SOME ASPECTS OF POLARIZATION IN IONIC CRYSTALS WITH ELECTRODE REACTIONS†

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(Received 20 November 1975; accepted in revised form 15 March 1976)

Abstract—Space charge polarization involving an electrode reaction with surface adsorption is examined. As recently demonstrated by Lányi, the presence of such a process may be represented using a complex, frequency-dependent rate constant. Lányi’s rate constant is shown to be normally a special case of a more general complex rate constant following from earlier work of Armstrong and others on electrode reactions with an adsorbed intermediate species. An exact expression, based on earlier work of one of the authors, is given for the impedance of a uni-univalent extrinsic-conduction system with mobile charges of only a single sign and for which the electrode processes involve such adsorbed intermediate species. Conditions are then found which reduce the exact results to the approximate expressions for series capacitance and resistance derived by Lányi for his special case of calcium-doped NaCl. These conditions are well satisfied for his specific choices of parameter values. Curves showing the exact frequency response of various series and parallel quantities are presented, together with complex impedance plane results. Finally, it is shown how under conditions that include the range of usual experimental interest the entire space-charge, electron reaction/adsorption system can be well represented by a simple equivalent circuit of frequency-independent elements.

INTRODUCTION

In the interesting and valuable paper by Lányi[1], “Polarization in Ionic Crystals with Incompletely Blocking Electrode”, a frequency-dependent, complex electrode-reaction rate constant, $k^* = k' + ik''$, is introduced in an effort to explain a.c. space charge polarization results for calcium-doped NaCl, probably measured in the range of 400–600°C. Lányi assumes that only cation vacancies are mobile (here termed a one-mobile situation) and states that his theoretical approach involving $k^*$ leads to better agreement with experiment than is possible with earlier theories which use a real, frequency-independent electrode rate constant[2–5].

Lányi suggests that his formalism, a generalization of earlier work[2–4] to a complex rate constant situation, particularly applies to polarization cells of the non-parent-metal electrode[6], such as Pt|NaCl|Pt, which he expects may sustain steady, stationary currents. Since his $k^*$ approaches zero as $\omega$, the radial frequency of the a.c. applied voltage, goes to zero, however, his treatment reduces to complete blocking in this limit and thus cannot lead to non-zero d.c. conductance, in contradistinction to the results of earlier theories. It is not clear whether Lányi includes time-invariant d.c. under “stationary” current. Note that a direct current may or may not be stationary even though it does not change perceptibly during the time of an experiment (or $\omega \to 0$). For such quasi-stationary situations, it is necessary that $k^*$ be non-zero at least down to $\omega_{\text{min}}$, the minimum frequency of measurement in the a.c. case.

Elsewhere, Lányi’s work has been shown to be a special case of a more general approach involving an electrode reaction with an adsorbed intermediate species present[7]. Quasistatic calculations leading to the differential capacitance arising in an electrolyte system when specific ionic adsorption takes place at an electrode are well known[8]. In addition, there has been considerable earlier work published on small-signal a.c. response in the adsorbed intermediate situation. In particular, it is worth citing 1970 and 1974 papers by Epelboin et al.[9, 10] and 1972 and 1974 papers by Armstrong et al.[11, 12] on the a.c. impedance of complex electrochemical reactions. Other earlier related work is cited by Armstrong. These calculations, which do not involve a complex rate constant approach, apply best to a supported electrolyte situation, however, and should be appreciably less applicable to Lányi’s unsupported case[7]. The complex rate constant approach, introduced by Lányi[1], can apply to either supported or unsupported conditions[7] and is thus more comprehensive. It has been shown elsewhere[7] how it may be extended to encompass more general electrode and bulk conduction conditions than those treated by Lányi.

The formal treatment of Ref. [7] demonstrates how the various specific parameters which enter the complex rate constant approach to electrode reactions with adsorption can be expressed in terms of more basic response parameters of the overall system. It also shows in principle how the a.c. response of the system may be calculated explicitly in the general intrinsic-extrinsic conduction case involving charges of both signs mobile.
No interpretive numerical or pictorial results are given, however, and the present paper remedies this lack for Lányi's specific case: strongly extrinsic n-type ionic Schottky-defect materials with positive charges taken immobile.

