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## ABSTRACT

Space charge polarisation is first defined and those aspects of it which will and will not be considered at length are distinguished. Basic equations of charge motion in solids and liquids are discussed for the situation where a single mobility is an adequate approximation for each mobile species. Rather general boundary conditions at the interface between the material of interest and its electrodes are introduced and intrinsic-carrier recombination is considered. Theoretical results are first discussed for quasi-static differential capacitance as a function of applied dc potential, both without and with some account of specific adsorption. Small-signal ac results and analysis methods are then described. After consideration of Maxwell-Wagner interfacial polarisation, the remainder of the paper deals with detailed ac response results for a homogeneous material and shows how bulk, surface reaction, recombination, and diffusion effects may be differentiated and analyzed.

## I. INTRODUCTION

Space-charge polarisation (SCP) is a widely encountered component of the electrical behavior of solids and liquids. In order to define it unambiguously, it is desirable to start with the more general phenomenon of electric polarisation.

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Electric polarisation arises from charge separation. Two kinds of electric polarisation are readily distinguished. Crude1v speaking, dielectric polarisation involves charge separation on an atomic or molecular scale, while SCP is associated with greater separations. Dielectric polarisation  $\vec{P}$  is defined as the dipole moment per unit volume of a material. It may involve both permanent and induced dipoles or either separately.  $\vec{P}$  is usually defined for a homogeneous material or at least for a homogeneous region of macroscopic dimensions of the material. For an isotropic or cubic medium exposed to an applied macroscopic electric field  $\vec{E}$ ,  $\vec{P}$  and  $\vec{E}$  are parallel and one can introduce the scalar  $\chi \equiv \vec{P}/\vec{E}$ , a quantity known as the polarisability or dielectric susceptibility. In CGS-Gaussian units, which will be used herein, the dielectric constant associated with  $\chi$  is  $\varepsilon \equiv 1 + 4\pi\chi$ . It is, properly, an intensive property of the material considered, the same for any region of greater than molecular dimensions and thus independent of sample volume.

One of Maxwell's equations may be expressed as  $\vec{\nabla} \cdot \vec{\mathbf{p}} = 4\pi\rho$ , where  $\vec{\mathbf{D}}$  is the electric displacement, given by  $(\vec{\mathbf{E}} + 4\pi\vec{\mathbf{P}})$ , and  $\rho$ is the net unbalanced charge per unit volume, the local space charge. For a homogeneous material,  $\vec{\nabla}\varepsilon = 0$ , and one obtains the following form of Poisson's equation

$$\vec{\nabla} \cdot \vec{E} = (4\pi/\epsilon)\rho \quad .$$
 (1)

Here all the dielectric polarisation has been subsumed in  $\epsilon$  and the SCP manifested in  $\rho$ . Thus the bulk dielectric properties of the material are accounted for by the intensive quantity  $\epsilon$  which will here be taken, as usual, independent of  $\rho$  and  $\vec{E}$ . The present work will, for simplicity, deal with a homogeneous, isotropic material, usually in a one-dimensional approximation. It will be assumed that all frequency dispersions associated with  $\epsilon$  occur appreciably above all SCP frequencies of interest. This criterion requires that the lowest-frequency dielectric dispersion region occurs appreciably above the radial frequency,  $\omega_{\rm D}$  =  $\tau_{\rm D}^{-1}$ , associated with the dielectric relaxation time of the bulk material,  $\tau_{\rm p}$ .

One might be tempted to conclude from Eq. (1) that SCP only occurs where  $E \neq 0$ . But this is clearly an insufficient condition. Ordinary ohmic current flow, as in a metal, involves  $E \neq 0$  but no significant charge separation. Only when  $\vec{\forall} \cdot \vec{E} \neq 0$ is there net charge separation and thus space charge. But  $\vec{\forall} \cdot \vec{E} \neq 0$  does not occur when  $E \neq 0$  in the bulk region (no electrode effects) of a homogeneous isotropic material held at constant temperature throughout. It is generally the presence of inhomogeneities and/or phase changes within the material or at its surfaces which leads to  $\rho \neq 0$ . Here, I shall primarily be concerned only with homogeneous, isotropic bulk material at constant

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temperature, and thus with SCP associated with surface boundaries and electrode regions. Nevertheless, it will be shown that SCP which arises from surface region discontinuities can under certain circumstances extend throughout the entire region between electrodes of a material of interest. Further, the existence of SCP requires inhomogeneity or discontinuity of a special kind, since in principle ohmic electrodes attached to a homogeneous, isotropic material need generate no SCP even though there is a phase transition at the interface from experimental material to (different) electrode material. From another point of view, if an electrode is reversible (infinitely rapid electrode kinetics) for all current carriers, it will fix the thermodynamic potentials of these carriers<sup>1</sup> and no SCP will occur. Since most SCP of interest arises from boundary phase discontinuities, it is clear that detailed boundary conditions are of crucial importance in determining SCP and its concomitant effects.

The usual experimental arrangement for the investigation of the electrical behavior of solids involves a parallelepiped of material, often in the form of a thin layer, between two plane, parallel, frequently identical electrodes. The electrodes are usually metallic but may sometimes be liquid electrolytes involving one or more of any ionic species which are mobile in the solid. Just as in liquid electrolyte experiments, it is sometimes desirable that all processes of interest be concentrated in the material near one electrode, the working electrode. The boundary parameters (and/or shape) of the other electrode, the indifferent electrode, are then taken so that  $\rho \simeq 0$  in its neighborhood and its influence on the electrical behavior of the system is usually negligible compared to that of the working electrode. Plane, parallel, equal size electrode arrangements are convenient for comparing experimental results with the predictions of theoretical models which approximate the situation by considering only one-dimensional current flow. All quantities herein which are proportional to electrode area, such as capacitance, will be given in specific form, per unit area, but will, nevertheless, usually be referred to as capacitance, conductance, etc.

Current-carrying entities in the electrodes and in the material under investigation may be of a variety of types: electrons and/or holes, positive and/or negative ions, and positive and/or negative defects such as cation vacancies. In addition, immobile charges may be present with which the mobile charge carriers may or may not recombine. In the present work, it will usually be assumed that the electrodes are electronic conductors and that the material being studied is essentially non-electronic, involving a single species of positive and a single species of negative ionic and/or defect charge carrier. Many of the theoretical results to be described are not limited to these conditions, however.

The question of detailed boundary conditions at an electrode is a delicate one still containing much terra incognita. Omitting the possibility of rectification, which will be done throughout this paper, one can distinguish a continuum of possible boundary effects for a given species of current carrier, ranging from complete blocking, through partial blocking, finally to zero blocking, ohmic, or open electrodes. Completely open or reversible electrodes generally involve an extremely large (infinite in the limit) heterogeneous rate constant for the charge species involved. Detailed discussion of electrode-contact characterization for various charge carrier conditions has been given by Kröger<sup>2</sup>. In the present work, the above continuum will be described by means of dimensionless boundary condition parameters, r, and r, for positive and negative mobile charge species, respectively. These parameters may be related to thermally activated heterogeneous rate constants or to surface recombination rates. Although they may sometimes be complex and frequency-dependent in ac situations, such possibilities will not be further considered herein. When  $r_{-} = 0$  for a given positive species at a given electrode, the contact is completely blocking for this species. At the other extreme when  $r = \infty$ , the contact is completely open. It is worth mentioning that complete blocking is an idealized, limiting condition, but one nevertheless that is well approximated in many experimental situations. It requires an infinite potential barrier between electrode and experimental material, which precludes mass transfer either over the barrier or by tunnelling through it. In this limit, the electrode and the material are not in thermodynamic equilibrium, and the electrochemical potential thus need not be the same in both.

Since the subject of SCP is an extremely broad one, it is necessary to limit its scope for the present discussion. First, no further consideration will be given to ordinary dielectric response, although electrical behavior arising from the presence of electric dipoles may often be confused with SCP behavior and <u>vice versa</u>, especially in blocking electrode situations and especially when a distribution of relaxation times is invoked to explain putative dielectric response behavior. Incidentally, it is worth mentioning that the expressions frequently used to describe a distribution of thermally activated relaxation times are inappropriate when applied over a range of temperatures and when the enthalpy involved in the thermally activated dipole behavior is itself distributed<sup>3</sup>.

Second, the present paper will not deal with current injection into insulators leading to space-charge limited currents. One and two carrier injection situations have been discussed quite thoroughly in the past<sup>4-6</sup>. Although the present work does deal with positive and negative carrier injection through the boundary conditions discussed above, it will always involve

situations (which may be semi-insulating) where there is a nonzero bulk-region concentration of positive and negative charge (with  $\rho = 0$ ) in thermal equilibrium under unperturbed conditions. Such a condition is much more applicable to solid state ionics than is the one considered in the conventional space-charge limited current situation, which invariably considers only electron and/or hole injection, usually deals with bulk rather than electrode effects of these injected carriers, and generally ignores intrinsic carrier generation.

Further, no consideration of ordinary transient response will be included. Much useful information can be obtained from charging and discharging measurements at different temperatures<sup>3</sup>. When the system responds in a linear range, however, the same information can be obtained from steady-state frequency response measurements<sup>7,8</sup>. On the other hand, in the nonlinear response region this is no longer the case, and it is inappropriate to derive frequency response results from a Fourier or Laplace transform of transient response results.

Finally, no discussion will be given of the powerful technique of ionic thermoconductivity, also known as thermally stimulated depolarisation<sup>9-11</sup>. This procedure is particularly useful in observing the relaxation of the polarisation of dipoles and/or the release of mobile charge from traps in the material. Neither of these processes is included in the present models, but thermally stimulated depolarisation measurements should certainly be made in parallel with ordinary transient and frequency response measurements whenever possible in order to characterize the system investigated more fully.

