BINARY ELECTROLYTE SMALL-SIGNAL FREQUENCY RESPONSE

J. ROSS MACDONALD

Texas Instruments Incorporated, MS-227, P.O. Box 5474, Dallas, Texas 75222 (U.S.A.)

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I. INTRODUCTION

Interest is rapidly growing in the frequency response of a variety of binary charge systems. In such systems, two types of charge carrier are dominant; they have opposite signs and may have any mobility values, including zero for one of them. Representative systems include aqueous or other liquid electrolytes without a supporting electrolyte, glass electrodes, fused salts, and a variety of solid materials. Electrodes may be completely blocking for the charge carriers or may allow a conduction current, often involving an electrode reaction, to occur. Systems of the type considered are not purely ohmic at all frequencies, even neglecting their omnipresent geometric capacitance, $C_g$, but usually exhibit strong frequency-dependent capacitative and resistive effects.

In earlier work, some discussion of experimental results and of the various theories put forward to explain these small-signal frequency response results has been presented. In particular, considerable analysis has been given of the uni-univalent situation with equal mobilities for the two types of carriers. Recently, a detailed theory has been published which involves arbitrary valences and mobilities and relatively general electrode boundary conditions. It does not include specific ionic adsorption explicitly, however. This microscopic, charge-motion theory neglects no diffusion terms and yields results which satisfy Poisson's equation exactly everywhere within the material considered. Although the new theory applies in the fully dissociated extrinsic conduction situation as well as for intrinsic conditions, only the latter type of conduction will be considered in the present paper. Thus, the response of heavily doped solids at low temperatures is not covered by the present work and will be considered elsewhere.

The general theory yields an exact analytic result for system impedance as a function of frequency, but this result depends on many parameters and is far too complex to be immediately transparent. In the earlier work, therefore, only its limit as the applied frequency goes to zero has been considered in detail. The purpose of the present paper is to (a) use computer calculations of the exact expression for total impedance to show some of the major types of frequency response to which the theory leads in the intrinsic case; (b) derive from the results simple approximate frequency response formulas for cases of especial interest; (c) present several approximate equivalent circuits applicable over limited frequency ranges and made up only of essentially frequency-independent elements together with Warburg circuit elements (where appropriate); and (d) finally to compare
unsupported and supported results where pertinent. Frequency response will be shown by means of impedance-plane plots, by curves showing frequency dependence of the real and imaginary parts of the total impedance of the system, and by frequency response plots of its total parallel capacitance and conductance, derived from the total admittance. All of these types of presentations (and many more) have been used in showing small-signal response in the electrolyte, dielectric, and semiconductor fields. Although they involve some or all of the same information in different ways, all these methods are separately useful in comparing experimental and theoretical results. The presentation of all these approaches should also help make those authors who only use one method exclusively more aware of the virtues of other methods.

Note that although the analytic results of the general theory depend on a linearizing assumption and thus apply in principle only for small-signal conditions, they need not necessarily be limited only to electrolyte situations where the potential of zero electrode charge and the equilibrium potential coincide. In the absence of specific adsorption but even in the presence of a non-zero direct current, the theoretical results may apply provided the system is sufficiently linear around the bias point that the static components of charge are essentially constant and independent of position within the material considered. There is then no static field gradient in the material. Also, under these conditions an applied a.c. potential amplitude appreciably greater than \( kT/e \) may be applied as well without necessarily destroying the applicability of the theory. Here \( k \) is Boltzmann's constant, \( T \) the absolute temperature, and \( e \) the protonic charge.

Although full comparison of theory and experiment requires (or derives) knowledge of the individual valence numbers \( z_p \) and \( z_n \) and of the individual mobilities \( \mu_p \) and \( \mu_n \) of the positive charge carriers (bulk concentration \( p \)) and negative charge carriers (bulk concentration \( n \)), in the normalized form of the theory only the ratios \( \pi_n = z_n/p \) and \( \pi_m = \mu_n/\mu_p \) are necessary. For convenience and greatest generality many of the frequency response curves presented herein will thus involve normalized quantities. As we shall see, however, elimination of normalization when necessary is a simple process.