LÁNYI'S SERIES CAPACITANCE

One of Lányi's most significant results in his expression for series capacitance per unit electrode area, \( C_0 \), as a function of \( \omega \). The unit-area qualifier will be omitted for brevity in the rest of this paper. In order to make direct contact with earlier work, it will be convenient to express Lányi's result in terms of dimensionless variables. Define the dielectric relaxation time as \( \tau_D = \epsilon/4\pi\sigma \), where \( \epsilon \) and \( \sigma \) are the bulk permittivity and conductivity. Introduce the normalized frequency \( \Omega = \omega\tau_D \). Further, let [2,4]

\[ r_* = \left( |D_0|k_0 \right) r_0 \]

and \( r_0 = \left( \kappa_0/k_0 \right) b_0 \), where the \( r_* \)'s are dimensionless boundary value parameters which are simply related to the real \( k_0 \) and \( k_0 \) rate constants introduced by Lányi. Here \( l \) is the separation length of identical plane parallel electrodes; \( D_0 \) is the diffusion coefficient for cation vacancies; \( k_0 \) and \( k_0 \) are ordinary electrochemical rate constants for forward and backward reactions; and \( b_0 \) is defined by Lányi as the thickness of the layer on the surface of the electrode in which neutralized ions may be deposited. An internal relaxation time associated with the adsorption process (not necessarily that measured externally for the system as a whole) may also be defined from \( r_{sl} \), as \( \tau = \tau_D / r_{sl} = b_0/k_0 \). One then finds, on using Lányi's derived frequency dependence for \( k^* \), the following expression for the complex, dimensionless boundary condition parameter \( r_*^2 \),

\[ r_*^2 = r_{sl}^2 = \frac{1}{|D_0|} k_0 r_{sl}^2 + i\pi r_{sl}^2 = \Omega r_{sl}^2 / (\Omega - i r_{sl}) = \Omega r_{sl}^2 / (\Omega + i r_{sl}). \]

The presence of specific adsorption has thus led to the replacement of the conventional constant boundary condition parameter by a frequency-dependent complex quantity. As \( \Omega \to 0 \), \( r_*^2 \to 0 \), and for \( \Omega \to \infty \), \( r_* \to r_{sl} \). Note that when \( r_{sl} = 0 \), \( r_*^2 = r_{sl}^2 \), equivalent to the frequency-independent quantity previously termed \( r_0 \) [5] or \( \rho [4] \). In the one-mobile situation, the corresponding boundary condition parameter for positive charges, \( r_0 \) or \( r_* \), may be taken identically zero [13].

In the conventional treatment, \( r_0 = 0 \) ensures that negative charges are completely blocked at the electrode while \( r_* \to \infty \) specifies an infinitely fast (relative to other system processes) electrode reaction rate. Further interpretation of \( r_* \) will be given later in this paper. The condition \( r_0 \to 0 \) leads to \( r_* \to \infty \). The resulting \( r_*^2 = r_{sl}^2 \) case may be physically interpreted as a parent metal electrode situation: that where the mobile charges in the material of interest are ions of the electrode atoms. Then the ions can discharge in the ordinary way, building up the electrode. There is therefore no effective adsorption and \( r_*^2 \) will be real and frequency independent.

Now define a Debye length in the one-mobile situation as \( L_{D1} \), and let \( M_1 = 1/2L_{D1} \).

\[ \frac{L_{D1}}{\epsilon} = \frac{kT}{4\pi e^2 \sigma n_0}, \]

(2)

where \( k \) is Boltzmann's constant, \( T \) is the absolute temperature, \( e \) is the protonic charge, and \( n_0 \) is the equilibrium bulk concentration of unassociated, mobile cationic vacancies. Lányi's approximate result for \( C_0 \) (his eqn 34) may now be written in the more transparent form

\[ C_0/C_S = \frac{r_{sl}^2(1 + \alpha)^2 + \Omega^2}{r_{sl}^2(1 + \alpha) + \Omega^2}, \]

(3)

where \( \alpha = L_{D1}/L_{D1} = (k_0/k_0) b_0 \), and \( L_{D1} \) is the appropriate Debye length. Note that the high frequency limiting value of the bulk conductance is \( G_S = R_{91}^{-1} = (1/\mu_0) \), where the Einstein relation \( \mu_0 = (kT/e)C_0 \), has been used in eqn (4), and \( \mu_0 \) is the vacancy mobility. The dielectric relaxation time, \( \tau_D \), is also equal to \( C_0 L_{D1} \). The quantity \( L_{D1} \) in (4) is an effective recombination or reaction length.