There are still many SCP areas of interest not excluded by the above limitations, particularly static and steady state situa-The static, zero-current condition with time-independent tions. electric field applied requires complete blocking of mobile carriers at at least one electrode. SCP can only be inferred under such static conditions by potential (or field) probe techniques. Alternating and direct steady-state non-zero current situations are of more interest because more can generally be learned from Note that a non-zero purely displacement current can flow them. across completely blocking contacts (if the capacitance of the blocking region or layer is non-zero) in response to an impressed alternating potential, since no mass flow between electrode and material is then involved. In steady-state ac and dc situations, any current-induced temperature variation in the material itself and between the bulk material and mobile carriers will be neglected, a particularly good approximation when the carriers are ionic rather than electronic.

The present work deals only with quasi-static and steady-

state conditions. It applies in situations where charge motion may be adequately described by means of mobilities and diffusion coefficients. Thus, certain hopping/percolation processes are excluded<sup>12,13</sup>. Further, it is assumed that the Einstein relation, D<sub>i</sub> = (kT/ez<sub>i</sub>)µ<sub>i</sub>, holds between diffusion coefficient, D<sub>i</sub>, and mobility, µ<sub>i</sub>, of a charge carrier of valence number z<sub>i</sub>. Here k is Boltzmann's constant, T is the absolute temperature, and e is the proton charge. The models to be described also assume that D<sub>i</sub> and µ<sub>i</sub> are independent of field, concentration, and position.

Two other idealizations, which like the above have usually been made in most past calculations, are inherent in the present approach. One is the neglect of all inertial effects of the charge carriers, effects which may tend to make them contribute a negative term to the effective dielectric constant of the material below their plasma frequencies<sup>14</sup>. The present models apply primarily, however, at frequencies so much lower than the plasma frequency that one would expect that other effects would dominate and the present approximation would be quite adequate. For reference, the plasma frequency of Ag ions at a concentration of  $10^{18}$  cm<sup>-3</sup> is of the order of 45 MHz.

A more stringent approximation under certain conditions is the neglect of discreteness-of-charge effects<sup>15,16</sup>, including the finite size of charge carriers such as ions<sup>17</sup>. This approximation may be expected to be weakest when the charges under consideration are completely blocked and when they may be specifically adsorbed at an electrode as well. This matter will be further considered in Section III.

Section II is concerned with the basic equations which describe the idealized situation defined by the above discussion. Then, in Section III the differential SCP capacitance of a system which may involve specific adsorption is considered as a function of dc bias. Section IV is concerned with ac response as a function of frequency in a variety of situations. First, certain aspects of the Maxwell-Wagner theory of interfacial polarisation are discussed; then, some data analysis methods are considered. Finally, Section IV-4 deals with the varieties of frequency response possible when a single species of mobile positive charge and a single species of mobile negative charge are present in a material, the mobilities and valences of the charges are arbitrary, and many different boundary conditions are possible. Because of the restriction to a single species of positive and a single species of negative charge, the situation considered corresponds to the unsupported electrolyte condition in liquid electrolytes, that which leads to maximum space charge.

# II. BASIC EQUATIONS

The basic equations consistent with the discussion of the last section will be given here in one-dimensional form. It will usually be assumed that symmetrical plane, parallel electrodes are placed at x = 0 and x = l. The situation to be considered involves an arbitrary amount of dissociation of intrinsic neutral centers of concentration  $n_{c}(x)$ , which arises from an originally unperturbed, homogeneous, neutral bulk concentration N. It will also be assumed that there may be present a homogeneous concentration,  $N_{D} \equiv N_{D}^{+} - N_{A}^{-}$ , of immobile charged impurity centers associated with extrinsic conduction. Here  $N_D^+$  and  $N_A^-$  are the individual concentrations of charged donor and acceptor centers. I It will be assumed for simplicity that any impurity centers present are fully ionized at all temperatures of interest. Thus, although the treatment may include generation-recombination of intrinsic centers, it takes all extrinsic centers always fully charged. This is equivalent to assuming shallow donor and/or acceptor energy levels and not too low temperatures. When  $N_{1} = 0$ , one deals with intrinsic rather than extrinsic conduction.

Let  $z_p$  and  $z_p$  be the valence numbers of positive and negative charge species of concentrations p and n and mobilities  $\mu_p$  and  $\mu_n.$  The current equation is

$$I = I_{p} + I_{n} + (\varepsilon/4\pi)\frac{\partial E}{\partial t}, \qquad (2)$$

where

$$I_p \equiv ez_p j_p$$
,  $I_n \equiv -ez_n j_n$ , (3)

and

$$\mathbf{j}_{\mathbf{p}} \equiv (\mu_{\mathbf{p}}\mathbf{p}\mathbf{E} - \mathbf{D}_{\mathbf{p}} \frac{\partial \mathbf{p}}{\partial \mathbf{x}}) , \qquad \mathbf{j}_{\mathbf{n}} \equiv -(\mu_{\mathbf{n}}\mathbf{n}\mathbf{E} + \mathbf{D}_{\mathbf{n}} \frac{\partial \mathbf{n}}{\partial \mathbf{x}}) .$$
 (4)

Poisson's equation becomes

$$\frac{\partial E}{\partial x} = (4\pi/\epsilon)\rho , \qquad (5)$$

where

$$\rho \equiv e(z_p p - z_n n + N_e) .$$
 (6)

The material will be taken electrically neutral ( $\rho$  = 0) in its unperturbed bulk region under thermal equilibrium conditions.

Since the field E is related to the electrostatic potential  $\psi$  by E = -(d $\psi/dx$ ), the applied voltage across the electrodes is given by

$$V_{a} = -\int_{0}^{\ell} E(x) dx$$
 (7)

The continuity equations  $^{18}$  may be written in the following generalized form  $^{19}$ 

$$\frac{\partial \mathbf{p}}{\partial t} = -z_{\mathbf{p}\mathbf{L}} \frac{\partial \mathbf{n}_{\mathbf{c}}}{\partial t} - \frac{\partial \mathbf{j}_{\mathbf{p}}}{\partial \mathbf{x}} , \qquad (8)$$

$$\frac{\partial \mathbf{n}}{\partial t} = -\mathbf{z}_{\mathbf{n}\mathbf{L}} \frac{\partial \mathbf{n}_{\mathbf{c}}}{\partial t} - \frac{\partial \mathbf{j}_{\mathbf{n}}}{\partial \mathbf{x}}, \qquad (9)$$

and

$$\frac{\partial n_{c}}{\partial t} = -k_{1}n_{c} + k_{2}(n^{z}nL)(p^{z}pL) .$$
 (10)

In the above,  $k_1$  is a temperature-dependent generation coefficient and  $k_2$  is a recombination coefficient. For generality, it has been assumed that an intrinsic neutral center dissociates into  $z_p$  positive charges each of valence number  $z_p$  and  $z_n$  negative charges of valence number z. The original neutrality of the center then requires that  $z_p z_p = z_n z_n$ . In all the work to be discussed here, whenever intrinsic generation-recombination is considered,  $z_n$  and  $z_n$  will be taken equal and  $z_n z_p z_n$  taken unity in order to avoid<sup>p</sup> the need to consider m-body mass-action recombination with m > 2.

Since one of Maxwell's equations leads directly to the condition  $\vec{\nabla} \cdot \vec{I} = 0$ , the total current (including both conduction and displacement terms) is space invariant at all times even in dynamic situations. This is often a useful condition in the onedimensional case since it allows one to write

$$I = \langle I \rangle \equiv \ell^{-1} \int_{0}^{\ell} I(x) dx$$
 (11)

for the current path x = 0 to x = l. The averaged form of I is often simpler to use in obtaining final results than the original form. Equations (2)-(11), the Einstein relation between  $D_i$ and  $\mu_i$ , and appropriate boundary conditions define the idealized situation considered. Note that no mobile charged aggregates

have been included. Any immobile charged aggregates may be included in N<sub>e</sub>. Some conditions which need to be met for the diffusion terms in Eqs. (4) to be appropriate have been given elsewhere for electronic charge carriers<sup>20</sup>. It should also be noted that models of the present genre are usually limited to conditions which ensure that maximum mobile charge concentrations are small compared to the concentration of intrinsic atomic or ionic sites in the material.

The boundary conditions considered herein are generalized forms of those suggested by Chang and Jaffé<sup>21</sup> which involve the dimensionless r and r parameters already mentioned. Using subscripts "L" and <sup>p</sup>"R" to <sup>n</sup>denote left and right electrodes, one can write these conditions for the conduction current components I and I as

$$I_{pL} = -r_{pL} (ez_{p} D_{p} / \ell) [p_{L} - p_{eL}] , \qquad (12)$$

$$I_{nL} = r_{nL} (ez_n D_n / l) [n_L - n_{eL}] , \qquad (13)$$

$$I_{pR} = r_{pR} (ez_p D_p / \ell) [p_R - p_{eR}] , \qquad (14)$$

and

$$I_{nR} = -r_{nR}(e_{n} D_{n} / \ell) [n_{R} - n_{eR}] .$$
 (15)

In the above, the subscript "e" denotes thermal equilibrium. Thus, the boundary conditions are linear in the boundary concentration perturbations from the zero-current equilibrium situation. Such linearity is necessary for small perturbations around equilibrium but cannot necessarily be expected to hold accurately for large perturbations. Note, however, that a boundary concentration perturbation must be zero when the corresponding  $r_{i}$ (i = n or p) is infinite. Also when  $r_{i}$  = 0, the current is zero even for large perturbations. Thus, the above expressions may be expected to apply more broadly near these limits.

