect compensation even at a single temperature.

### III. Solubility product equilibrium ( $\Lambda_j \rightarrow 0$ limit)

When the charge carrier concentrations obey the solubility product law (82) rather than the intrinsic center dissociation/association equilibrium expression (A9), a somewhat different approach is required. Formally, the present case is the limit of (A9') as  $\Lambda_I \rightarrow 0$  and  $\tilde{N}_I^0 \rightarrow \infty$  while  $\Lambda_I \tilde{N}_I^0 = 1$ , but since Eqs. (A6) and (A7) no longer apply, the procedure of Part II is not generally useful here. On replacing (A6), (A7) and (A9) by the single solubility product expression (82), normalizing variables, and eliminating  $\tilde{N}_{j0}^*$ , one obtains the usual electroneutrality condition

$$\tilde{p}_0 - \frac{\Lambda_A \tilde{N}_A^0}{\tilde{p}_0 + \Lambda_A} = \tilde{n}_0 - \frac{\Lambda_D \tilde{N}_D^0}{\tilde{n}_0 + \Lambda_D}, \quad (\text{A31})$$

which may be solved together with  $\tilde{n}_0 \tilde{p}_0 = 1$  by conventional iterative techniques.

An interesting special case is that of complete extrinsic dissociation, for which  $\Lambda_A \rightarrow \infty$  and  $\Lambda_D \rightarrow \infty$ . In this situation, specific values of  $\tilde{n}_0$  and  $\tilde{p}_0$  may be found using the above results or from Eqs. (A29) or (A29') and (A8') with  $\Lambda_I = 0$ , in agreement with expressions presented earlier<sup>6</sup> by one of us.

## APPENDIX B: SMALL-SIGNAL ac EQUATIONS

### I. DERIVATION OF THE $[a_{jm}]$ MATRIX

When one uses the notation of Appendix A, the incremental parts of Eqs. (4)–(9) become

$$i\omega N_{Ii} = -k_{Ie} N_{Ii} + k_{Ir}(n_0 p_i + p_0 n_i), \quad (\text{B1})$$

$$i\omega N_{ji} = -k_{je} N_{ji} + k_{jr}(N_{j0}^* y_{ji} + y_{j0} N_{ji}^*), \quad (\text{B2})$$

$$i\omega y_{ji} = -i\omega(N_{Ii} + N_{ji}) + \mu_j [(-1)^j y_{j0} E_i' + (kT/e z_j) y_{ji}^*], \quad (\text{B3})$$

and

$$E_i' = (4\pi e/\epsilon) [z_1(p_i - N_{1i}^*) - z_2(n_i - N_{2i}^*)], \quad (\text{B4})$$

where superscript primes denote differentiation with respect to  $x$ , and  $j=1,2$ . Equations (B1) and (B2) may be rewritten as

$$N_{Ii} = c_{I0}^{-1} h_I (n_0 p_i + p_0 n_i), \quad (\text{B1}')$$

and

$$N_{ji} = -N_{ji}^* = h_j y_{ji}, \quad (\text{B2}')$$

where

$$h_I \equiv (\Lambda_I + i\Omega \xi_I)^{-1}, \quad (\text{B5})$$

$$h_j \equiv \left( \frac{\Lambda_j \tilde{N}_j^0}{\Lambda_j + i\Omega \xi_j + \tilde{y}_{j0}} \right) \left( \frac{1}{\Lambda_j + i\Omega \xi_j + \tilde{y}_{j0}} \right), \quad (\text{B6})$$

and  $\Omega \equiv \omega \tau_D$ . Since  $h_j$  only involves  $y_{j0}$  in the  $\pi_x = 1$ , partial-dissociation case,  $c_{I0}$  has been used here to define  $\tilde{y}_{j0}$  with no loss in generality. The  $\xi$ 's are ratios of relaxation times, given by

$$\xi_I \equiv (\tau_D k_{Ir} c_{I0})^{-1} \equiv \tau_I / \tau_D, \quad (\text{B7})$$

and

$$\xi_j \equiv (\tau_D k_{jr} c_{I0})^{-1} \equiv \tau_j / \tau_D, \quad (\text{B8})$$

where  $\tau_D \equiv R_\infty C_g$  is the dielectric relaxation time of the bulk material.