Equation (3) shows that \( C_0 \to C_0 \) for \( \Omega \gg r_{sl} (1 + \alpha) \); i.e. \( \omega \gg \tau_p^{-1} (1 + \alpha) \). This limit is essentially correct [14] for a fully dissociated, one-mobile, situation as long as the resulting \( \Omega < 1 \), the main area of interest in space charge polarization experiments [13-15]. But note that \( r_{sl} (1 + \alpha) \) may possibly exceed unity. Then \( C_0 \) no longer reduces exactly to \( C_0 \) and must be calculated in the \( \Omega \gg 1 \) region from the exact results developed later in this paper. When \( r_{sl} \neq 0 \) and \( \Omega > 0 \), \( C_0 \to C_0 \) as \( C_0 \to \infty \), possibly much greater than \( C_0 \). Note that the smaller \( r_{sl} \) and thus the larger \( \alpha \), however, the lower the frequency range at which the transition to \( C_0 \) takes place. Clearly, \( \alpha \) determines the amount of low-frequency-limiting capacitance of the system, \( C_0 = \alpha (r_{sl}/2r_{sl}^2) C_0 \), arising directly from specific adsorption.

When \( r_{sl} \neq 0 \) and \( r_{sl} = 0 \), eqn (3) yields

\[ C_0 \to C_0 [1 + (r_{sl}/2r_{sl}^2) \Omega^2], \]

(5)

which goes to \( \infty \) as \( \Omega \to 0 \). Lányi argues that this reduction leads to the Beaumont-Jacobs (BJ) series capacitance [4], which he states also follows a \( \omega^{-2} \) dependence at low \( \omega \) values. This conclusion is incorrect. Beaumont and Jacobs implicitly take \( r_{sl} = 0 \) and actually work with the components of the polarization admittance of their system [4, 5, 16], \( Y_1 = Y_1 - G_1 - J 0 \), and \( Y_T \) is the total admittance. They calculate no series expressions themselves. The parallel components of \( Y_1 = G_1 - J 0 \) should not be used directly to obtain series components from \( Z_1 = R_{11}^{-1} \) as Lányi evidently did since this procedure does not in general lead to a physically significant series capacitance.

The BJ results are actually consistent [13] with the very general equivalent circuit shown in Fig. 1 [5, 13-16] for which \( G = R_{91}^{-1} = R_{91}^{-1} + R_{91}^{-1} \). In the one-mobile BJ
situation, where \( r^*_p = r_{sp} = \rho \), the d.c. resistance, \( R_D \), is not infinite, as it is in Lányi's treatment, unless \( \rho = 0 \). In fact, one finds [5, 13, 15], \( R_D = (1 + 2\rho^2)R_\infty \) and \( R_\infty = (1 + 0.5p)R_\infty \). The circuit of Fig. 1 is constructed with a maximum number of frequency-independent elements, includes the necessary \( C_2 \) and \( R_E \) in their proper places, and puts all frequency dependent elements in the impedance \( Z \). When the series quantities \( C_1(\omega) \) and \( R_1(\omega) \) are calculated[13] from the BJ result for \( Z_r \), one finds that both \( C_1 \) and \( R_1 \) properly approach constant values as \( \omega \to 0 \). This result was, in fact, well known long before Lányi's work [5, 11-16]. The quantities \( C_1 \) and \( R_1 \) are the physically significant series elements here. It is not physically meaningful, however, to express the total \( Z \) only in terms of overall series elements (not \( C_1 \) and \( R_1 \)) when \( R_D < \infty \) since the series capacitance thus obtained will then indeed show a \( \omega^{-2} \) dependence as \( \omega \to 0 \). Since the high-frequency-limiting resistance \( R_\infty \) is made up from \( R_D \), the discharge or d.c. resistance, and \( R_E \) in parallel, it is clear that when \( R_D = \infty \) and the d.c. conductance is zero, \( R_E \) is just \( R_\infty \). As the following work demonstrates, this is just the case in Lányi's \( r_{sp} \neq 0 \) situation of pure adsorption. It is not the case, however, where the situation is not restricted to pure adsorption and \( R_D \) is finite.