Let us now consider that the applied potential difference V<sub>a</sub> is made up of a possibly large static part V<sub>a</sub> and a small perturbation part  $\delta V_a$ , so that  $V_a = V_{a0} + \delta V_a$ . Then the current, field, and concentrations will also each divide into a static part and a perturbed part. But since the basic equations governing the system are nonlinear, it will not generally be possible to write I, and the other quantities, in the separated form  $I = I_0(V_{a0}) + \delta I(\delta V_a)$  with a linear dependence of  $\delta I$  on  $\delta V_a$ . If  $\delta V_a$  is sufficiently small [generally <<(kT/e)], however, the The static and differential capacitances of the system are of particular interest and relevance for completely blocking electrodes. If the total amount of stored SCP charge at  $V_a = V_{ao}$ is designated  $q_o$ , then the static or integral capacitance is  $C_s \equiv q_o/V_{ao}$ . Similarly, if at a given  $V_a = V_{ao}$  an additional small perturbation  $\delta V_a$  is applied, the differential capacitance is given by  $C_d \equiv (dq/dV_a) = [d(V_a C_s)/dV_a = \delta q/\delta V_a$ , where  $\delta q$  is the change in q arising from  $\delta V_a$ . The differential capacitance is usually of more interest than is  $C_s$ .

The small-signal ac response of the system may be calculated from the above equations around the bias point  $V_{ab}$  by taking, for example,  $\delta V = V_1 \sin(\omega t)$ , where  $V_1$  is the amplitude of the sinusoidal perturbation of radial frequency  $\omega$ . When V<sub>1</sub> << (kT/e), all higher-order harmonics in the Fourier expansion of quantities such as I, E, n, and p may be neglected compared to the fundamental, and the admittance  $Y(V_a) \equiv \delta I/\delta V$  is a well-defined quantity which may be calculated from the above equations. The explicit separation of the equations into a nonlinear set depending only on V and a linearized ac perturbation set dependent on  $\delta V = V_1 \exp(i\omega t)$  is necessary to solve the equations in the most expeditious way<sup>22</sup>. First the nonlinear dc equations must be solved, then the resulting steady-state inhomogeneous fields, concentrations, etc. must be used in the perturbation set of equations to obtain the final ac current or admittance. In general, this sort of sequential calculation must be done numerically by computer simulation. The equations can, however, be solved exactly for small-signal ac response when V = 0 and the equilibrium state of the system is one with  $E(x) = {}^{a0}$  for all  $x^{22}$ . Results of such a solution for completely symmetrical electrodes will be discussed in Section IV-4.

There is one further complication which needs consideration. It causes E(x) not to be zero near surfaces even in thermal equilibrium. Although an isolated ionic single crystal such as AgCl may be taken macroscopically neutral, Frenkel<sup>23</sup> pointed out long ago that in thermal equilibrium the surface of the crystal should be charged and this charge balanced by a diffuse space charge of opposite sign adjacent to the surface. In this instance, the above non-ideal surface dipole arises from any difference in the energy required to form positive and negative defects in the crystal<sup>23<sup>-</sup>26</sup>. Even the presence of an essentially completely blocking electrode adjacent to the surface may be expected, however, to modify the surface-region dipole through imaging effects. The presence of a partially blocking electrode, which requires in equilibrium that the electrochemical potential of any charge carrier crossing the interface be the same in the electrode and in the material next to it, may be expected to affect

the surface dipole region even further. More discussion of this phenomenon, which may be characterized by a diffusion potential  $V_{\rm D}$  which determines the strength of the dipole, has been given elsewhere<sup>26</sup>.

Several interesting cases may be distinguished. With complete blocking of both positive and negative mobile charge carriers in the material, i.e.  $(r_p, r_n) = (0,0)$ , the surface charges may be considered to be specifically adsorbed according to an electrical adsorption isotherm which generally depends on both  $V_D$  and the applied p.d.,  $V_a$ . If the surface charges are not completely blocked, then it seems sensible to conclude that there are no specifically adsorbed surface charges, and charge on the electrode alone balances that in the diffuse layer. Finally, if the diffuse layer charge is not blocked and that on the surface is, one would expect that in general any diffuse layer charge would be balanced both by specifically adsorbed charge and by charge on the electrode. The complete-blocking,  $V_D \neq 0$  situation will be discussed further in the next section.

## III. COMPLETE BLOCKING: QUASI-EQUILIBRIUM

Both positive and negative mobile species are taken to be completely blocked in the work considered in this section. Two situations have conventionally been examined: a single blocking electrode at x = 0 with the material of interest extending to  $x = \infty$  in the right half space, and alternatively, two blocking electrodes at x = 0 and at  $x = \ell$ . A good experimental approximation to the first of these arrangements is to place a blocking working electrode at x = 0 and an indifferent or ohmic electrode at x = l and ensure that l is large compared to the bulk Debye Theoretical and, where possible, experimental curves of length. potential, field, and charge concentrations versus x are instructive in such situations. Representative results are given in Refs. 20, 27-34, not all applying just to complete blocking. References 28, 29, and 31 include the substantial effect of intrinsic recombination on the curve shapes when one species of carrier is immobile. Space limitations preclude detailed discussion of such shapes here. A brief summary of some of the theoretical work through 1963 on static space charge distributions has been given elsewhere<sup>35</sup>.

It is worthwhile to summarize expressions for diffuse-layer differential capacitance,  $C_d$ , in various blocking situations. For simplicity, all  $C_d$  results will be given only for the  $z_n = z_p = 1$  case. In the present completely blocking case,  $C_d$  can be measured quasi-statically as  $(\delta q / \delta V_a)$  or, when the system is linear, as the low-frequency limiting value of parallel ac capacitance. For a single blocking electrode with  $V_p = 0$  and no

specific adsorption, the intrinsic-conduction diffuse double layer differential capacitance is then given  $by^{27}$ 

$$C_{d} = (\varepsilon/4\pi L_{D})\cosh(V_{a}^{*}/2) , \qquad (16)$$

where  $V_a^* \equiv V_a/(kT/e)$  and  $V_a$  is the applied potential difference. When both carriers are mobile, the appropriate Debye length reduces to

$$L_{D} = L_{D2} \equiv [\varepsilon kT/4\pi e^{2}(z_{n}^{2}n_{i} + z_{p}^{2}p_{i})]^{1/2}$$
$$= [\varepsilon kT/8\pi e^{2}c_{i}]^{1/2}, \qquad (17)$$

where n and p are the bulk intrinsic concentrations, satisfying the electroneutrality condition  $z_n = z_p p_i$ ; in the present  $z_n = z_p = 1$  case,  $n_i = p_i \equiv c_i$ . When say only the negative carriers are mobile,

$$L_{D} = L_{D1} \equiv [\epsilon kT/4\pi e^{2} c_{1}]^{1/2}$$
 (18)

Eq. (16) and subsequent C<sub>d</sub> expressions hold adequately only as long as the diffuse layer charge carrier concentrations remain small compared to the concentration of intrinsic entities (atoms or ions) which make up the material. Grimley<sup>36,37</sup> has given a  $V_{\rm D}$  = 0 treatment, applied specifically to Schottky defect carriers, where this restriction is relaxed. Nevertheless, Eq. (16), which includes no finite-size corrections, has usually been found adequate for liquid electrolyte experimental results<sup>17</sup>.

The situation is somewhat more complicated in the twoelectrode case. Assume again that  $V_D = 0$  and there is no specific adsorption, so that E = 0 throughout the material before the application of  $V_a$  across the electrodes. Then<sup>27</sup>

$$C_{d} = (\varepsilon/8\pi L_{D2}) \operatorname{ctnh}(M) \operatorname{cosh}(V_{a}^{*}/4) , \qquad (19)$$

where

$$M = \ell/2L_{p2} .$$
 (20)

The two factors of two present here and not in Eq. (16) arise from the equal division of V<sub>a</sub> across the two interphase regions and from the series combination of equal diffuse layer capacitance for these regions to give the total capacitance. Note that when V<sub>a</sub>  $\rightarrow$  0 and ( $\ell/L_D$ )  $\rightarrow$  0, Eq. (19) reduces to  $\epsilon/4\pi\ell$ , just the geometrical capacitance C<sub>g</sub> of the material. Thus, the purely SCP part of C<sub>d</sub> is

$$C_{SCP} = C_d - C_g = C_g[(M) \operatorname{ctnh}(M) \cosh(V_a^*/4) - 1]$$
 (21)

Again when  $V_a \rightarrow 0$ , it is clear that for M > 3,

$$C_d \cong MC_g = \epsilon/8\pi L_{D2} \equiv C_o$$
, (22)

just the ordinary unbiased capacitance of two diffuse double layers in series. This capacitance is intensive as far as  $\ell$ -dependence is concerned, in accord with its approximate localization near the electrodes.

For either one or two electrodes, the situation is more complicated when one species of charge is immobile but bimolecular recombination between positive and negative charges can  $occur^{28,29}$ . Note that it is an idealization to speak of applying V across completely blocking electrodes because of possible potential drops between the electrodes and the material studied. One can place the material to be investigated in an electric field, i.e., between capacitor plates, and calculate the applicable V from integration of the actual resulting field in the material from x = 0 to  $\ell$  as in Eq. (7). Note that when  $V_D = 0$ ,  $V_a$  must be zero when the electrode charge,  $q_m$ , is zero. The system may often be realized experimentally by placing very thin insulating layers between metallic electrodes and the material. If the capacitances of these layers are much greater than C, for the material, then the V (across the material) which should be used in Eq. (19) will be well approximated by the actual p.d. applied across the electrodes. The case where the potential drop across such an insulating layer is not negligible has also been considered<sup>28,38</sup>.