One may now eliminate  $N_{Ii}$ ,  $N_{ji}$ , and  $E_i'$  from Eq. (B3) using (B1'), (B2'), and (B4). Further,  $N_{j0}^*$  may be eliminated using (A20). Now if we let  $X \equiv x/L_D$  and  $Y_{ji} \equiv y_{ji}/z_j y_{j0}$ , Eq. (B3) may be rewritten as

$$\begin{aligned} \frac{d^2 Y_{ji}}{dX^2} = & \delta_j [(1 + h_j) Y_{ji} - (z_k/z_j)^2 (1 + h_k) (y_{k0}/y_{j0}) Y_{ki}] \\ & + (i\Omega \lambda_j) \{ [1 + h_j + h_I (y_{k0}/c_{I0})] Y_{ji} \\ & + [h_I (z_k/z_j) (y_{k0}/c_{I0})] Y_{ki} \}, \end{aligned} \quad (\text{B9})$$

which can finally be put in the form

$$\frac{d^2 Y_{ji}}{dX^2} = a_{jm} Y_{mi}, \quad (\text{B9}')$$

where  $j=1,2$ ,  $m=1,2$ , and the dimensionless  $[a_{jm}]$  matrix involves only bulk properties of the material such as  $G/R$  rate constants.  $[a_{jm}]$  and its eigenvalues are of central importance in the calculation of  $Z_{TN}$ . Its components may be written as

$$a_{11} \equiv \Delta_1 + i\Omega(\lambda_{e1} + \epsilon_2 f_I), \quad (\text{B10})$$

$$a_{12} \equiv -\Delta_2 + i\Omega \epsilon_2 f_I, \quad (\text{B11})$$

$$a_{21} \equiv -\Delta_1 + i\Omega \epsilon_1 f_I, \quad (\text{B12})$$

and

$$a_{22} \equiv \Delta_2 + i\Omega(\lambda_{e2} + \epsilon_1 f_I), \quad (\text{B13})$$

where

$$\Delta_j \equiv \delta_j (1 + h_j), \quad (\text{B14})$$

$$\lambda_{ej} \equiv \delta_j / \epsilon_j, \quad (\text{B15})$$

and

$$f_I \equiv 2\phi b h_I. \quad (\text{B16})$$

In arriving at these results,  $\pi_x$  was taken unity in all terms which disappear in the limit of full dissociation. Thus, since  $h_I \rightarrow 0$  as  $\Lambda_I \rightarrow \infty$ , we can write, for example,  $\lambda_1 h_I (n_0/c_{I0}) = \lambda_1 h_I \tilde{n}_0 = \epsilon_2 f_I$ . Note that in the absence of extrinsic recombination ( $h_j = 0$ ),  $\Delta_j = \delta_j$  and  $\lambda_{ej} = \lambda_j$ . Similarly, when intrinsic centers are fully dissociated,  $f_I = 0$ . The  $a_{jm}$  expressions do not, however, assume  $\pi_x = 1$  in the full intrinsic-extrinsic dissociation limit since  $\pi_x$  appears explicitly in the  $\epsilon_j$  and  $\delta_j$  terms remaining in this limit.

### II. EIGENVALUES

Although the expressions for the  $a_{jm}$  elements derived in the last section are far more general than those given earlier<sup>6</sup> which neglect dynamic  $G/R$  effects, we shall try to maintain maximum generality by dealing as far as

possible with the general  $a_{jm}$  symbols rather than the specific expressions given in Eqs. (B10) to (B13). The eigenvalue equation for  $[a_{jm}]$  leads to the  $\theta_j^2$  eigenvalues satisfying

$$\theta_j^4 - (a_{11} + a_{22})\theta_j^2 + (a_{11}a_{22} - a_{12}a_{21}) = 0. \quad (\text{B17})$$

Root relations immediately yield the useful exact results

$$\theta_1^2 + \theta_2^2 = a_{11} + a_{22} \equiv B, \quad (\text{B18})$$

and

$$\theta_1^2 \theta_2^2 = a_{11}a_{22} - a_{12}a_{21} \equiv A/4. \quad (\text{B19})$$

Equation (B18) may be rewritten as

$$(\theta_1^2 - a_{11}) = -(\theta_2^2 - a_{22}), \quad (\text{B18}')$$

and

$$(\theta_1^2 - a_{22}) = -(\theta_2^2 - a_{11}), \quad (\text{B18}'')$$

expressions useful in later developments of the present work.