**EXACT RESULTS FOR THE ONE-MOBILE CONDUCTION SITUATION**

Lányi's expressions for series capacitance and resistance are derived for a uni-univalent situation in which only negative charges are mobile. An exact solution of the general space charge-electrode reaction problem has been given, however, in which valences of positive and negative charges are taken arbitrary and both positive and negative species may be mobile with arbitrary mobilities [5]. Further, this solution involves arbitrary \( r_p \) and \( r_n \) boundary condition parameters instead of the Lányi special choices \( r_p = 0 \) and \( r_n \) given by eqn (1). Thus, the above solution may be readily extended to include more general complex frequency-dependent expressions for \( r_p \) and \( r_n \) than those applicable in Lányi's special situation.

For example, consider the work of Armstrong and collaborators [11, 12] on reactions with adsorbed intermediates which results directly in expressions for the faradaic admittance of the surface processes. As shown above, Lányi's complex rate constant obeys the limiting conditions \( r^*_p \to 0 \) as \( \omega \to 0 \) and \( r^*_n \to r_{sp} \) as \( \omega \to \infty \). Since finite rate constants contribute to the admittance of the system and since Armstrong's analysis shows that the limiting values of the contribution to the conductance \( G \), from electrode processes only, are (for the Armstrong-Henderson model) \( G \to R_\infty^{-1} \) (not the \( R_\infty \) of the present paper) as \( \omega \to \infty \) and \( G \to R^{-1} + R_\infty^{-1} \) as \( \omega \to 0 \), the effect of an adsorbed intermediate species can cause the complex rate constant \( r^*_p \) to go to zero as \( \omega \to 0 \) but to some finite value, say \( r_{sp} \). This additional dimensionless boundary condition parameter, which will be zero (Lányi) or positive in most but not all [11] cases of interest, here determines the \( R_D \) and \( R_E \) of Fig. 1 through \( R_D = R_0/R_\infty = [1 + (2/\rho)a_0] \) and \( R_E = R_0/R_\infty = 1 + (r_{sp}a_0) / 2 \) in the one-mobile situation. The expressions for the normalized quantities \( R_D \) and \( R_E \) are more complicated in the general case [5, 13, 15] but still involve \( r_{sp} \) and its analogue \( r_p \). The more general form of \( r^*_p \) consistent with the Armstrong-Henderson analysis is, therefore,

\[
r^*_p = r_{sp} = \frac{(r_{sp} - r_{sp})}{1 + i\omega},
\]

which correctly satisfies the above limiting conditions. In order to make contact with Lányi's complex rate constant \( r^*_p \) (eqn 1) we identify the above time constant \( \tau \) with \( n_o/(\tau_1 \tau_2) \), giving

\[
r^*_p = \frac{\Omega^2 r_{sp} + \Omega r_{sp} + i(\Omega r_{sp} - r_{sp})}{r_{sp} + \Omega^2},
\]

which reduces to Lányi's rate constant,

\[
r^*_n = \frac{\Omega^2 r_{sp} + \Omega r_{sp} - r_{sp}}{r_{sp} + \Omega^2},
\]

in the limit \( r_{sp} \to 0 \). The above very heuristic derivation of \( r^*_n \) has been avoided in subsequent work [7]. There, an \( ab \) initio calculation leads to eqn (5) above for \( r^*_p \) and to explicit expressions for \( r_{sp} \) and \( \tau \) as well in terms of more basic properties of the material of interest and the electrode reactions present.

Consider now an extrinsic or intrinsic conduction situation involving, for simplicity, equal valence numbers for positive and negative mobile charges but arbitrary mobilities for these species. When an adsorbed intermediate species is present, the exact impedance results for this case may be obtained merely by replacing the \( r_{sp} \) and \( r_{p} \) factors appearing in the full solution [5] by \( r^*_p \) and \( r^*_p \) terms of the form of eqn (5). Such replacement is valid for eqns (A33) to (A43) of Ref. [5] but, because eqn (A43) involves the \( \Omega = 0 \) values of \( r^*_p \) and \( r^*_n \), the analysis leading to an explicit expression for the \( Z = R_\infty + (i\omega C_1)^{-1} \) of Fig. 1 must be slightly generalized when \( r^*_p \) and \( r^*_n \) are frequency dependent.