Let us now consider the possible presence of specifically adsorbed surface charge, q<sub>s</sub>, with V<sub>D</sub> not necessarily zero. Denote the total, integrated diffuse layer charge by q<sub>d</sub>. For a single blocking electrode many Debye lengths away from any other electrode (M >> 1), the relation q<sub>m</sub> + q<sub>s</sub> + q<sub>d</sub> = 0 must hold. The differential capacitance may be calculated from C<sub>d</sub>  $\equiv$  dq<sub>m</sub>/dV<sub>a</sub> when the dependences of q<sub>s</sub> and q<sub>d</sub> on V<sub>a</sub> are known. Although q<sub>d</sub> should most properly be given by Grimley's expression<sup>36</sup> modified to include V<sub>D</sub> and arbitrary valences, for illustrative simplicity I shall here use the conventional z<sub>n</sub> = z<sub>p</sub> = 1 diffuse layer result<sup>26,27</sup>

$$q_d = -A_1 \sinh[0.5(v_D^* + v_a^*)]$$
, (23)

where

$$A_1 \equiv (\epsilon kT/2\pi eL_D) \equiv (4kT/e)C_o$$
, (24)

and  $V_D^* = V_D^{\prime}(kT/e)$ .

One next requires electrical adsorption isotherms for the individual components of  $q \equiv q_s^+ + q_s^-$ . For simplicity in writing equations, let us alternatively denote all positive-related (p and +) quantities with a subscript "1" and negative ones with a subscript "2". Assume that there are  $N_{\pm}^+ \equiv N_{\pm}$  and  $N_{\pm}^- \equiv N_{\pm}^-$  surface adsorption sites occupied by positive and negative charges, respectively. Then,  $q_{\pm} \equiv (-1)^{1+j} e_{\pm} N_{\pm}$ , with j = 1, 2. Further assume that there is a fixed maximum number of adsorption sites for charge of each sign, N and N  $m_{\pm}^- m_{\pm}^-$ . Then the maximum surface charge components are  $q_{\pm}^- = (-1)^{1+j} e_{\pm} N_{\pm}^-$ . Under these conditions the Langmuir isotherm is an appropriate choice<sup>26</sup> except that it takes no account of planar interaction between adsorbed entities, important when N  $\equiv N_{\pm} + N_{\pm}^-$  begins to become an appreciable fraction of N or N  $m_{\pm}^- N_{\pm}^-$ .

$$(N_{\rm s}^{\pm}/N_{\rm sm}^{\pm}) = [1 + \exp(\Delta G^{\pm}/kT)]^{-1},$$
 (25)

where the  $\triangle G$ 's are electrochemical free energies of adsorption from the bulk, referenced to  $(N_s^{-}/N_{sm}^{+}) = 0.5$  at  $\triangle G^{-} = 0$ .

Following conventional practice, one may separate each  $\Delta G^{\pm}$ into a chemical part independent of applied potential,  $\Delta G^{\pm}$ , and a potential dependent part, ez  $\lambda^{+}V_{a}$  or  $-ez \lambda^{-}V_{a}$ . The  $\lambda^{\pm}$  quantities introduced here are usually of the order of unity or less and are included to account at least approximately for discreteness of charge effects<sup>15,16</sup>. Thus,  $\lambda^{\pm}V_{a}$  are micropotentials rather than the macropotential, V. Separation of  $\Delta G^{\pm}$  yields  $\Delta G^{\pm}_{a} \equiv$  $(\Delta G_{a}/kT) \equiv \Delta G^{-}_{a} - (-1)^{+}(z_{a}\lambda_{a}V^{*}_{a})$ . Finally, let  $\psi^{*}_{a} \equiv 0.5(V^{*}_{D} + V^{*}_{a})$ . Then the foregoing equations lead for  $z_{n} = z_{p} = 1$  to

$$C_{d} = (2C_{o})\cosh(\psi_{o}^{*})$$
  
+ (e/4kT)  $\sum_{j=1}^{2} (-1)^{1+j} (\lambda_{j}q_{smj}) \operatorname{sech}^{2}(\Delta G_{j}^{*}/2)$ . (26)

A term equivalent, for  $\lambda^{\pm} = 1$ , to the first of the sech<sup>2</sup> expressions above has been cited by Pleskov<sup>39</sup> for the differential capacitance of electron surface states on a semiconductor surface. Note that  $\rho_{,}$ , defined as  $e\lambda_{j}|q_{smj}|/8kTC_{o} \equiv (\lambda_{j}/2A_{1})|q_{smj}|$ , will usually be much larger than unity.

Raleigh, in unpublished work<sup>40</sup>, has considered a simpler version of the present case, that which follows when the diffuse layer contribution is ignored,  $N_{sm}^+ = N_{sm}^- \equiv N_{sm}^-$ ,  $\Delta G_o^{\pm} = 0$ , and

 $\lambda \pm = 1$ . Thus, when V = 0, N<sup>+</sup> = N<sup>-</sup> = 0.5N , a very special condition. Under these circumstances Eq. (26), rewritten for arbitrary  $z_n$  and  $z_p$ , reduces to just

$$C_{d} = (2\rho C_{o}) \operatorname{sech}^{2}(V_{a}^{*}/2) , \qquad (27)$$

where  $\rho \equiv (eN_{m})(z_{m} + z_{m})/2A_{1}$ . The maximum value of the symmetrical C curve,  $2\rho C = (e/4kT)[(eN_{m})(z_{m} + z_{m})]$ , will generally be much larger than 2C. Raleigh adjusts  $(z_{m} + z_{m})$  somewhat arbitrarily to yield agreement between  $2\rho C$  and the peak of an experimental AgBr curve for C taken near the melting point of AgBr for a single blocking electrode situation<sup>41,42</sup>. He then finds good agreement between theory and experiment near the peak. Better agreement over a wider potential range could probably be achieved with inclusion of diffuse layer effects and with  $\Delta G_{-}^{+}$  values non-zero and unequal. Raleigh takes the negative surface charges as Br; it seems more likely that silver ion vacancies, which have appreciably higher mobility, would predominate.

When  $\Delta G^{\dagger} = \Delta G^{-}$ , there is no equilibrium Frenkel space-charge double layer; instead, positive and negative adsorbed charges are of equal concentration when V = 0. It is thus clear that when  $V_{D} \neq 0$ ,  $eV_{D}$  must be a function of  $(\Delta G^{+} - \Delta G^{-})$ . Thus, the  $V_{D}$  which appears in  $\psi$  is not independent of the values of  $\Delta G^{\pm D}$ . The matter has been considered in some detail previously<sup>26</sup> for the This case of  $(\Delta G^{\pm}/kT) >> 1$ , which allows the Langmuir/Fermi distributions of Eq. (25) to be reduced to Maxwell-Boltzmann distributions. An explicit linear relation between  $(\Delta G^{+} - \Delta G^{-})$  and  $V_{D}$  and  $ln|q_{sm}^{+}/q_{-}^{-}|$  was found and used to calculate  $C_{d}$  curves for a two-blocking-electrode situation. Some of the results derived, particularly those for  $\lambda^{\perp} \sim 0$ , were qualitatively similar to the Raleigh AgBr experimental results, which show a central peak, unequal minima, and final rises. But in this two-electrode situation, most of this sort of behavior arose from unequal splitting for V. 4 0 of V between the two electrode regions, even for the M >> 1 case. The results were compared to an earlier, less accurate calculation<sup>43</sup> which erroneously assumed splitting of V into equal parts. Conditions are depicted very diagrammatically in Fig. 1 for the  $V_D > 0$  case. There "e" and "s" denote electrode and surface regions. As  $V_a$  increases, one diffuse layer grows and the other decreases until finally the signs of the leftregion diffuse charge and the right-region surface charge change, as shown in Fig. 1-c.

Even if Eq. (26), with appropriate values of  $\Delta G_{\rho}^{\pm}$ ,  $\lambda^{\pm}$ ,  $N_{sm}^{\pm}$ , and  $V_{D}$ , could fit Raleigh's AgBr data excellently, there remains an important stumbling block arising from the finite size of specifically adsorbed ions. Figure 1-d shows a crude picture of some ions specifically adsorbed on a metal electrode, say



Fig. 1. (a) - (c). Signs of charge concentrations at electrodes (e), surfaces (s), and in diffuse layers for  $V_D > 0$ . (d). Specifically adsorbed charge at electrode surface.

platinum. The charge centroids of such ions are located at the inner Helmholtz plane<sup>15</sup>, and the ion material between the center of charge of an ion and charges in the metal should have a low "dielectric constant," insofar as this concept is meaningful. 0ne may expect an inner layer capacitance to be present associated with the charge-free region between the electrode and the inner Helmholtz plane. The approximate plane-parallel capacitor formed when charges in the metal and the adsorbed layer are smeared in their planes cannot be expected<sup>44</sup> to have an effective capacitance even as large as 100  $\mu$ F/cm<sup>2</sup>. But Raleigh finds a maximum capacitance of nearly 500  $\mu$ F/cm<sup>2</sup> at V = 0. One would expect that the considerably smaller inner-region capacitance would be in series with any adsorption and diffuse layer capacitances and would dominate the combination. The solution to the problem of the missing inner layer capacitance is still unclear. It is possible, however, that it is essentially shorted out by partial charge transfer between the electrode and specifically adsorbed charges,

## IV. STEADY-STATE AC RESULTS

## I. Introduction

The most general situation of interest for a homogeneous material with a single species of mobile positive charge and a

single species of mobile negative charge would involve two electrodes with different boundary conditions (r, r, and  $V_D$ / adsorption all different for the two electrodes), and extrinsic-intrinsic conduction with trapping and recombination. The applied p.d.,  $V_a$ , would, in general, be made up of a static part  $V_{a0}$  and an alternating part  $V_{a1}$ , not necessarily small. For simplicity, and because this general situation has not yet been fully worked out, results for much simpler conditions will be discussed here.