The solution of (B17) may be written

$$\theta_j^2 = 0.5[B + (-1)^{j+1}(B^2 - A)^{1/2}]. \quad (\text{B20})$$

It follows that

$$(B^2 - A)^{1/2} = \theta_1^2 - \theta_2^2. \quad (\text{B21})$$

The assignment of the 1 and 2 subscripts to the plus and minus solutions is arbitrary here but the particular choice above will be maintained throughout. In order to avoid the possibility of a small difference between large numbers, Eq. (A23) may be applied to (B20), yielding, for example,  $\theta_2^2 = 0.5A/[B + (B^2 - A)^{1/2}]$ . It turns out to be desirable to reduce this expression even further. To do so, one may apply the relation

$$[B + (B^2 - A)^{1/2}]^{-1} = (2B)^{-1} [1 + \{A/[B + (B^2 - A)^{1/2}]\}^2], \quad (\text{B22})$$

leading to

$$\theta_2^2 = \left(\frac{A}{4B}\right) \left[1 + \frac{A}{\{B + (B^2 - A)^{1/2}\}^2}\right]. \quad (\text{B23})$$

Once  $\theta_2^2$  is calculated,  $\theta_1^2$  may be obtained from

$$\theta_1^2 = B - \theta_2^2. \quad (\text{B18}')$$

When  $|B/A| \gg 1$ ,  $|\theta_2^2| \ll 1$  and  $\theta_1^2$  approaches  $B$ .

When one substitutes Eqs. (B10) to (B13) in (B18) and (B19), the following results are obtained after simplification:

$$A = 4i\Omega\psi(b_e + u_e f_I), \quad (\text{B24})$$

$$B = u_e + i\Omega(d_e + f_I), \quad (\text{B25})$$

where

$$\psi \equiv 1 + i\Omega, \quad b_e \equiv \lambda_{e1}\lambda_{e2}, \quad (\text{B26})$$

and

$$u_e \equiv \Delta_1 + \Delta_2, \quad d_e \equiv \lambda_{e1} + \lambda_{e2}. \quad (\text{B27})$$

In the absence of extrinsic recombination (either because  $\Lambda_j^{-1}$  or  $\bar{N}_j^0$  ( $j = 1, 2$ ) are zero),  $b_e = b$ ,  $d_e = d$  and  $u_e = 1$ .

Further, as  $\Omega \rightarrow 0$ ,  $\theta_2^2$  is proportional to  $i\Omega$  and the limiting value of  $\theta_1^2$  is a constant (see Appendix C).

In addition to  $\theta_j^2$ , we shall also need

$$\gamma_j \equiv (M\theta_j) \coth(M\theta_j), \quad (\text{B28})$$

and

$$t_j \equiv \gamma_j - 1. \quad (\text{B29})$$

Since  $M\theta_2 \rightarrow 0$  as  $\Omega \rightarrow 0$ ,  $t_2 \rightarrow (M^2\theta_2^2/3) - [(M^2\theta_2^2)^2/45] \dots$  in this limit.

### III. ADMITTANCE DERIVATION AND SIMPLIFICATION

The general method of solution of the basic equations has already been discussed in detail<sup>6</sup> and need not be repeated. It leads to the following expression for

$$Y_{2N} \equiv Y_{TN}\psi \equiv -2Q_s/D_2. \quad (\text{B30})$$

The formal expression for  $Q_s$  given earlier<sup>6</sup> is still applicable when one uses the present more general expressions for the  $a_{jm}$  and remembers that  $\rho_j \equiv r_j/2$  may be complex here. The  $D_2$  term requires minor modifications, however. First, redefine the earlier  $c_j$  and  $f_j$  as follows:  $c_j \equiv C_{kj}$  and  $f_j \equiv f_{kj} \equiv 1 + C_{kj}$ , where as usual,  $j$  and  $k$  must always differ. Then

$$C_{kj} \equiv a_{kj}^{-1}(\theta_k^2 - a_{kk}), \quad (\text{B31})$$

which can be rewritten, using (B18), as  $C_{kj} = a_{kj}^{-1}(a_{jj} - \theta_j^2)$ , and, using (B17), as  $a_{jk}/(\theta_k^2 - a_{jj})$ . It follows from the above results that

$$a_{kj}C_{kj} = -a_{jk}C_{jk}, \quad (\text{B32})$$

which must replace the  $\delta_k c_k = -\delta_j c_j$  relation used in the earlier work, a result to which it reduces in the absence of dynamic  $G/R$  effects.