Frequency response results and complex impedance plane plots for the above rather general situation will be published elsewhere. The general expressions for the admittance \( Y \) or the impedance \( Z \) are quite complicated in this situation but simplify greatly in the present one-mobile case. They will, therefore, be given here for this situation only, using the general expression of eqn (5) for \( r^*_p \) rather than the eqn (1) special form following from Lányi's work. In the one-mobile situation with negative charges mobile, \( r^*_p \) may be taken identically zero since immobile carriers do not react at the electrodes.
Consider normalized quantities, denoted by a subscript "N." Normalize capacitances with \( C \), resistances and impedances with \( R \). If \( \mu_n \) and \( \mu_p \) are the mobilities of the mobile species, the present one-mobile limit involves \( \pi_m = \mu_n/\mu_p \to \infty \). The parameter \( \pi_m = z_m/z_p \) of the general theory is unity here in the equal valence number case. Then let \( \gamma_m = \gamma_p \approx \gamma \). Simplification in the \( \pi_m \to \infty \) limit is easiest when the \( \theta_i \) eigenvalues of the theory are chosen as in eqns (A7) and (A8) of Ref. [15]. Then \( \theta_i \to i = 1 \) and \( \theta_i \to \delta_i(1 + i \Omega) \), where

\[
\delta_n = n_{00}(n_0 + p_0),
\]

and \( n_0 \) and \( p_0 \) are equilibrium bulk values of the negative and positive charge concentrations. In the \( \pi_m = 1 \) intrinsic conduction situation, \( n_0 = p_0 \), while when the system is strongly \( n \)-type extrinsic, as in Lányi’s doped NaCl case, \( n_0 \gg p_0 \).[5]

Next, define \( M = 1/2L_0 \), where \( L_0 = L_0; = (ekT/4\pi(z_0 e)^2(n_0 + p_0)^2) \). Note that \( M(d_0) = M \), when \( \pi_m = 1 \) and \( L_0 \) is generalized to include \( z_0 \). Let

\[
\begin{align*}
\tau_1 &= M_\theta \cdot \text{ctnh}(M_\theta) - 1 \\
&= M_1(1 + i \Omega)^{-1} \cdot \text{ctnh}(M_1(1 + i \Omega)) - 1,
\end{align*}
\]

and

\[
\begin{align*}
\tau_m &= (\tau_{n-} - \tau_{n0}).
\end{align*}
\]

Then, the exact expression for \( Y_{N0} = Z_{N0} \) when \( \pi_m \to \infty \) is

\[
\begin{align*}
Y_{N0} = (i\Omega g_{a0})[i\tau_1(1 + i \Omega)^{-1} + 0.5 \xi_m \tau_{n-} (1 + i \Omega \xi_m)^{-1}],
\end{align*}
\]

where

\[
\begin{align*}
g_{a0} &= 1 + 0.5 \xi_m, \\
\xi_m &= \tau_{n-}/[\tau_{D0} - 1] \cdot \text{ctnh}(M_1(1 + i \Omega)).
\end{align*}
\]

To obtain the special Lányi situation, it is only necessary to let \( \tau_{D0} \to 0 \). Incidentally, Lányi makes the approximation \( \text{ctnh}(M_1(1 + i \Omega)) \approx 1 \), adequate when \( M_1 \gg 1 \), the usual experimental case.

As before, let a subscript 0 denote the \( 0-0 \) limit. It immediately follows from (11) that

\[
C_{N0} = g_{a0}(s + \beta), \tag{14}
\]

and

\[
R_{N0} = g_{a0} \left[ \frac{(0.5 r_1 - 1) + \xi_{n0} \beta}{(s + \beta)^2} \right]. \tag{15}
\]

where

\[
\begin{align*}
s &= M_1 \cdot \text{ctnh}(M_1) - 1 = r_1 - 1, \\
\beta &= 0.5 \xi_{n0} \tau_{n-},
\end{align*}
\]

When \( \tau_{D0} = 0 \), \( \beta = M_1 \alpha \). The total parallel capacitance in the \( \Omega \to 0 \) limit, \( C_{P0} = C_{N0} + C_{N1} \), is, in normalized form,

\[
C_{P0} = (1 - g_{a0}) + g_{a0}(r_1 + \beta). \tag{18}
\]

Thus, \( C_{P0} \) will greatly exceed \( C_{P0} = M_1 \alpha \), when \( g_{a0}(r_1 + \beta) \gg M_1 \). When \( \alpha < 1 \) and \( \xi_{n0} = 1 \), this condition reduces to \( \alpha \gg 1 \) for the usual \( M_1 \gg 1 \) situation. Specific adsorption, where \( \alpha \) can be much larger than unity, can thus lead to a total low frequency capacitance much greater than the ordinary double layer capacitance \( C_0 \) [8, 9–12].