Finally, the description of a given space-charge situation with electrodes completely blocking or able to sustain charge transfer reactions requires parameters which define the specific boundary conditions at the electrodes. In the general theory, these dimensionless parameters are denoted \( r_p \) and \( r_n \). When two identical electrodes are considered, these parameters are taken to be the same at both. Complete blocking occurs when \( r_p = r_n = 0 \). On the other hand, for example, when \( r_p = 0 \) and \( r_n = \infty \), a condition we shall frequently consider herein, positive carriers are completely blocked and negative ones completely free to discharge or to appear at the electrodes. The condition \( r_n = \infty \) is thus indicative of an infinitely rapid reaction rate for the negative carriers. The later presentation of theoretical results is facilitated through use of the derived boundary condition quantities \( g_p = 1 + (r_p/2) \) and \( g_n = 1 + (r_n/2) \). A glossary of symbols used herein is presented at the end of the paper.

II. BASIC EQUIVALENT CIRCUITS

The exact equivalent circuit found in the earlier work is shown in Fig. 1a.
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Fig. 1. Exact equivalent circuits involving the frequency-dependent admittance $Y_i$. The two circuits are electrically equivalent. Here $G_{EN} = G_E/G_x$ and $G_x = G_D + G_F$.

Figure 1b provides an alternative circuit which exhibits the same overall impedance, $Z_T$, as that of Fig. 1a at all frequencies. These circuits apply for the case of two identical plane-parallel electrodes separated by a distance $l$. The effects of any electrode roughness are ignored here. Most of the results considered herein apply to the situation of two identical electrodes, the usual one for solids. Modifications in element values to make circuits applicable for the usual aqueous electrolyte situation of a single small working electrode and a much larger indifferent electrode will be discussed later. A comparison will be made later of the present results with the conventional equivalent circuit used in the supported case (see Fig. 20a).

All circuit elements herein apply for unit electrode area. Thus, the geometrical capacitance $C_g$ is given in the present case by $e/4\pi l$, where $e$ is the dielectric constant of the basic material in the absence of mobile charge. Now let $Y_\lambda = Z^{-1} = G_p + i\omega C_p$, where $G_p$ and $C_p$ are the parallel conductive and capacitative elements of the total admittance $Y_\lambda$ and $\omega$ is the radial frequency. It will be convenient hereafter to deal primarily with normalized quantities. Let us thus write $Y_{TN} = G_{PN} + i\omega C_{PN}$, where $\Omega = i\omega \tau_p \equiv i\omega C_g R_x$. The subscript "N" will be used herein to indicate normalization of capacitances with $C_g$, resistances with $R_x$, conductances with $G_x = R_x^{-1}$, and time constants with $\tau_D$. $G_\infty$ is the high-frequency limiting conductance of the system and is given by $(e/l)(z_n \mu_p n_l + z_n \mu_n n_l)$, equal to $(e/2l)(z_n \mu_p n_l + z_n \mu_n n_l)$, since $z_n n_l = z_p n_p$ because of electroneutrality in the bulk.