The expression for  $e_j$ , appearing in  $D_2$  of the earlier work, now becomes  $e_j \equiv 1 - C_{jk} = 1 - C_{jk} - 2\theta_j^2 H_{jk}$ , where  $H_{jk} \equiv \Delta_j - \Delta_k C_{jk}$ . Replace  $f_3 \equiv 1 - c_1 c_2$  of the earlier analysis by

$$f_s \equiv 1 - C_{12}C_{21} \equiv \frac{\theta_1^2 - \theta_2^2}{\theta_1^2 - a_{kk}}, \quad (\text{B33})$$

where a subscript "s" will be employed to indicate quantities independent of the permutation of 1 and 2 subscripts.

Since the desired  $Y_{sN} \equiv -(1 + Z_{2N})$ , we may now use (B30) with the corrected  $D_2$  to obtain, after considerable algebra,

$$Y_{sN} = \frac{D_2 - 2Q_s}{2Q_s} = \frac{h_s + Y_{MN}}{g_s + N_s}, \quad (\text{B34})$$

where

$$h_s \equiv \rho_1 \rho_2 + \epsilon_1 \rho_1 + \epsilon_2 \rho_2, \quad (\text{B35})$$

$$g_s \equiv 1 + \rho_s \equiv 1 + \epsilon_1 \rho_2 + \epsilon_2 \rho_1, \quad (\text{B36})$$

and

$$N_s \equiv f_s^{-1} \sum_{j=1}^2 f_{jk}(1 - f_{kj}\epsilon_j)t_j. \quad (\text{B37})$$

In the presence of specific adsorption or surface states,  $\rho_j$  is complex. When adsorbed species either do not

react further at all (pure adsorption) or subsequently react to form a neutral species maintained at constant concentration, only a single adsorption relaxation time,  $\tau_a$ , is involved for each adsorbing species.<sup>7,14</sup> This simplest situation is the only one which will be explicitly considered here. Let  $\xi_{ja} \equiv \tau_{ja}/\tau_D$ . Then

$$\rho_j \equiv \frac{\rho_{j0} + i\Omega \xi_{ja} \rho_{j\infty}}{1 + i\Omega \xi_{ja}}, \quad (\text{B38})$$

where  $\rho_{j0}$  and  $\rho_{j\infty}$  are real constants and  $\rho_j$  is thus real and frequency independent when  $\rho_{j0} = \rho_{j\infty}$ .

The normalized admittance  $Y_{MN}$  is more complicated. It can be written as

$$Y_{MN} \equiv G_s + \sum_{j=1}^2 G_{jk} t_j, \quad (\text{B39})$$

where

$$G_s \equiv M_s t_1 t_2 - N_s, \quad (\text{B40})$$

and

$$G_{jk} \equiv f_s^{-1} [g_{jk} J_{jk} + C_{kj} K_{jk} g_{jl}]. \quad (\text{B41})$$

Here  $g_j \equiv 1 + \rho_j$ ,  $J_{jk} \equiv 1 - \theta_j^{-2} H_{jk}$ , and  $K_{jk} \equiv J_{jk} - f_{jk}$ . Finally,

$$M_s \equiv 1 - f_s^{-1} \sum_{j=1}^2 \theta_j^{-2} H_{jk} f_{kj}. \quad (\text{B42})$$

As the above results show, the full result for  $Y_{sN}$  is still exceptionally complicated, with several hierarchical levels. Further simplification is desirable and possible if one makes extensive use of Eqs. (B17) to (B19) and (B10) to (B13). After much algebra,  $M_s$  reduces greatly and becomes just

$$M_s \equiv i\Omega \psi^{-1} \equiv [1 + (i\Omega)^{-1}]^{-1}. \quad (\text{B42}')$$

Similarly,  $N_s$  reduces to

$$N_s \equiv I_{12} [(\theta_1^2 - u_e \psi) t_1 - (\theta_2^2 - u_e \psi) t_2], \quad (\text{B37}')$$

where  $I_{12} \equiv (\theta_1^2 - \theta_2^2)^{-1}$ . The quantity  $N_s + 1$  is given by the above expression with  $t_j \rightarrow \gamma_j$ . Now let

$$Y_{MN} \equiv Y_{MN}^0 + Y_{MN}^1, \quad (\text{B43})$$

where  $Y_{MN}^0$  is the completely blocking ( $\rho_j = 0$ ) limit of  $Y_{MN}$ . One finds

$$Y_{MN}^0 \equiv (i\Omega \psi^{-1} I_{12}) [\Gamma_{12}^{-1} t_1 t_2 + (\theta_1^2 - u_e \psi) t_2 - (\theta_2^2 - u_e \psi) t_1]. \quad (\text{B44})$$