Consider a homogeneous, isotropic material between two identical electrodes without  $V_D$ /adsorption. Take  $V_{a0} = 0$  and consider that  $(V_{a1})_{max} << kT/e$ . Finally, only results for intrinsic conduction without trapping will be discussed, although a theory for extrinsic-intrinsic conduction without trapping has been given<sup>22</sup>. Most of the results following from the equations of Section II will be for zero recombination (full dissociation) of intrinsic carriers, i.e.  $k_1 = k_2 = 0$ , but some findings of current calculations which include intrinsic generation-recombination will be mentioned at the end of this section.

Before discussing detailed ac SCP results for a homogeneous material, a simplified SCP approach for inhomogeneous conditions will be examined in the next subsection and methods of data analysis examined in the following one.

## 2. Interfacial Polarisation

As its name implies, interfacial polarisation (IP) arises from mobile charges piling up at interfaces in a material. For example, the N-layer Maxwell-Wagner (MW) capacitor<sup>45,46</sup> consists of a series of layers, each of specified dielectric constant and conductivity, lying parallel to plane, parallel electrodes. Alternatively, one or more species of conducting particles of specific shapes may be considered to be dispersed in a carrier medium with different electrical properties<sup>45-47</sup>.

Interfacial polarisation theory is simplified because no detailed account is included in it of mobilities, valences, recombination, or specific conditions at interfaces; instead everything is subsumed in the dielectric constant and conductivity assigned to each layer. More properly, the equations of Section II should be solved for each region with appropriate boundary conditions at each interface. Since this is usually impractical, it is interesting to compare results of the lumped-constant IP approach with those following from the detailed solution of the transport-continuity equations even for a homogeneous material.

The usual MW N-layer IP equivalent circuit made up of frequency-independent lumped-constant elements is shown at the



Fig. 2. Two equivalent circuits for interfacial polarisation.

right in Fig. 2. It is known as the Voigt model when used to describe mechanical viscoelasticity effects (with reinterpretation of the r's and c's) and describes a retardation situation<sup>8,48</sup>. Each parallel circuit represents the properties of a single layer. An alternate circuit, the Maxwell model, is shown at the left of Fig. 2. It conventionally describes a relaxation situation and is the usual model applied to describe a discrete or continuous  $(N = \infty)$  distribution of relaxation times for dielectric materials. As shown, these two circuits can have identical impedances at all frequencies if the relations between their elements are correctly chosen. It is possible to calculate the elements on the left directly from those on the right but the reverse solution cannot be carried out (for N > 1) explicitly and exactly. The following relations are applicable, however:

Maxwell-Wagner IP has frequently been invoked to explain observations of very large low-frequency apparent or effective dielectric constants (e.g., 49,50). It is often implied or stated that the high (apparent) dielectric constant is a true property of the material. Such is not the case; the error comes from calculating and using a properly intensive quantity, dielectric constant, in a situation where it is inapplicable. The problem is illustrated by the following simple example. Consider a two-layer MW situation with equal true dielectric constants,  $\varepsilon$  4,6. Assume that the layer thicknesses are  $d_1$  and  $d_2$ , with  $d = d_1 + d_2$  and  $d_1 << d_2$ , and take the resistivity of layer one much larger

than that of layer two. Now if the effective low-frequencylimiting dielectric constant of the combination is calculated, one obtains  $\varepsilon_{eff} \cong (d_2/d_1)\varepsilon_0 >> \varepsilon_0$ . But clearly this is not a true dielectric constant; it has been arrived at using d rather than the proper d (<<d), and the resulting  $\varepsilon_{eff}$  is not an intensive property. In general, whenever a material is expected to be inhomogeneous and/or whenever space charge can occur near boundaries and electrodes it is wise initially not to calculate properly intensive quantities such as dielectric constant and conductivity, even with the appellation "apparent" or "effective," but instead to deal only with actual capacitances and conductances or specific (unit area) values of such quantities. Once the dependencies of frequency-independent circuit elements on electrode separation have been found, it may be possible to interpret some of them in terms of intensive bulk properties. will certainly not be possible to do so, however, for all elements arising from interface-related processes.

Another way an incorrect or misleading large effective dielectric constant or capacitance can be obtained from even an N = 2 Voigt-model circuit is if experimental impedance data associated with such a circuit are interpreted in terms of a series capacitance and series resistance:  $Z_T \equiv R_S + (i\omega C_S)^{-1}$ , where  $Z_T$ is the total impedance. The N = 2 circuit leads to a frequency dependence of  $_2C_S$  of the following form: As  $\omega$  decreases,  $C_S$  increases as  $\omega^{-2}$  from a high-frequency value of  $c_1$  (assuming  $c_1 << c_2$ ), saturates over an appreciable frequency interval at  $(c_1 + c_2)$ , and then finally increases indefinitely again proportional to  $\omega^{-2}$ . This rise, of course, should not be interpreted in terms of a dielectric constant increase; it appears because of inappropriate analysis of the circuit. For example, the total parallel admittance,  $Y_T \equiv Z_T^{-1} \equiv G_P + i\omega C_P$ , leads to a  $C_P$  which properly saturates at  $(c_1 + c_2)$  as  $\omega \to 0$ .

Figure 3 shows two circuits which are electrically equivalent and arise from the SCP theory<sup>22</sup> to be discussed in IV-4. Here the dc discharge conductance is  $G_p$ ,  $G_\infty \equiv R_\infty^{-1} \equiv G_p + G_p$ , and  $G_{DN} \equiv G_D/G_\infty$ ,  $G_{EN} \equiv G_E/G_{\bullet}$ . Note that the elements of  $Y_1 \equiv G_1 + i\omega C_{1P}$  and of  $Z_1 \equiv Y_1 \equiv R_1 + (i\omega C_1)^{-1}$  are all frequency dependent in general. There are, however, two important conditions for which the circuit of Fig. 3 can be well approximated as an N = 2 type of circuit over an appreciable frequency range. Define Case A as that where in the range of interest C. is essentially frequency independent and either R. is as well, Case A<sub>1</sub>, or, the usual case, A<sub>2</sub>, R<sub>1</sub> << R<sub>E</sub>  $\equiv G_E^{-1}$ . Case B is that where over a given frequency range the frequency dependencies of the series-connected elements R<sub>1</sub> and C<sub>1</sub> are just those which lead to frequency independent values of the parallel elements,  $G_{1P}$  and  $C_{1P}$ . There are two Case B situations where the N = 2 circuit is well approximated. The first, of lesser interest, Case B<sub>1</sub>,

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# Fig. 3. Two exact equivalent circuits following from detailed theory<sup>22</sup> of charge motion in solids and liquids.

occurs when  $G_{iP}$  may be neglected, i.e.  $\omega C_{iP} >> G_{iP}$ ; it is then essentially equivalent to Case A<sub>2</sub>. Case B<sub>2</sub>, on the other hand, occurs when  $G_D$  may be neglected:  $G_{iP}^{-1} + G_E^{-1} << G_D^{-1} \equiv R_D$ . Then the circuit becomes like that of Fig. 3-b but with  $D_{G-1G}^{-1}D_{G}$ . replaced by  $G_{iP}$ ,  $G_{EN}^{-Y}$  by  $C_{iP}$ , and  $R_{\infty}$  by  $R_E$ , essentially equal to  $R_{\infty}$  for this high dc resistance case. It can be shown<sup>51</sup> that such a circuit corresponds exactly to an N = 2 arrangement of the kind shown at the right of Fig. 2.

#### 3. Data Analysis

Since even results for a homogeneous material with electrode effects and/or recombination can sometimes lead to a simple N = 2parallel-series circuit, it is of interest to discuss how data associated with such a circuit might best be analyzed. The initial aim of analysis should be to determine the frequencyindependent values, if any, of the capacitative and conductive elements of the equivalent circuit. Then, investigation of the

dependence of these elements on temperature and electrode spacing, together with any other information known about the system, should help one decide to what degree the results arise from a MW IP or a homogeneous SCP system. Note that discussion of a N = 2 circuit is sufficient since N = 2 methods may be applied sequentially to pairs of a system exhibiting N > 2 circuit behavior.

In addition to an examination of the frequency response of series and parallel components of the circuit impedance/admittance, another approach may be particularly valuable. This analysis method involves plotting the real versus imaginary parts of some such complex quantity as admittance<sup>52,53</sup> or impedance<sup>54-56</sup> as parametric functions of frequency. Such Argand or "circle diagrams" have been used for many years in electrical engineering; when complex dielectric constant is the quantity considered, they are known as Cole-Cole plots<sup>57</sup>.

There are four complex quantities worth investigating. Consider normalized forms denoted by a subscript "N", where resistances are normalized with  $R_{\infty}$  and capacitances with C. Let  $Y_T \equiv Z_T^{-1}$  be the total admittance. Then we may write,<sup>g</sup>

$$\mathcal{M} \equiv i\Omega Z_{\rm TN} = C_{\rm SN}^{-1} + i\Omega R_{\rm SN} , \qquad (28)$$

$$z_{TN}^{*} \equiv R_{SN} + i(\Omega C_{SN})^{-1} , \qquad (29)$$

$$Y_{TN} \equiv G_{PN} + i\Omega C_{PN} , \qquad (30)$$

and

$$K_{DN} = (Y_{TN}/i\Omega)^* = C_{PN} + i\Omega^{-1}G_{PN}$$
, (31)

where the asterisk denotes complex conjugation and  $\Omega \equiv \omega C R_{\infty}$  as before. In the above, is the complex modulus of Hodge  $\frac{e_{1}}{2}$  al.<sup>58</sup>, and  $K_{DN}$  is the conjugate of the complex effective dielectric constant in normalized form<sup>59</sup>. Note that  $\mathcal{M} = K_{DN}$ . All the quantities defined above have positive imaginary parts. These parts are plotted on the positive y-axis <u>versus</u> the real parts of a given complex quantity on the positive x-axis.