The remaining elements appearing in the circuits of Fig. 1 are $Y_i$, $G_E$, and $G_D$. Only $Y_i$ depends on frequency. The frequency dependences of the elements of $Z_i = Y_i^{-1}$, $R_i$, and $C_i$ will be considered in detail later. Note that we can write $Z_{IN} = R_{IN} + (i\Omega C_{IN})^{-1}$. Finally, it turns out that $G_{EN} = R_{EN}^{-1} = g_n/g_p g_n$ and $G_{DN} = R_{DN}^{-1} = 1 - G_{EN}$. Thus, $G_D + G_E = G_x$. Now $g_n = g_p f_n + g_p g_n$, and $g_n$ and $g_p$ have already been defined. Here $\tau_n = (1 + (\pi_m)^{-1})^{-1} = \mu_p/(\mu_n + \mu_p)$ and $r_p = (1 + (\pi_m)^{-1})^{-1} = \mu_n/(\mu_n + \mu_p)$. These definitions lead to $G_{EN} = \tau_n [1 + (r_n/2)]^{-1} + \mu_p [1 + (r_p/2)]^{-1}$ and $G_{DN} = \tau_n [1 + (2/r_n)]^{-1} + \mu_p [1 + (2/r_p)]^{-1}$. Thus when $r_p = r_n = 0$, $G_{EN} = 1$ and $G_{DN} = 0$. On the other hand, when $r_p = 0$ and $r_n = \infty$, $G_{EN} = \epsilon_p$ and $G_{DN} = \epsilon_n$. Note that since in general $G_{EN}^{-1} G_{DN} = R_{EN} - 1$, the term $G_{EN}^{-1} G_D$ in Fig. 1b may be rewritten as $(R_{EN} - 1) G_x = (R_{DN} - 1)^{-1} G_x$.

Figure 2a shows the low-frequency-limiting form of the circuit of Fig. 1a. Here the subscript "0" denotes the $\omega \to 0$ values. The exact formula for $R_{IN}^0$ is very lengthy, but various expressions for $R_{IN}^0$ in specific cases of interest have been given earlier. The general expression for $C_{IN}^0$ is, however,
Here \( M = \frac{1}{2L_D} \) measures the number of Debye lengths contained in the half-cell distance \((l/2)\). In the present case

\[
L_D = \left[ \frac{ekT}{4\pi e^2(z_n^2 n_i + z_p^2 p_i)} \right]^{\frac{1}{2}}
\]

(2)

When the bulk concentrations \( n_i \) and \( p_i \) are given on a molar basis, \( k \) should be replaced by the gas constant \( R \) and \( e \) by \( F \), the Faraday. Incidentally, many of the intrinsic conduction results of the present paper, such as Eqn. (1), apply also in the extrinsic case when \( \delta_p, \delta_m, \) and \( \delta_p \) are redefined for the extrinsic situation.

The quantity \( r = M \coth(M) \) in eqn. (1) will be essentially equal to \( M \) for all \( M \) values of usual interest. Since \( M \) may be far greater than unity, \( C_{IN0} \) also may be much greater than unity. Now when \( r_p = r_n = 0 \), the completely blocking electrodes condition, \( C_{IN0} = r - 1 \). The total low-frequency-limiting capacitance is then

\[
C_{po} = C_g + C_{i0} = r C_g \geq M C_g = \varepsilon/8\pi L_D.
\]

This is indeed, as it should be, the usual small-signal intensive double layer capacitance arising from two identical double layers in series. Note that when \( M \gg 1 \) and \( r_p \neq r_m \), eqn. (1) shows that \( C_{IN0} \) and \( C_{P0} \) may greatly exceed the ordinary double-layer value. It is the large diffusion pseudocapacitance represented by the first term of eqn. (1) that leads to the most interesting behavior inherent in the present situation. Such pseudocapacitance only appears when charges of opposite sign discharge unequally at the electrodes and is at a maximum when charge of one sign is completely blocked and the other completely free to discharge (e.g., \( r_p = 0, r_n = \infty \), or \( r_p = \infty, r_n = 0 \)).

Figure 2b represents the high-frequency-limiting form of the equivalent circuits of Fig. 1. The remaining elements, \( C_g \) and \( R_{go} \), are of course independent of electrode boundary conditions in this frequency region defined by \( \Omega = \omega \tau_D > 0.1 \). Note that for \( \Omega = 1 \), where \( \omega \) is equal to the inverse of the basic dielectric relaxation time \( \tau_D \), the reactance associated with \( C_g \) is equal in magnitude to \( R_{go} \).