The specific adsorption capacitance and resistance arise from the terms involving \( \beta \) in eqns (11), (14) and (15).

These results agree with earlier ones[5, 13, 15] when \( \beta = 0 \). In particular, when \( \tau_{D0} = 0 \) the resulting value of \( \tau_{D0} \) is just the exact, two-electrode diffuse layer capacitance found for complete blocking in the limit of small applied potential difference[17, 18]. This is a required result here when \( \tau_{D0} = 0 \) and \( \beta = 0 \), but not otherwise, one may identify Lányi’s \( R \) and \( C \) with the present \( R \) and \( C \). Lányi’s approximate result for \( R \) may be written in the form

\[
R_{C0} = \frac{1}{\tau_{D0}} \left[ \frac{r_2(1 + 2 \alpha \tau_0) + \Omega^2}{r_2(1 + \alpha^2) + \Omega^2} \right]. \tag{19}
\]

Equations (3) and (19) do, in fact, agree with (14) and (15), respectively, for \( \alpha = 0 \) when Lányi’s assumption \( M_1 \gg 1 \) is made. Then \( r_1 = M_1 = s \). The exact results for \( C_{n0} \) and \( R_{n0} \) which follow immediately from eqn (11) may be shown to reduce to eqns (3) and (19), respectively, under the following conditions: (a) \( \tau_{D0} = 0 \); (b) \( M_1 = 1 \); (c) \( M_1 \gg r_{n-} \); (d) \( \Omega \ll 1 \); and (e) \( \xi_{n0} = 1 \). All these conditions are well satisfied in Lányi’s work. Equations (3) and (19) should not be used in place of (11), when some of these conditions are not satisfied.

**PARAMETER VALUES**

In comparing theory with Lányi’s experimental results for NaCl, it is of interest to consider the magnitudes of various quantities which occur in the theory yet are not directly specified by Lányi. From Lányi’s theoretically expected value of \( C_{n0} \approx 0.8 \mu \text{F/cm}^2 \) at 400°C, one obtains \( L_0 = 33.2 \text{ Å} \) on taking \( \epsilon = 6 \) for NaCl. In turn, this result yields \( n_0 = 1.74 \times 10^{14} \text{ cm}^{-3} \), slightly smaller than the value of \( 2.24 \times 10^{14} \text{ cm}^{-3} \) expected for 100 ppm doping with CaCl and no association. (Lányi erroneously quotes \( \tau_{D0} = 1.25 \times 10^{18} \text{ cm}^{-3} \) instead of \( 2.24 \times 10^{18} \text{ cm}^{-3} \). It is not entirely clear what value Lányi found for bulk conductivity at 400°C. Using his lower quoted value of \( 2.5 \times 10^{-6} \text{ (ohm-cm)}^{-1} \), one finds \( D_0 = 4.04 \times 10^{-7} \text{ cm}^2/\text{sec} \) from the present value of \( n_0 \). With \( l = 0.1 \text{ cm} \), one obtains \( C_{n0} = 5.31 \mu \text{F/cm}^2 \) and \( G_n = 2.5 \times 10^{-5} \text{ mho/cm}^2 \), leading to \( \tau_0 = 2.13 \times 10^{-7} \text{ sec} \) and \( M_1 = 1.51 \times 10^3 \). This value of \( \tau_0 \) corresponds, for \( \Omega = 10^{-2} \), to a frequency of about 7.5 Hz. On employing Lányi’s values of \( k_0 = 3.9 \times 10^{-7} \text{ cm/sec} \) and
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(k_0/l_0) = 0.85 sec^{-1}, one finds L_0 = 4.59 \times 10^{-7} cm, yielding \( \alpha = 1.38 \). It follows from this result and the above value of \( M_T \) that (r_0/r_1) = 4.16 \times 10^3. On the other hand, the relation (r_0/r_1) = (l/l_0) \times 10^3 yields 5.34 \times 10^3, showing a small discrepancy in some of the above input figures.

Agreement is adequate in view of the uncertainty in some of these figures. The relations (r_0/r_1) = (l/l_0) \times 10^3 finally yield \( r_0 \approx 0.097 \) and \( r_1 \approx 1.81 \times 10^3 \).