What sort of shapes arise from these plots? Admittanceplane curves for several different circuits have been presented by Bauerle<sup>53</sup>, and complex dielectric constant and complex conductivity-plane curves given for several other circuits by Grant<sup>60</sup>. For the N = 2 circuit, it turns out that  $\mathcal{M}$  and  $Z_{\mathrm{TN}}^*$ plots lead to two connected but well distinguishable semicircles with circle centers on the real axis provided the two time constants of the circuit are well separated. But as Hodge <u>et al</u>. have demonstrated <sup>58</sup>,  $\mathcal{M}$  shows good semicircle separation when the time constant difference arises primarily from a difference in resistances, e.g.,  $r_2/r_1 >> 1$ , and  $Z_{TN}$  shows such separation when the difference comes from an appreciable difference between the two capacitances of the circuit. In all cases, both semicircles are present, but their sizes are very different in the above limiting cases. Generally, when one type of plot shows two distinguishable semicircles, only one will be apparent on the other. In the absence of further information, it is thus a good idea to construct both  $\mathcal{M}$  and  $Z_{TN}$  plots initially. When two joined semicircles appear, all  $N^{TM} = 2$  circuit element values may be obtained from the real-axis intercepts and the frequencies at which the peaks of the semicircles occur.

The other two kinds of plots have been used more in the past but are generally not quite as instructive as the first two. For the N = 2 circuit, they never give two semicircles but, at best, lead to a single semicircle melding into a vertical line at its right end. Thus, the fact that there are two time constants present does not show up so clearly, and not all the circuit element values follow as readily from these plots. There thus seems to be little reason to use  $Y_{\rm TN}$  and  $K_{\rm DN}$  plots rather than  ${\bf M}$  and  $Z_{\rm TN}$  ones, at least in the initial stages of an investigation.

By restricting attention to the complex dielectric constant, Volger<sup>46</sup> concluded that in an N-layer MW situation, (N-1) relaxation times rather than N occur. As we have seen, this need not be the case. Bauerle<sup>53</sup> used an N = 3 circuit to analyze data on zirconia-yttria by admittance plane methods. He found only two connected semicircles but omitted any parallel capacitance across one of his three resistances. This omitted capacitance can be identified as C<sub>g</sub> to good approximation. Since there is always some geometric capacitance in any real situation, it should properly not have been omitted. At sufficiently high frequencies, it leads to a semicircle in the Z<sub>TN</sub> plane or a vertical line in the Y<sub>TN</sub> plane. Bauerle's data did not extent to high enough frequencies to show this effect.

In almost all SCP cases of interest, the time constant  $\tau_{D} \equiv R_{\infty}C_{g}$  will be appreciably shorter than other time constants present in the system. Furthermore, in most cases, C will also be much smaller than other capacitances present. Under these conditions, the parallel combination of C and  $R_{\infty}$  may be placed in series with the rest of the circuit to<sup>g</sup>a high degree of approximation. For the special Cases A and B already discussed in connection with Fig. 3, the rest of the circuit may be well approximated by another resistance and capacitance in series, yielding an N = 2 Voigt-model circuit. Finally, whenever one

wishes to fit impedance/admittance data to a theoretical model, it will be a good idea to do such fitting using generalized least squares, a technique which allows both the real and imaginary parts of the data to be statistically weighted in determining parameter estimates and their uncertainties<sup>61</sup>.

# 4. Detailed Results for a Homogeneous Material

Over the years since 1952 there has been considerable work devoted to the solution of the equations of Section II for the small-signal ac situation with various simplifications and idealizations (e.g., 21, 22, 54-56, 59, 62-64). Here, I shall discuss recent work<sup>22,55,56</sup> which essentially subsumes most earlier results. Consider an intrinsic-conduction material, initially without recombination, and with identical plane, parallel electrodes. Further, V<sub>p</sub> is taken zero, no specific adsorption effects are included, and the finite size of charge carriers is neglected. To define such a system as far as its normalized impedance is concerned, one may use the following parameters: ( $r_p$ ,  $r_n$ ;  $\pi_m$ ,  $\pi_z$ ; 0, M). Here  $\pi_m \equiv \mu_n/\mu_p$ ,  $\pi_z \equiv z_n/z_p$ , and the zero denotes intrinsic conduction. Because of symmetry ( $r_n$ ,  $r_p$ ;  $\pi_m$ ,  $\pi_z$ ; 0, M) defines the same normalized situation.

It is found that the exact equivalent circuit of Fig. 3 can usually be well approximated by the N = 3 circuit of Fig. 4. Here  $R_3 \equiv R_{\infty}$  and  $C_3 \equiv C_g$ ;  $R_2$  and  $C_2$  can generally be taken frequencyindependent, and  $R_1^{e}$  and  $C_1$  must be taken frequency-dependent in part of the frequency range<sup>55,56</sup>. Insofar as time constants may be defined for the three subcircuits, one usually finds  $\tau_1 >> \tau_2 >> \tau_3 \equiv \tau_D$ .

Figure 5 shows the simple frequency response for  $C_{PN} \equiv C_p/C_p$  found with completely blocking, equal mobility, and equal valence



Fig. 4. Approximate equivalent circuit following from detailed SCP theory<sup>22</sup>. R<sub>1</sub> and C<sub>1</sub> are generally frequency dependent.



Fig. 5. Normalized parallel capacitance <u>vs</u> normalized frequency for complete blocking and several values of  $M \equiv \ell/2L_{p2}$ .

conditions. Here Fig. 4 reduces to an N = 2 Voigt model with  $Z_1 = 0$ ,  $R_2 = \infty$ , and  $C_2 = MC_g \equiv C_o$ , just the ordinary diffuse layer capacitance for two layers in series. Somewhat similar results are obtained when  $r_p = r \neq 0^{55,56}$ . Note that these results are an example of Case  $A_2$  reduction discussed in Section IV-2.

Figure 6 gives some results for another limiting case. Here  $\rm Z_2$  = 0, and, in general,

$$Z_{1N} \approx [\pi_{m} (i\Omega bM^{2})^{\frac{1}{2}} ctnh (i\Omega bM^{2})^{\frac{1}{2}}]^{-1} , \qquad (32)$$

where  $b \equiv \delta_n \delta_p / \epsilon_n \epsilon_p$ ,  $\delta_n \equiv (1 + \pi_z^{-1})^{-1}$ ,  $\delta_p \equiv (1 + \pi_z)^{-1}$ ,  $\epsilon_n \equiv (1 + \pi_n^{-1})^{-1}$ , and  $\epsilon_p \equiv (1 + \pi_n)^{-1}$ . This approximate expression for  $Z_{1N}$  holds<sup>56</sup> when  $r_p = 0$  for any  $\pi_n$  and  $\pi_z$ , not just the unity values of Fig. 6. Note that the  $\Omega$  dependence in Fig. 6 involves appreciable regions with  $\Omega^{-3/2}$  rather than the conventional  $\Omega^{-2}$  behavior apparent in Fig. 5. In the intermediate frequency range, where the ctnh function is unity,  $Z_{1N}$  reduces to an ordinary diffusional Warburg impedance. Such an impedance must be modified as above, however, for a finite length of material, since as  $\Omega \rightarrow 0$ , there will eventually be less than one diffusion length available in  $\ell$ .

For M >> 1, the usual case, the total low-frequency-limiting capacitance,  $C_{PO}$ , which follows from Eq. (32), is



Fig. 6. Normalized parallel capacitance <u>vs</u> normalized frequency for  $(r, r_n) = (0, \infty)$  boundary conditions and several M values.

$$C_{PO} \approx (\delta_n \delta_p M^2 / 3) C_g \approx (M/12) C_o$$
, (33)

where the second form applies when  $\pi_z = 1$ . Notice that for large M,  $C_{p0}/C_0$  may greatly exceed unity. This large capacitance is connected with diffusion in a restricted space (x = 0 to  $\ell$ ) and is extensive, directly proportional to  $\ell$ ! It is of especial interest, both for its size and its genesis. Earlier work<sup>59,63</sup> shows conclusively that for M >> 1,  $C_{p0}$  is not primarily associated with stored space charge in the material when r and r are very different. It is a diffusional rather than a<sup>P</sup>SCP capacitance, is sometimes called a pseudocapacitance, and is associated with the energy stored in the chemical reaction which occurs at the electrode when r or r is not zero<sup>65</sup>. When r = r  $\neq 0$ , on the other hand, there are still reactions present but no diffusion-related delay which can lead to diffusion capacitance<sup>56</sup>.

Figure 7 shows some more complicated results which can appear when  $0 \le r_n \le \infty$ . Here  $g_n \equiv 1 + (r_n/2)$ . The different values of  $\pi_n$  are used to give greater separation between some of the curves, but the possible effect of  $\pi_n$ , which has of course a limited range, is much smaller than that of  $r_n$  and  $\pi_n$ . Note that  $\Omega^{-m}$ regions occur with values of m = 2, 1.5, 1, and 0.5, all slopes which are frequently encountered experimentally. When  $r_n > 0$  as



Fig. 7. Normalized parallel capacitance  $\underline{vs}$  normalized frequency for several  $(0,r_n)$  situations.

well, all intermediate slopes from m = 0 to 1.5 are also possible<sup>55</sup>. Generally, most measurable structure occurs in the curves when there is a large difference in mobilities and the more mobile species is much more strongly blocked than the other. Accurate capacitance measurements over a wide frequency range can be made in this  $R_D >> R_E$  case but not when  $R_E >> R_D$ .

It has been shown<sup>21,55,56,63,64</sup> that when the dimensionless quantities r and/or r are neither zero nor infinite, they may be related to heterogeneous reaction rate constants,  $\xi_i$ . The result is  $\xi_i \equiv (D_i/\ell)r_i$ , where i = p or n. Since  $\xi_i$  is associated with an electrode reaction, it cannot depend on  $\ell$ . Thus, both r and r must be proportional to  $\ell$  when they are neither zero nor<sup>P</sup>infinite and are associated with thermally activated reaction rates or surface recombination rates.