If accurate measurements can be carried out for \( \Omega > 0.1 \), experimental values of \( C_g \) and \( R_{go} \) are best obtained from this region.

Finally, it will be useful to introduce the notation used in the earlier work to designate a specific binary electrolyte situation: \((r_p, r_n, \pi_m, \pi_z, 0, M)\). Values
of these normalized parameters, together with a value of \( \Omega \), entirely define a specific case of the theory in its normalized form; i.e., they allow a specific value of \( Z_{TN} \) or \( Y_{TN} \) to be calculated. Because of the symmetry of the situation in normalized form, it turns out that for any \( \Omega \) the case \((r_m, r_n; \pi_m, \pi_z; 0, M)\) yields the same value of \( Z_{TN} \) as does \((r_p, r_n; \pi_m, \pi_z; 0, M)\) for any specific set of values of these quantities. Thus, when a situation such as \((0, r_n; \pi_m, \pi_z; 0, M)\) is examined for a range of \( r_n \) values and for \( \pi_m, \pi_z \geq 1 \), it is unnecessary to consider separately the case \((r_p, 0; \pi_m, \pi_z; 0, M)\). For this reason, I shall here be concerned with, e.g., \((0, \infty; \pi_m, \pi_z; 0, M)\), not with \((\infty, 0; \pi_m, \pi_z; 0, M)\).

III. IMPEDANCE-PLANE RESULTS

The circuits of Fig. 1 lead directly to the basic relation

\[
Z_{TN} = \frac{(Z_{IN} + R_{EN})}{1 + (\Omega + G_{DN})(Z_{IN} + R_{EN})}
\]

from which it is clear that when \(|(\Omega + G_{DN})(Z_{IN} + R_{EN})| \approx 1\), \((Z_{TN} - R_{EN}) \approx Z_{IN}\). One situation where the above condition holds is that for \((0, \infty; \pi_m, \pi_z; 0, M)\) with \(10 M^{-2} < (\Omega/\pi_m) < 1\) and \(\pi_m \ll 1, M \gg 1\), and \(\pi_m M < 1\). Then \(G_{DN} = \varepsilon_n \approx \pi_m \ll 1\) and \(R_{EN} = 1 + \pi_m \approx 1 = R_{\infty}\). Thus, when the above conditions apply, simple subtraction of the bulk resistance \(R_\infty\) from the total measured impedance \(Z_T\) yields the "interface" impedance \(Z_i\). As we shall see later, \(Z_i\) is not always a true interface impedance since it is not always completely intensive.

The above sort of results apply when charge of one sign is nearly or completely blocked, that of opposite sign discharges with an infinite or very large reaction rate, and the discharging charge carriers have a much smaller mobility than those that are completely or nearly completely blocked. As we shall see later, this is a very important and interesting case and is overtly consistent with the usual electrochemical practice of subtracting \(R_\infty\) from the total impedance in order to obtain intensive circuit element quantities associated with processes occurring near and at the working electrode.

Another case of some interest is that where

\[
Z_{TN} \approx Z_{3N} = (1 + i\Omega)^{-1}
\]

which yields simple Debye dispersion behavior with the single time constant \(\tau_D\). As we shall see, this is the usual result found with \(M \gg 1\) under any other conditions at frequencies for which \(\Omega > 0.1\). It follows immediately from eqn. (3) for the above \(\pi_m \ll 1\) case when \(|Z_{IN}| \ll R_{EN} \approx 1\). In addition, in the equal mobility case \((0, \infty; 1, \pi_z; 0, M)\), where \(R_{EN} = 2\) and \(G_{DN} = 0.5\), with \(M \gg 1\) and when \(|Z_{IN}| \ll R_{EN}\), eqn. (3) again leads to eqn. (4). Finally, the uninteresting case \((\infty, \infty; \pi_m, \pi_z; 0, M)\) involves just \(C_g\) and \(R_\infty\) in parallel and thus leads to \(Z_{TN} = Z_{3N}\) at all frequencies.