Finally,  $Y_{MN}^1$  may be written

$$Y_{MN}^1 \equiv (\psi^{-1} I_{12}) \sum_{j=1}^2 W_j t_j, \quad (\text{B45})$$

where

$$W_j \equiv \sum_{m=1}^2 \rho_m P_{jm}, \quad (\text{B46})$$

and

$$P_{j1} \equiv (\epsilon_1 + i\Omega)(\theta_1^2 - a_{jj}) + (-1)^{j+1} \epsilon_1 a_{12}, \quad (\text{B47})$$

$$P_{j2} \equiv (\epsilon_2 + i\Omega)(\theta_1^2 - a_{kk}) + (-1)^{j+1} \epsilon_2 a_{21}. \quad (\text{B48})$$

Since it turns out that as  $\Omega \rightarrow 0$ ,  $Y_{MN}$  and  $N_s \rightarrow 0$ ,

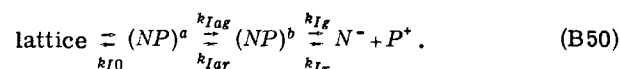
$$Z_{sN0} \equiv \frac{g_{s0}}{h_{s0}} = \frac{1 + \epsilon_1 \rho_{20} + \epsilon_2 \rho_{10}}{\rho_{10} \rho_{20} + \epsilon_1 \rho_{10} + \epsilon_2 \rho_{20}}, \quad (\text{B49})$$

in agreement with  $(R_{DN} - 1)$  calculated from (25).

#### IV. TREATMENT OF "STRUCTURED" INTRINSIC AND IMPURITY NEUTRAL CENTERS

The present small-signal formalism may readily be generalized to include the possibility that intrinsic and extrinsic neutral centers exist in more than one form, i.e., changes in the structure of the neutral centers can occur without dissociation which leads to mobile charge carriers. We will then be able to distinguish between situations in which these changes will have a significant effect on small-signal response and those in which they will not.

To illustrate how the generalization is achieved we consider a Schottky or Frenkel defect conductor in which bound charge carrier pairs can exist in two forms,  $(NP)^a$  and  $(NP)^b$ , differing in the separation of the charges, which take part in the reaction sequence



The rate laws governing  $N_{Ib} \equiv [(NP)^b]$  and  $N_{Ia} \equiv [(NP)^a]$  are thus

$$\left(\frac{\partial N_{Ib}}{\partial t}\right) = -(k_{Irg} + k_{Iar})N_{Ib} + k_{Ir}np + k_{Iag}N_{Ia} \quad (\text{B51})$$

and

$$\left(\frac{\partial N_{Ia}}{\partial t}\right) = -(k_{Iag} + k_{Ia0})N_{Ia} + k_{Iar}N_{Ib} + k_{Ia0}N_{Ia0}. \quad (\text{B52})$$

It has been here assumed that the rate of formation of  $(NP)^a$  from the unperturbed lattice is  $k_{Ia0}(N_{Ia0} - N_{Ia})$ , an approximation valid for low imperfection densities. The ratio  $k_{Iag}/k_{Iar}$  is taken to be finite and nonzero and we set  $k_{Ia0} = 0$  in the Schottky case.

For small-signal ac conditions we define the incremental quantities  $N_{Iai}$  and  $N_{Ibi}$  by  $N_{Iai} \equiv N_{Ia0} + N_{Iai} \exp(i\omega t)$  and  $N_{Ib} \equiv N_{Ib0} + N_{Ibi} \exp(i\omega t)$  and write the small-signal equations

$$i\omega N_{Ibi} = -(k_{Irg} + k_{Iar})N_{Ibi} + k_{Ir}(n_0 p_0 + p_0 n_i) + k_{Iag}N_{Iai}, \quad (\text{B53})$$

and

$$i\omega N_{Iai} = -(k_{Iag} + k_{Ia0})N_{Iai} + k_{Iar}N_{Ibi}. \quad (\text{B54})$$

In the present case it is also necessary to replace Eq. (B1) by

$$i\omega N_{It} = -k_{Irg}N_{Ibi} + k_{Ir}(n_0 p_0 + p_0 n_i), \quad (\text{B1A})$$