Figure 8 shows the general form of the  $Z_{TN}^{\star}$  impedance plane plot following from the present theory<sup>55,56</sup>. The various arcs can be of any size relative to each other and all three do not necessarily show up simultaneously. Arc 1, which occurs at the



Fig. 8. Typical form of normalized impedance plane plot following from detailed SCP theory without recombination.

lowest frequencies, arises from the  $Z_1$  of Fig. 4 and is associated with diffusion. The 45° region is that where conventional infinite-length Warburg response is well approximated. In the present normalized form, the size of arc 1 is independent of  $\ell$  and depends primarily on  $\pi_m$ . With  $Z_T^{\star}$  rather than  $Z_{TN}^{\star}$  plotting, the arc 1 size will be directly proportional to  $\ell$  since  $R_{\infty} \propto \ell$ .

The central arc arises from Z<sub>2</sub> and is associated with finite electrode reaction rates; it is usually very well approximated by a semicircle with C<sub>2N</sub>  $\cong$  M and R<sub>2N</sub>  $\cong$  2/( $\varepsilon$  r +  $\varepsilon$  r). When either  $\varepsilon$  r or  $\varepsilon$  r is infinite, R<sub>2N</sub> = 0 and no reaction arc appears. When r = r<sup>p</sup>  $\ge 0$  or r = 0, r << 1 +  $\pi$ , arc 1 does not appear or may be too Small to measure. This is an N = 2 situation, an illustration of Case A<sub>2</sub> discussed earlier. In normalized form, the size of arc 2 is inversely proportional to  $\ell$  through r and/or r, but in unnormalized form it is essentially independent of  $\ell$  and p involves circuit elements associated only with the interphase-electrode region. Finally, arc 3, which again is an excellent semicircle, arises from bulk effects, involves R<sub>w</sub> and C<sub>2</sub> only, is independent of  $\ell$  in normalized form with a height of 0.5, and its size is directly proportional to  $\ell$  for unnormalized conditions. Note that its peak occurs at  $\Omega \equiv \omega \tau_p = 1$ .

Arc 2 is not always found to be a perfect semicircle with its center on the real axis, as demonstrated by Fig. 9. When  $\pi_m \sim M$ ,



Fig. 9. Normalized impedance plane plot showing calculated arc 2, arising from slow electrode reaction, for several  $\pi_{m}$ ,  $\pi_{z}$  values.

the resulting arc may be quite well approximated by a depressed semicircle, one with its center below the real axis. Many experimental data lead to depressed semicircles of this kind, although the depression is often greater than that apparent here, the maximum found thus far for the present theory. Figure 10 shows a situation where arc 1 is much larger than the other arcs and the effect of variable M is examined. Experiment frequently yields curves which approximate some of those shown in Fig. 10, although the available experimental frequency range usually does not allow all three arcs to be completely covered. Even coverage of parts of several arcs may allow analysis of the data to yield estimates of mobilities, boundary parameters, etc<sup>56</sup>, how-In the usual M >> 1 case, it is generally wise to conever. struct both  $Z_{TN}$  and  $Y_{TN}$  complex plane plots when initially analyzing data.

Up to this point the discussion has been limited to full dissociation results ( $k_1 = k_2 = 0$ ). Some work has been published which deals with generation-recombination (GR) effects when only one charged species is mobile<sup>66</sup>, but unpublished work in progress yields particularly interesting results in the  $r_p \neq r_n$  two-mobile case ( $\pi_m$  neither zero nor infinite). Consider the M >> 1 situation with  $k_1$  and  $k_2$  non-zero. Two new parameters describing geminate GR are  $\Lambda \equiv k_1/k_2c_1$  and  $\xi_r \equiv (k_2c_1)^{-1}/\tau_p$ , where  $(k_2c_1)^{-1}$  is the effective recombination time. It turns





out for  $\pi = 1$  that  $(c_1/N) = \Lambda/(1 + \Lambda)$ , where  $(c_1/N)$  is the dissociation ratio; thus for small dissociation  $\Lambda \cong (c_1/N)$ , and when  $\Lambda \to \infty$ ,  $c_1 \to N$ , full dissociation.

First, consider the low-frequency-limiting value of the parallel capacitance,  $C_{p0} = C_{p} + C_{10}$ . In the general situation (r, r;  $\pi_{m}, \pi_{z}$ ; 0, M) take r = 0, r  $\geq 1, \pi_{m} << 1, \pi_{z} = 1$ , and M  $\geq 1$ . Then one finds that the dominant part of  $C_{p0}$  is

$$C_{P0} \cong (M^2 C_g / 12) (1 + 2\Lambda^{-1}) ,$$
 (34)

in agreement with Eq. (33) when  $\Lambda \ \rightarrow \ \infty.$  This expression may be rewritten as

$$C_{PN0} \cong (1/3) (\ell/4)^2 [8\pi (z_e^e)^2 (2N - c_i^2)/\epsilon kT] ,$$
 (35)

where  $z_e$  is the common value of  $z_n$  and  $z_p$ . For  $c_i = N$ , the capacitance involves noncombining positive and negative charges each of bulk concentration N, just as expected. But when  $c_i << N$ , the capacitance is twice as large! Note that it is then far larger than the value calculated conventionally with  $c_i$  replacing

 $(2N - c_i)$ . Evidently, not only does  $c_i << N$  GR make it possible for all centers of bulk concentration N to contribute to  $C_{P0}$ , but it adds a further factor of two increase, probably related to the dynamics of GR itself. It is physically plausible to expect all originally neutral centers to contribute since the zero-frequency limit of the capacitance allows sufficient time for every neutral center to eventually dissociate and the resulting charges separate in the applied field.

GR also leads to interesting results in the non-zero  $\Omega$  range. One often finds a new  $Z_{TN}^{*}$  complex-plane arc, located between arcs 1 and 2 or 2 and 3 of Fig. 8. There are then four arcs possible. An example where all four appear with reasonable separation is (0, 10; 4x10<sup>-3</sup>, 1; 0, 10<sup>-4</sup>) with  $\Lambda = 10<sup>-4</sup>$  and  $\xi_r = 4x10<sup>-4</sup>$ . The maximum values of  $Im(Z_{TN}^{*})$  are found to be about 58, 50, 23, and 0.5, as  $\Omega$  increases, for the diffusion, GR, reaction, and bulk arcs, respectively. Not all four arcs appear well separated under many conditions; in particular, the GR and reaction ones frequently meld together.

When  $(r_p, r_n) = (0, \infty)$ , there is no reaction arc, and the GR arc turns out to be a semicircle without depression when  $\pi_m \xi_r \approx 1$ . This semicircle is an instance of Case B<sub>2</sub>, discussed above. On the other hand when  $\xi_r >> \pi_n^{-1}$ , the GR arc may be of virtually the same shape as the finite-Warburg diffusion arc. The possibility of confusion between these two arcs thus arises but can be resolved from their different dependencies on length,  $\ell$ . The size of the unnormalized GR arc is independent of  $\ell$ , as it should be. Data which include even a part of the GR arc should allow the GR parameters to be estimated.

Finally, it is worth noting that when the Langevin<sup>67,68</sup> diffusion-limited theory for  $k_2$  is used to evaluate  $\xi_r$ , one finds  $\xi_r = 1$ , not a well-known result. While it is, in fact, reasonable to expect that the shortest recombination time would be  $\tau_p$ , when the mean free path of a charge carrier is large compared to the range of its screened Coulomb potential, one might expect that  $\xi_r$ could be much greater than unity. Lax<sup>68</sup> has discussed a situation where electrons are the major charge carriers and finds that the Langevin  $k_2$  is much larger than experimentally observed values. To the degree that this may also be the case in solids with ionic/ vacancy charge carriers, one needs to examine  $\xi_r > 1$  effects there as well as those for  $\xi_r = 1$ .

#### REFERENCES

- 1. F. A. Kröger, <u>The Chemistry of Imperfect Crystals</u>, (North-Holland Publishing Company, Amsterdam, 1964), p. 880.
- 2. Ref. 1, pp. 879-908.