One common way of delineating some aspects of impedance behavior is to show the circle diagram or Cole–Cole plot, where the imaginary part of an impedance is plotted versus its real part with frequency as a parametric variable. Alternatively, admittance-plane circle diagrams may be plotted, as in early space-charge measurements on KBr. Here, since their use seems somewhat more com-
mon, I shall present only impedance-plane results and will later illustrate directly how the components of the total admittance depend on frequency. Figures 3–6 thus present impedance-plane plots, in terms of normalized quantities, for some specific \((r_p, r_n; \pi_{m}, \pi_{2}; 0, M)\) cases of interest. Since the imaginary part of the normalized impedance is always capacitative, its negative has been used here for the ordinate scale. Note that infinite frequency occurs at the \((0, 0)\) point and zero frequency is approached at the right. In addition, where appropriate, points corresponding to the three basic normalized frequency conditions \(M^2Q = 1, MQ = 1,\) and \(\Omega = 1\) have been shown on the curves of Figs. 3–6. The normalized parametric frequency variable \(\Omega\) increases from right to left here.

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Fig. 3. Impedance-plane plots of normalized impedance components for \((0, 0; 1, 1; 0, M)\) and \((0, \infty; 1, 1; 0, M)\) situations and several \(M\) values.

Figure 3 shows how the size of \(M\) affects the shape of the curves for the two extreme cases \((r_p, r_n) = (0, 0)\) and \((0, \infty)\). Figure 3a indicates that in the completely blocking situation where \(R_{EN} = 1\) and \(G_{DN} = 0\), \(Z_{TN} \approx 1 + Z_{IN} \approx 1 + (i\Omega C_{IN})^{-1}\) for \(\Omega \ll M^{-1}\), and thus the reactance of the double-layer capacitance dominates in this region. Alternatively, when \(\Omega > 0.1\) and \(M > 10^2\), \(Z_{TN} \approx Z_{TN^0}\). Note that in terms of \(Z_T\) rather than \(Z_{TN}\), the semicircle lies between \(\text{Re}(Z_T) = 0\) at \(\Omega \rightarrow \infty\) and \(\text{Re}(Z_T) = R_r\) at \(\Omega \sim 0.1\).

Figure 3b shows that in the usual case of \(M > 10^2\), two connected arcs appear for \((0, \infty; 1, 1; 0, M)\), while they become merged as \(M\) decreases towards zero. Here for large \(M\) and \(\Omega \gtrsim M^{-1}\), only the Debye dielectric relaxation semicircle appears. In the opposite extreme, as \(\Omega \rightarrow 0\), \(Z_{TN} \rightarrow Z_{TN^0}\). Since \(|Z_{IN^0}| = \infty\), eqn. (3) shows that \(Z_{TN^0} = R_{DN}\). Whenever both \(r_p\) and \(r_n\) are not simultaneously zero, \(R_{DN}\) is finite. Here, in the equal mobility case, \(R_{DN} = \varepsilon_n^{-1} = 1 + \pi_m^{-1} = 2\). Further detailed consideration of circle diagrams and other response curves for the equal-mobility cases \((0, 0; 1, 1; 0, M)\) and \((0, \infty; 1, 1; 0, M)\) has been given earlier\(^2,3\).

The dashed line in Fig. 3b through the point \((1, 0)\) is drawn with a slope of 45 degrees. Where the second arc is well approximated by this line, \(\text{Re}(Z_{TN}) \approx 1 +\)
[\text{Im}(Z_{TN})]. But this is just the result one finds when a Warburg impedance is in series with a bulk resistance \(R_x\). Thus, such a straight line segment of an arc in the impedance plane may be (and usually is) an indication of Warburg behavior, although it is also necessary that the Warburg part of the impedance be proportional to \(\omega^{-3}\). Such behavior will be considered in much more detail later. It appears when diffusion to an electrode of mobile entities influences cell behavior appreciably.

\[\begin{align*}
\text{Re} (Z_{TN}) & \quad \text{(a)} \\
\text{Re} (Z_{TN}) & \quad \text{(b)}
\end{align*}\]

Fig. 4. Impedance-plane plots for \((0, \infty; \pi_m, 1; 0, 10^4)\) situations with \(\pi_m < 1\). The \(0 \leq \text{Re}(Z_{TN}) < 1\) region has been omitted from the bottom plot.