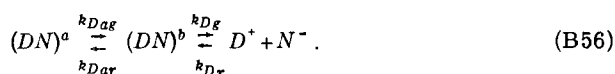
so that  $N_{It}$  is the net incremental rate at which the charge carriers recombine. After eliminating  $N_{Iai}$  and  $N_{Ibi}$  from the above three equations one obtains Eq. (B1') with

$$h_I \equiv \frac{1}{i\Omega \xi_I} \left[ \frac{(1 + i\Omega \xi_{Ib} - k_{Irg}\tau_{Ib})(1 + i\Omega \xi_{Ia}) - k_{Iag}k_{Iar}\tau_{Ia}\tau_{Ib}}{(1 + i\Omega \xi_{Ia})(1 + i\Omega \xi_{Ib}) - k_{Iag}k_{Iar}\tau_{Ia}\tau_{Ib}} \right], \quad (\text{B55})$$

where  $\tau_{Ia} \equiv (k_{Iag} + k_{Ia0})^{-1}$ ,  $\tau_{Ib} \equiv (k_{Irg} + k_{Iar})^{-1}$ ,  $\xi_{Ia} \equiv \tau_{Ia}/\tau_D$ , and  $\xi_{Ib} \equiv \tau_{Ib}/\tau_D$ . When only a single step in the reaction sequence (B50) is significant on the time scale of a half cycle of the lowest frequency applied signal,  $h_I$  reduces to the form of Eq. (B5). If  $k_{Ia0}$ ,  $k_{Iar}$ , and  $k_{Iag}$  are all much smaller than  $\omega$  so that the significant step is the

formation and dissociation of  $(NP)^b$ , Eq. (B5) itself applies. If  $k_{Iag}$  and  $k_{Iar}$  are both much larger than  $\omega$  and  $k_{Ig}$ , while  $k_{I0} \ll \omega$ , the significant step is again the formation and dissociation of  $(NP)^b$ , but with a quasi-equilibrium established between  $(NP)^a$  and  $(NP)^b$ . In this case the form of Eq. (B5) is again obtained but with  $\Lambda_I$  replaced by  $k_{Iag}k_{Ig}/[(k_{Iag}+k_{Iar})k_{Irc}c_{I0}] = \Lambda_I N_{Ib0}/(N_{Ia0}+N_{Ib0})$ . Finally, for Frenkel defects it is conceivable that  $k_{Iag}$ ,  $k_{Iar}$ , and  $k_{Ig}$  all might be much larger than both  $\omega$  and  $k_{I0}$ , so that the significant process is spontaneous defect formation from the unperturbed lattice. In this case one obtains the form of Eq. (B5) with  $\Lambda_I$  negligible [see discussions following Eq. (108)] and  $\xi_I$  replaced by  $k_{Iag}k_{Ig}/\tau_{DC}c_{I0}k_{Irc}k_{I0}$ .

We illustrate the treatment of extrinsic neutral centers for the donor case (the acceptor case is precisely analogous) again assuming two forms of neutral complex differing in charge separation and consider the reaction sequence



We define  $N_{Da} \equiv [(DN)^a]$ ,  $N_{Db} \equiv [(DN)^b]$ , and  $N_D \equiv N_{Da} + N_{Db}$ . Conservation of chemical species ensures that  $N_D^0 \equiv N_D + N_D^+$  is constant. When one writes the small-signal equations governing  $N_{Di}$ ,  $N_{Dai}$ , and  $N_{Dbi}$  and eliminates the latter two variables, one obtains Eq. (B2') with

$$h_D \equiv \left( \frac{\Lambda_D \tilde{N}_D^0}{\Lambda_D + \tilde{n}_0} \right) \times \frac{[\tau_{Da}(1 - k_{Dg}\tau_{Db}) + \tau_{Db}(1 + i\Omega\xi_{Da})]}{(\tilde{n}_0 + i\Omega\xi_D)[\tau_{Db}(1 + i\Omega\xi_{Da}) + \tau_{Da}] + k_{Dg}\tau_{Db}(\xi_D - \tilde{n}_0\xi_{Da})\tau_D}, \quad (B57)$$

where  $\tau_{Da} \equiv k_{Dag}^{-1}$ ,  $\tau_{Db} \equiv (k_{Dg} + k_{Dar})^{-1}$ ,  $\xi_{Da} \equiv \tau_{Da}/\tau_D$ , and  $\xi_{Db} \equiv \tau_{Db}/\tau_D$ . For  $k_{Dar} \ll k_{Dg}$  or for  $k_{Dar} \gg k_{Dg}$  and  $k_{Dag} \gg \omega$ , this result reduces to the form of Eq. (B6).