- 3. J. R. Macdonald, J. Appl. Phys. <u>34</u>, 538 (1963).
- N. Sinharay and B. Meltzer, Solid State Electronics <u>7</u>, 125 (1964).
- 5. M. A. Lampert and P. Mark, <u>Current Injection in Solids</u>, (Academic Press, New York, 1970).
- G. P. Owen and A. Charlesby, J. Phys. C: Solid State Phys. <u>7</u>, L400 (1974).
- J. R. Macdonald and M. K. Brachman, Rev. Mod. Phys. <u>28</u>, 393 (1956).
- J. R. Macdonald and C. A. Barlow, Jr., Rev. Mod. Phys. <u>35</u>, 940 (1963).
- C. Bucci and R. Fieschi, Phys. Rev. Lett. <u>12</u>, 16 (1964);
  C. Bucci, R. Fieschi, and G. Guidi, Phys. Rev. <u>148</u>, 816 (1966).
- 10. B. K. P. Scaife, J. Phys. D: Appl. Phys. 7, L171 (1974).
- H. M. Gupta and R. J. Overstraeten, J. Phys. C: Solid State Phys. <u>7</u>, 3560 (1974).
- 12. H. Scher and M. Lax, Phys. Rev. <u>B7</u>, 4491, 4502 (1973).
- 13. H. Scher and E. Montroll, Phys. Rev. <u>B15</u>, to be published.
- C. Kittel, Introduction to Solid State Physics, 4th Ed., (John Wiley, New York, 1971), p. 270.
- C. A. Barlow, Jr. and J. R. Macdonald, Adv. in Electrochem. and Electrochem. Eng. <u>6</u>, 1 (1967).
- 16. W. R. Fawcett, J. Chem. Phys. <u>61</u>, 3842 (1974).
- M. J. Sparnaay, Rec. Trav. Chim. <u>77</u>, 872 (1958); J. Electroanal. Chem. <u>37</u>, 65 (1972).
- G. Jaffé, Ann. Physik <u>16</u>, 217, 249 (1933); Phys. Rev. <u>85</u>, 354 (1952).
- 19. J. R. Macdonald, J. Appl. Phys., to be published.
- 20. J. R. Macdonald, Solid State Electronics 5, 11 (1962).
- 21. H. Chang and G. Jaffé, J. Chem. Phys. 20, 1071 (1952).
- 22. J. R. Macdonald, J. Chem. Phys. <u>58</u>, 4982 (1973).
- 23. J. Frenkel, <u>Kinetic Theory of Liquids</u> (Oxford University Press, New York, 1946), p. 36.
- 24. K. L. Kliewer and J. S. Koehler, Phys. Rev. <u>140</u>, A1226 (1965).
- 25. L. M. Slifkin, J. de Physique <u>34</u>, C9-247 (1973).
- 26. J. R. Macdonald, J. Appl. Phys. <u>45</u>, 73 (1974).
- 27. J. R. Macdonald, J. Chem. Phys. 22, 1317 (1954).
- 28. J. R. Macdonald, J. Chem. Phys. <u>29</u>, 1346 (1958).
- 29. J. R. Macdonald, J. Chem. Phys. <u>30</u>, 806 (1959).
- 30. P. M. Sutton, J. Am. Ceram. Soc. <u>47</u>, 188 (1964).
- P. M. Sutton, J. Am. Ceram. Soc. 47, 219 (1964).
  J. W. Mayer et al., Phys. Rev. 137, A295 (1965).
- 33. M. Maitrot et al., Rev. de Phys. Appl. <u>6</u>, 369 (1971).
- 34. R. P. Buck, J. Electroanal. Chem. 46, 1 (1973).
- 35. J. R. Macdonald, J. Chem. Phys. 40, 3735 (1964).
- 36. T. B. Grimley, Proc. Roy. Soc. (London) A201, 40 (1950).
- 37. D. O. Raleigh, Electroanal. Chem. 6, 87 (1973).
- 38. D. Miliotis and D. N. Yoon, J. Phys. Chem. Solids 30,

	12/1 (10/0)
30	1241 (1909). Yu V Plackov Prog in Surf and Mombrana Sai 7 57
39.	(1073)
40	D O Raleigh private communication
41	D O Raleigh and H R Crowe Solid State Comm 8 955
71.	(1970).
42.	D. O. Raleigh, J. Electrochem. Soc. 121, 633 (1974).
43.	E. Fatuzzo and S. Coppo, J. Appl. Phys. 43, 1457 (1972).
44.	R. D. Armstrong, J. Electroanal. Chem. 52, 43 (1974).
45.	A. R. von Hippel, Dielectrics and Waves, (John Wiley,
	New York, 1954), pp. 228-234.
46.	J. Volger, Prog. in Semiconductors 4, 207 (1960).
47.	L. K. H. Van Beek, Physica 26, 66 (1960).
48.	J. Schrama, Thesis, Univ. of Leiden (1957), pp. 32, 60.
49.	I. S. Goldstein, J. Appl. Phys. 45, 2447 (1974).
50.	H. H. Byer and L. G. Bobb, J. Appl. Phys. 45, 3739 (1974).
51.	I. M. Novosel'skii et al., Soviet Electrochemistry 8, 546
	(1972).
52.	J. R. Macdonald, J. Chem. Phys. 23, 275 (1955).
53.	J. E. Bauerle, J. Phys. Chem. Solids 30, 2657 (1969).
54.	J. R. Macdonald, J. Electroanal. Chem. 32, 317 (1971).
55.	J. R. Macdonald, J. Electroanal. Chem. 53, 1 (1974).
56.	J. R. Macdonald, J. Chem. Phys. 61, 3977 (1974).
57.	K. S. Cole and R. H. Cole, J. Chem. Phys. 9, 341 (1941).
58.	I. M. Hodge et al., J. Electroanal. Chem. 58, 429 (1975).
59.	J. R. Macdonald, J. Chem. Phys. 54, 2026 (1971).
60.	F. A. Grant, J. Appl. Phys. 29, 76 (1958).
61.	D. R. Powell and J. R. Macdonald, Computer J. 15, 148 (1972);
	16, 51 (1973). Also, J. R. Macdonald, Am. J. Phys. 43, 372
	(1975).
62.	J. R. Macdonald, Phys. Rev. <u>92</u> , 4 (1953).
63.	R. J. Friauf, J. Chem. Phys. 22, 1329 (1954).
64.	J. H. Beaumont and P. W. M. Jacobs, J. Phys. Chem. Solids
	<u>28, 657 (1967).</u>
65.	J. R. Macdonald, J. Appl. Phys. <u>44</u> , 3455 (1973).
66.	J. R. Macdonald, J. Phys. C: Solid State Phys. 7, L327
	(1974); <u>8</u> , L63 (correction) (1975).
67.	P. Langevin, Ann. Chim. Phys. <u>28</u> , 289, 433 (1903).
68.	M. Lax, Phys. Rev. <u>119</u> , 1502 (1960).

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## DISCUSSION

ARMSTRONG : In superionic conductors the Debye length is often less than a typical atomic size, which suggests that your theories are not directly applicable in this case.

MACDONALD : To some degree this conclusion is doubtless true. Instead of an ordinary diffuse double layer extending over many crystal planes being present, the double layer capacitance may be a sort of inner-layer capacitance associated with charge in the plane immediately next to the electrode. Although this would effect the d.l. capacitance which arises in my theory, it should not necessarily have a large effect on the reaction, diffusion and recombinaison terms in the theory. It seems likely that most of the results of my theory would still be applicable, perhaps with a very large value of M(=e/2LD) inserted in appropriate parts of the theory.

WAGNER : Would you please provide us with a physical picture of the capacitance and/or pseudocapacitance for a (0,0) completely blocking and ( $\infty$ ,0) partially blocking electrodes ?

MACDONALD : The (0,0) double layer capacitance is often taken to be a diffuse (space distributed) space charge capacitance arising from the competing effects of electric field and diffusion. It was originally discussed by Gouy and by Chapman. The  $(\infty,0)$  or  $(0,\infty)$  low-frequency limiting capacitance is more complicated. It arises when a Warburg impedance is limited because the associated diffusion length fills the entire space between electrodes. At sufficiently low frequencies this must happen for any finite electrode separation. This low-frequencylimiting capacitance is <u>not</u> a pure space charge capacitance but is associated with diffusion to an electrode, and, in the usual case, with electron transfer there.

VOÏNOV : When you represent an interface by a capacitor (double layer) in parallel with a resistance (electrode reaction) do you imply that in open-circuit the capacitor is not charged ?

MACDONALD : I only assume the capacitor is charged when some potential difference occurs across it. In either a.c. or d.c. experiments, potentials are present which determine the charge on a given capacitor and, sometimes, determine its magnitude as well.

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BONANOS : In most experimental situations the system of electrodes, interfaces, bulk, grain boundary properties etc. are effectively connected in series. What is the relevance of the Voight and Maxwell models in such situations ?

MACDONALD : The Voigt and Maxwell models are entirely equivalent electrically for proper element choices. One will generally use the one which a) arises naturally from theory and/or b) affords the most transparent explanation of the various physical processes assumed to be present.

HENISCH : How is the contour of the built-in diffusion barrier modified by the induced displacement of charge carriers in the bulk ?

MACDONALD : The barrier depends on the potential difference between bulk and surface. In equilibrium this potential difference is just the diffusion potential  $V_{D}$ . In other cases, the appropriate potential is  $(V_{\Pi}+\psi_{A})$ where  $\psi_{a}$  is the electrostatic potential difference. The expression for the contour of the barrier, i.e.  $\psi(X)$ (where  $\psi$  is the mean electrostatic potential) as a function of X, is too complicated to give here. In principle, it should be possible to eliminate a barrier by the application of a potential difference opposite to  $V_{D}$ . But when one uses symmetric electrodes with a similar or identical barrier at each, the application of an external potential difference increases the barrier height at one electrode and decreases it at the other. Thus there will never be a condition where both barriers are simultaneously absent.

HEYNE : Can you clarify what exactly you mean by <u>un</u>coupled ? I understand that coupling by Poisson's equation is always present.

MACDONALD : In the supported electrolyte case a large concentration of a supporting solute is present. The positive and negative ions of this fully dissociated salt are usually assumed to be completely blocked. In addition, the charges of interest (perhaps only partly blocked) are present at a much lower concentration. Therefore, the field gradient is primarily established by the high concentration species, and the low concentration ones are largely uncoupled. In other words, a charge in the concentration of the low-concentration negative species at a given location need not be compensated by a corresponding charge in the concentration of the low-concentration positive species.

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RALEIGH : Could you comment on the relative nature of Warburg impedance in supported and unsupported electrolytic media ? The concept of a Warburg impedance in an unsupported medium may be confusing, since it was originally derived for field-free diffusion in supported electrolytes.

MACDONALD : The Warburg impedance arises at frequencies where diffusion to an electrode is the rate limiting step. It can therefore appear in either supported or unsupported situations, with appropriate differences arising from the different effects of Poisson equation charge coupling in the two cases. The original derivation of the Warburg impedance was for a single electrode (semi-infinite) situation. All realizable situations involve finite dimensions. Therefore, one would expect the finite length Warburg formula to apply in most cases rather then the original infinite length one.