Figure 4 shows circle diagram results for \((0, \infty; \pi_m, 1; 0, 10^4)\). \(\pi_m\) variation for \((0, 0; \pi_m, 1; 0, M)\) has relatively little effect here, but this is clearly not the case when both charges are not blocked. Further, \(\pi_z\) values different from unity within the range \(0.25 \leq \pi_z \leq 4\) set by available ionic valences make little difference in the shapes of the arcs of Figs. 3-6; significant effects of \(\pi_z\) variation will be demonstrated later for some other types of plots. Note the different scales used for the two parts of Fig. 4. In addition, the \(\Omega > 0.1\) semicircle has been omitted from
Fig. 4b for simplicity. Also, the line marked \( \pi_m \to 0 \) in Fig. 4a and 4b is the limit curve that the arc approaches as \( \pi_m \) approaches zero, not the actual limit when \( \pi_m = 0 \). There is a discontinuity in shape between curves for \( \pi_m \) arbitrarily small but non-zero \( (R_{DN} \text{ finite}) \) and that for \( \pi_m = 0 \) \( (R_{DN} \text{ infinite}) \). In the latter case, the charge carrier which is free to discharge has no mobility and therefore cannot discharge. Thus, the cases \( (0, \infty; 0, \pi_z; 0, M) \) and \( (0, 0; 0, \pi_z; 0, M) \) must lead to exactly the same results, as is indeed found. Finally, note that when the discharging carrier has much higher mobility than the blocked one, e.g. the \( \pi_m = 9 \) curve of Fig. 4b, the right-hand arc is very small compared to the dielectric relaxation semicircle. Thus, for such cases as \( (0, \infty; \pi_m, \pi_z; 0, M) \) with \( \pi_m \gg 1 \), it will be difficult to subtract out the dominating effect of dielectric relaxation and obtain accurately the small remaining effects arising from electrode processes. As we shall see later, this is a low \( Q \) \( (Q = \text{quality factor}) \) and high dissipation factor situation.

Figure 5 shows how the shape of the circle diagram depends on \( r_n \) when \( r_n = \infty \) and on \( r_n \) when \( r_n = 0 \) for the \( \pi_m = \pi_z = 1 \) case. Only part of the dielectric relaxation semicircle has been shown in Fig. 5a. Note that the heights of the arcs at the right are here proportional to \( (1+r_p)^{-1} \). The curves of Fig. 5b are interesting since they exhibit a total of three connected arcs when \( r_n < \infty \). Clearly, the size of the middle arc depends directly on \( r_n \). Further, the middle arc remains coincident with a semicircle over most of its extent, indicating a second single-time-constant Debye
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dispersion in this region with a time constant dependent on \( r_n \). Clearly, if frequency response measurements aren't extended to sufficiently high frequencies and if \( R_x \) and \( C_x \) are unknown, this middle semicircle might possibly be mistaken for the final \( \Omega > 0.1 \) semicircle. The low-frequency arc meets the \( \text{Re}(Z_{TN}) \) axis at the low-frequency-limiting value of \( R_{DN} \). Here, \( R_{DN} = \varepsilon_n^{-1} \left[ 1 + (2/r_n) \right] = 2 \left[ 1 + (2/r_p) \right] \). Further, the cusp at the beginning of this arc occurs at approximately \( \text{Re}(Z_{TN}) = \left[ 1 + (2/\varepsilon_n r_n) \right] \). Thus, the radius of the middle semicircle is \((\varepsilon_n r_n)^{-1}\), here equal to \((2/r_p)\).