In order to account for his experimental results using a form of eqn (4), L\'anyi required values of \( C_0 \) and \( \alpha \) about 2.5 times larger than those above. He heuristically achieved them by reducing the \( L_0 \) appearing in the expression for \( C_0 \) and the first term given for \( \alpha \) in eqn (4) by the factor exp (-\( \phi_0/2kT \)), where \( \phi_0 \) is a Frenkel-layer static potential difference between the free surface of the material and the bulk[19]. His assumed value of \( \phi_0 = -0.39 \) volt yields 28.8 for the above factor at \( T = 400^\circ \). Then \( M_T = 4.35 \times 10^6 \) and \( \alpha \) becomes 70.9. It is likely that this method of introducing \( \phi_0 \) will at best be a poor first approximation[5, 19], but it will be followed here since no exact approach is yet available. The 28.8 factor leads to \( r_0 = 2.57 \times 10^{-16} \) sec and to \( r_1 = 2.18 \times 10^{-10} \) sec. It appears that somewhat better agreement with L\'anyi's experimental results for \( C_T(\omega) \) of NaCl may be obtained with the slightly different choices \( M_T = 3 \times 10^6 \) and \( r_1 = 5.05 \times 10^{-10} \) sec, leading to \( \zeta_0 = 1.98 \times 10^{-6} \). These values, together with \( r_0 = 0.097 \) and \( \chi = 2000 \) will be employed in the subsequent calculations. Here \( \chi \) is a measure of the extrinsic/intrinsic concentration ratio[5]. Theoretical results are essentially independent of \( |\chi| \) in the strongly extrinsic region where \( |\chi| > 10^4 \). The value of \( \alpha \) following from the above choices is 32.01.

**NUMERICAL RESULTS AND DISCUSSION**

The above numerical values of the parameters have been used in a computer program to calculate \( Z_{TN} \) and related quantities using eqn (11) for the one-mobile case. Figure 2 shows some of the results as a function of normalized frequency \( \Omega \). Here the normalized parallel quantities \( C_{PN} \) and \( G_{PN} \) follow from \( Y_{PN} = Z_{TN} = G_{PN} + i\Omega C_{PN} \), and, in the \( r_0 = 0 \) case, \( R_{DN} = \infty \), \( R_{DN} = 1 \), and \( Z_{TN} = (Z_{TN} + 1)/(1 + i\Omega Z_{TN} + 1) \).

Figure 2 shows that at sufficiently large \( \Omega \), \( R_{DN} \) and \( C_{PN} \) are both proportional to \( \Omega^{-1} \). \( C_{PN} \) here reaches its high-frequency limiting value of unity by \( \Omega \approx 10^{-2} \). At this same value of \( \Omega \), \( R_{DN} \) has substantially reached the limiting value of \( (2M_T)^{-1} \approx 1.667 \times 10^{-7} \) which follows from eqn (19). It turns out that the approximate eqns (3) and (19) yield results for \( C_{PN} = C_0/C_T = C_{PN} \) and \( R_{DN} = R_{DN} \) for the present parameter values within better than one per cent of the exact values for the range \( 0 \leq \Omega \approx 10^{-1} \). The true \( C_{PN} \) and \( R_{DN} \) values begin to drop below the L\'anyi high-frequency limiting values, however, for \( \Omega > 10^{-1} \) and are about 10% lower by \( \Omega = 1 \). Such drops are usually not significant, however, since most interesting behavior occurs for \( \Omega < 1 \).

It is the presence of specific adsorption (\( \alpha > 0 \)) which causes \( R_{DN} \) to be large here and \( C_T \) and \( C_{PN} \) to rise above their essentially common \( \Omega \to 0 \) value of \( C_{PN} = M_T = 3 \times 10^6 \) when \( \alpha = 0 \). The approximate \( \Omega^{-1/2} \) frequency dependence of \( C_{PN} \) and \( C_T \), apparent in the figure has been observed experimentally fairly frequently. Its appearance is insufficient evidence to ensure that specific adsorption is present, however, since it has been shown[13, 15] that similar behavior can occur when both positive and negative charges are mobile and \( \tau_f \) is real and constant. Detailed analysis of experimental results over a wide frequency range will, in general, be required to allow discrimination between the various situations which can lead to \( \Omega^{-1/2} \) behavior. Further, the limiting \( C_T \) slope found for \( \alpha \) appreciably bigger than its present value of 32 is actually \( -2 \), not \( -1.5 \). The \( \approx -1.5 \) slope evident in Fig. 2 thus arises here from the limited extent of the \( C_{DN} \) rise and is not an intrinsic feature of specific adsorption.