## V. INTRINSIC G/R EFFECTS AT $\Omega = 0$

Examination of Eqs. (B1'), (B2'), and (B9) indicates that when  $i\Omega h_I$  vanishes in the  $\Omega \rightarrow 0$  limit, intrinsic G/R effects are absent in this limiting case. If  $\Lambda_I$  is set equal to zero in (B5), as may be appropriate for electronic semiconductors<sup>11</sup> and in simple models for Frenkel defect materials (see Sec. V),  $i\Omega h_I$  remains nonzero as  $\Omega \rightarrow 0$ , and intrinsic G/R effects will be present and will be reflected in the values of  $R_{TN0}$  and  $C_{PN0}$ . From the more general treatment of the last section we have as  $\Omega \rightarrow 0$

$$i\Omega h_I \rightarrow \frac{k_{I0}k_{Iar}\xi_I^{-1}}{k_{Iag}k_{Ig} + k_{I0}(k_{Ig} + k_{Iar})}, \quad (B58)$$

an expression which vanishes if  $k_{I0} = 0$ . A simple physical interpretation may be given for these results: If intrinsic charge carrier recombination leads only to the formation of neutral centers, G/R effects will be absent for  $\Omega = 0$  since the concentration of the neutral centers must be constant in the  $\Omega = 0$  steady state. If however the charge carriers can in effect annihilate each other (either directly or after forming bound complexes), as is the case for electron-hole and vacancy-interstitial

recombination, this process can occur at a nonzero rate even under dc steady-state conditions.

## APPENDIX C: EXPANSION TO FIRST ORDER IN $\Omega$

Here we list quantities expanded to first order in  $\Omega$ , i.e.,  $Y(\Omega) = Y_0 + i\Omega Y_f + \dots$ , as  $Y: Y_0; Y_f$ . Where first-order terms are not needed, only  $\Omega \rightarrow 0$  values will be given.