Although Fig. 5a shows that as \( r_p \) becomes larger the low-frequency arc becomes smaller and smaller relative to the \( Z_{3N} \) semicircle, and thus electrode processes become more and more difficult to isolate, this trend may be counteracted, provided \( r_p \) is not too large, by the presence of a sufficiently small \( \tau_m \) ratio. The curves of Fig. 6 show results for \( \pi_m = 9^{-1} \), \( r_n = 2 \), and \( r_p \) variable. Again, three arcs appear with at least one very large compared to the dielectric relaxation semicircle.

The very rapid reduction of the sizes of the two lower frequency arcs of Fig. 6 as \( r_p \) increases from zero arises primarily from the very strong dependence of \( G_{DN} \) on \( r_p \), especially when \( \pi_m \ll 1 \), not so much from changes of \( Z_{IN} \) with \( r_p \). When three arcs are present, they will be numbered from right to left in order of increasing frequency: 1,2,3. When an arc such as No. 2 is missing, the remaining arcs will maintain their original numbers: 1 and 3.

![Fig. 6. Impedance-plane plot for the \((r_p, 2; 9^{-1}, 1; 0, 10^4)\) situation.](image)

The sizes of the three normalized arcs which appear when \( 0 \leq r_p < r_n < \infty \) are of particular interest since many experimental results show two or three arcs of the present types. Frequently, the dielectric relaxation semicircle (arc No. 3) either has not been measured or is much smaller than the other two arcs. It is often found that the low-frequency right arc is much larger than the middle semicircle and, in many cases, measurements are not extended to sufficiently low frequencies to allow much curvature in the right arc to show up. Then only an approximately straight line often at about a 45° slope appears. In this case, measurements remain in the approximate Warburg frequency response region and do not approach the low-frequency saturation region. It is worth mentioning that some authors\(^{13,14}\), working with glass membrane electrodes, have observed arcs 1 and 3 (or more probably 2 and 3) and have ascribed the higher frequency arc to the basic material under investigation and the lower frequency arc to a hydrolyzed surface film on the material. The present results show that such an assumption is unnecessary and that a single homogeneous material can yield both arcs.

Let us now consider the important three-arc \((0, r_n; \pi_m, \pi_x; 0, M)\) situation.
It turns out that an approximate expression for $Z_{TN}(\Omega)$ can be obtained which extends eqn. (4) to lower frequencies and includes separate terms for each of the three possible arcs, thereby partitioning $Z_{TN}$ into three normalized impedances frequently dominant in different frequency regions. An exact partition of this type has already been presented in the two-arc $(0, \infty; 1, 1; 0, M)$ situation. The approximate relation applying in the present case is, for $M \geq 10$,

$$Z_{TN} \approx \sum_{j=1}^{3} Z_{jN} \tag{4'}$$

where

$$Z_{1N} \approx 2\left[\pi \gamma_{2} + i\Omega \left(\frac{\delta_{p}}{\varepsilon_{p}}\right)^{2}(r_{1} - 1)\right] \equiv \left[\frac{G_{1N} + i\Omega C_{1N}}{1 + \frac{1}{G_{1N} + i\Omega C_{1N}}}\right]^{-1} \tag{4''}$$

and

$$Z_{jN} \equiv \left[\frac{G_{jN} + i\Omega C_{jN}}{1 + \frac{1}{G_{jN} + i\Omega C_{jN}}}\right]^{-1} \quad (j=2,3) \tag{4'''}$$

Here, $\gamma_{2} \equiv (ibM^{2}\Omega)^{1/2} \coth (ibM^{2}\Omega)^{1/2}$; $b \equiv \delta_{p}/\varepsilon_{p} \varepsilon_{n}$; $\Omega \equiv (1 + i\Omega)^{1/2}$; $G_{2N} \equiv (b\varepsilon_{n}/r_{n}/2)$; $C_{2N} \equiv r \approx M$; $G_{3N} \equiv 1$; and $C_{3N} \equiv 1$. Equation (4') is exact for $(0, \infty; \pi_{m}, \pi_{e}=\pi_{m}; 0, M)$, and in other cases is most accurate when $b\Omega \ll 1$. It may be further simplified, with little loss of accuracy, by taking $t = 1$ for all $\Omega$.