Although curves such as those in Fig. 2 are useful, an overall view of system response can be obtained by plotting the real and imaginary parts of \( Z_f \) or \( Z_{TN} \) in the complex plane as parametric functions of \( \omega \) or \( \Omega \), as in Fig. 3. The small left-hand semicircle in Fig. 3 arises from \( C_T \) and \( R_f \) in parallel; it is a bulk effect, independent of electrode boundary conditions, and occurs for \( \Omega \approx 0.1 \). Only when appreciable structure appears to the right of this semicircle, for \( \Omega \approx 0.1 \), will it generally be possible to explore electrode reaction, adsorption, diffusion, etc. effects[13, 15].
The following numerical results for the $r_{ax} = 0.2$ case demonstrate the quality of the present equivalent circuit approximation:

$$
\Omega \begin{bmatrix}
Z_{N1} \\
1.997 - 2.996 i \\
2.024 - 3.031 i \\
9.924 - 3.135 i \\
9.945 - 3.102 i \\
10.695 - 5.262 i \\
10.695 - 5.257 i
\end{bmatrix}
$$

The top numbers of each pair are the exact results; the bottom numbers are the appropriate ones following from the equivalent circuit of Fig. 4 together with eqns (14) and (15) for $C_{NO}$ and $R_{NO}$, respectively. As usual, $C_s = M_C$. A generalized, slightly more accurate circuit applicable when charges of both signs may be mobile will be presented in a later paper.

Frequently in the past, the admittance $Y_T$ has been plotted in the admittance plane or the effective complex dielectric constant, which is proportional to $(\omega)^{-1}Y_T$, has been plotted in the complex plane as Argand diagrams. It is worth emphasizing that whenever the equivalent circuit can be well approximated by a series combination of parallel RC circuits each associated with a single, well-defined physical process as in Fig. 4, it is more natural and preferable to plot $Z_T$ or $Z_{NO}$ in the complex impedance plane instead of $Y_T$ or $Y_{NO}$. Then, each parallel section can contribute a separate arc in the plane, provided the time constants of the sections are sufficiently well separated. Plotting $Y_T$ or $(\omega)^{-1}Y_T$ instead mixes together the effects of the separate parallel sections and renders analysis considerably more difficult, particularly when more than two sections are present. Even when the arcs in the impedance plane are not semicircles with centers on the real axis or when the time constants are close enough together to give some melding of arcs, impedance plane plotting is usually preferable to either of the other types of plots.

It is important to note that the general approach of Ref. [5], illustrated herein, can involve an $r_T$ of any form and frequency dependence, not just the $r_T^*$ of eqn (5). It also takes direct and integral account of any diffusion of the charged species to and from the electrode without the necessity of the somewhat ad hoc later introduction of such diffusion by Armstrong [12]. On the other hand, neither the present procedure nor those of Lanyi and Armstrong account explicitly for any diffusion (in/on the electrode) of the intermediate species. In Armstrong’s situation, it is assumed that both unadsorbed species are in the (liquid) solution and that both may diffuse. Because the present work takes proper account of the motion of the charged species in the material of interest, it automatically leads to such quantities as $C_{ax}$, $R_{ax}$, $R_s$, and $C_s$ rather than requiring them to be added heuristically to the equivalent circuit, as in Armstrong’s case.

The impedance and capacitance behavior of space charge systems with charge of one or both signs mobile and the $r_T^*$ of eqn (5) will be considered in detail elsewhere for various values of $r_{ax}$, $r_{ax}$, and $\xi_{ax}$. It will be shown that...
when \( r_n \neq 0 \) \( Z_r \) may show inductive behavior over an appreciable frequency range, in agreement with experimental observations[10, 20] and the predictions of Armstrong's work[11, 12], and, when \( r_n < 0 \), the low frequency limiting differential resistance, \( R_0 \), can even be negative as well.

Acknowledgements—The valuable suggestions and computer analysis of Dr. J. A. Gerber are highly appreciated. We also appreciate useful correspondence with Dr. Š. Lányi.

REFERENCES
15. Macdonald J. R., J. Chem. Phys. 61, 3977 (1974). The \( \varepsilon_0 \) of eqn (A6) of this paper should be replaced by \( \varepsilon_p \).