$$\begin{aligned} \rho_j: & \rho_{j0}; \xi_{ja}\rho_{jm} \\ \rho_s: & (\epsilon_1\rho_{20} + \epsilon_2\rho_{10}); (\epsilon_1\rho_{2f} + \epsilon_2\rho_{1f}) \\ g_j: & (1 + \rho_{j0}); \rho_{jf} \\ g_s: & (1 + \rho_{s0}); \rho_{sf} \\ h_s: & (\rho_{10}\rho_{20} + \epsilon_1\rho_{10} + \epsilon_2\rho_{20}); [\rho_{1f}(\epsilon_1 + \rho_{20}) + \rho_{2f}(\epsilon_2 + \rho_{10})] \\ h_j: & [\Lambda_j\tilde{N}_j^0/(\Lambda_j + y_{j0})^2]; [-\xi_j h_{j0}/(\Lambda_j + \tilde{y}_{j0})] \\ h_I: & \Lambda_I^{-1} \equiv \tilde{N}_I^0 - 1; -\xi_I h_{I0}^0 \\ f_I: & 2\phi b \Lambda_I^{-1}; 2\phi b h_{If} \\ \Delta_j: & \delta_2(1 + h_{j0}); \delta_j h_{jf} \\ u_e: & (\Delta_{10} + \Delta_{20}); (\Delta_{1f} + \Delta_{2f}) \\ u_e\psi: & u_{e0}; (u_{e0} + u_{ef}) \\ \lambda_e: & \epsilon_j^{-1}\Delta_{j0}; \lambda_j h_{jf} \\ b_e: & \Delta_{10}\Delta_{20}/\epsilon_1\epsilon_2; (\Delta_{10}\Delta_{2f} + \Delta_{20}\Delta_{1f})/\epsilon_1\epsilon_2 \\ c_e: & (\lambda_{e20} - \lambda_{e10}); (\lambda_{e2f} - \lambda_{e1f}) \\ d_e: & (\lambda_{e10} + \lambda_{e20}); (\lambda_{e1f} + \lambda_{e2f}) \\ a_{jf}: & \Delta_{j0}; (\Delta_{jf} + \lambda_{ej0} + \epsilon_k f_{I0}) \\ a_{jk}: & -\Delta_{k0}; (\epsilon_k f_{I0} - \Delta_{kf}) \\ A: & 0; 4(b_{e0} + u_{e0} f_{I0}) \\ B: & u_{e0}; (u_{ef} + d_{e0} + f_{I0}) \\ (A/4B): & 0; (u_{e0}^{-1} b_{e0} + f_{I0}) \\ \theta_1^2: & u_{e0}; [u_{ef} + u_{e0}^{-1}(\Delta_{10}\lambda_{e10} + \Delta_{20}\lambda_{e20})] \\ \theta_2^2: & 0; (u_{e0}^{-1} b_{e0} + f_{I0}) \\ (\theta_1^2 - u_e\psi): & 0; u_{e0}^{-1}\epsilon_1\epsilon_2 c_{e0}^2 \\ (\theta_2^2 - u_e\psi): & -u_{e0}; u_{e0}^{-1} b_{e0} + f_{I0} - (u_{e0} + u_{ef}) \\ q: & \text{Equation (73)} \\ \theta_1: & \sqrt{u_{e0}}; (\theta_1^2)_f/2\sqrt{u_{e0}} \\ \theta_2: & \text{Equal real and imaginary terms involving } \sqrt{\Omega} \\ \coth(Y_0 + i\Omega Y_f): & \coth(Y_0); -Y_f \operatorname{csch}^2(Y_0) \\ \gamma_1: & (M\theta_{10}) \coth(M\theta_{10}); M\theta_{1f} [\coth(M\theta_{10}) - (M\theta_{10}) \operatorname{csch}^2(M\theta_{10})] \\ \gamma_2: & 1; (M^2/3)(u_{e0}^{-1} b_{e0} + f_{I0}) \\ t_1: & [(M\theta_{10}) \coth(M\theta_{10}) - 1]; \gamma_{1f} \\ t_2: & 0; \gamma_{2f} \\ P_{1f}: & 0; u_{e0}^{-1}\Delta_{k0}\lambda_{ek0} \\ p_{2f}: & \epsilon_j u_{e0}; u_{e0}^{-1}\Delta_{j0} [u_{e0} + \epsilon_j(\lambda_{ej0} - \lambda_{ek0}) + \epsilon_j(u_{ef} - f_{I0})] \end{aligned}$$

$$\begin{aligned}
(\theta_1^2 - a_{jj}): & \Delta_{k0}; u_{e0}^{-1} \Delta_{k0} (\lambda_{ek0} - \lambda_{ej0}) + \Delta_{kf} - \epsilon_k f_{I0} \\
(\epsilon_j + i\Omega)(\theta_1^2 - a_{jj}): & \epsilon_j \Delta_{k0}; u_{e0}^{-1} \Delta_{k0} \lambda_{ek0} + \epsilon_j (\Delta_{kf} - \epsilon_k f_{I0}) \\
(\epsilon_k + i\Omega)(\theta_1^2 - a_{jj}): & \epsilon_k \Delta_{k0}; u_{e0}^{-1} \Delta_{k0} [u_{e0} + \epsilon_k (\lambda_{ek0} - \lambda_{ej0})] \\
& + \epsilon_k (\Delta_{kf} - \epsilon_k f_{I0}) \\
W_1: & 0; u_{e0}^{-1} (\rho_{10} \Delta_{20} \lambda_{e20} + \rho_{20} \Delta_{10} \lambda_{e10}) \\
W_2: & u_{e0} (\epsilon_1 \rho_{10} + \epsilon_2 \rho_{20}); u_{e0} (\epsilon_1 \rho_{1f} + \epsilon_2 \rho_{2f}) \\
& + \sum_{j=1}^2 \rho_{j0} [u_{e0}^{-1} \Delta_{j0} \{u_{e0} + \epsilon_j (\lambda_{ej0} - \lambda_{ek0})\} \\
& + \epsilon_j (u_{ef} - f_{I0})] \\
N_s: & 0; u_{e0}^{-2} \epsilon_1 \epsilon_2 C_{e0}^2 t_{10} + \gamma_{2f} \\
Y_{MN}^0: & 0; t_{10} \\
Y_{MN}^1: & 0; u_{e0}^{-1} (W_{1f} t_{10} + W_{20} t_{2f}) \\
Y_{MN}: & 0; (1 + u_{e0}^{-1} W_{1f}) t_{10} + u_{e0}^{-1} W_{20} t_{2f}
\end{aligned}$$

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