The partition represented by eqn. (4') leads directly to an approximate equivalent circuit made up of three parallel $GC$ sections in series when $0 < r_{n} < \infty$. The quantity $Z_{2N}$ is zero when $r_{n} = \infty$, causing arc 2 to disappear. Although $Z_{1N}$ may be represented either as a frequency-dependent resistance in series with a frequency-dependent capacitance or as a conductance and capacitance in parallel, the parallel representation is best in the low frequency saturation region because it makes it clear that $\text{Re}(Z_{TN})$ is overtly finite, as it should be when $r_{p}$ and $r_{n}$ are not both zero. For $\Omega \rightarrow 0$, eqns. (4'), (4''), and (4''') lead to the exact result

$$Z_{TN} \rightarrow Z_{1N} = R_{1N} + R_{2N} + R_{3N} = \pi_{m}^{-1} + (2\varepsilon_{n}/r_{n}) + 1 = \pi_{m}^{-1}[(1 + (2/r_{n})] = R_{DN}. \text{When } \Omega > 10(bM^{2})^{-1}, Z_{2N} \text{ shows approximate Warburg frequency response, while } G_{1N} \text{ and } C_{1N} \text{ approach their low-frequency-limiting values for } \Omega < 2.5(bM^{2})^{-1}. \text{ Note that } Z_{2N} \text{ is independent of } \pi_{m} \text{ and } Z_{1N} \text{ depends on it primarily through } b, \text{ a quantity symmetric in } \delta_{n} \text{ and } \delta_{p}. \text{ Incidentally, although eqn. (4') holds approximately even for } r_{n} = 0, \text{ it can be considerably improved for this situation by multiplying } Z_{1N} \text{ by } \delta_{n}^{2} \text{ when } r_{n} = 0 \text{ and } \pi_{m} \text{ is appreciably less than unity. This factor is otherwise inapp}$$

The expression for the second semicircle (arc 2) is particularly interesting. Here, $C_{2} \equiv MC_{g}$ is just the ordinary double-layer capacitance when $M \gg 1$ and $r_{n} = r_{e} = 0$. This does not mean, however, that either $C_{p}$ or $C_{i}$ is equal to $C_{2}$ over the full frequency range where this semicircle is dominant. When $\pi_{m} = 1$, neither $C_{p}$ nor $C_{i}$ remains near $MC_{g}$ over an appreciable frequency region, even though the impedance-plane shape is well approximated by a semicircle. When $\pi_{m} \ll 1$, on the other hand, $C_{1N}$ decreases to approximately $M$ and then remains near it over an appreciable region, especially when $r_{n} \ll M$. It further turns out that $C_{1N}$ reaches $M$ at a lower $\Omega$ value than does $C_{1N}$ and then remains near $M$ while $C_{1N}$ does. The maximum of this semicircle is $-\text{Im}(Z_{2N}) = (\varepsilon_{n}/r_{n})^{-1}$ and occurs at $\Omega = (\varepsilon_{n}/r_{n}/2M)$. Clearly, $\langle\varepsilon_{n}/r_{n}\rangle^{-1}$ may greatly exceed 0.5, the maximum of arc 3. Under some conditions, such as $r_{p} = r_{n} = r_{e}$, arc 1 is completely missing and only arcs 2 and 3 appear. In other possible conditions, arc 1 is so much smaller in size than arc 2 that it
can be entirely neglected.

The quantity \( Z_{1N} \) yields the right arc (arc 1), which always appears to some degree, as in Figs. 3b, 4, 5 and 6, when \( 0 \leq r_n < r_n^* \). To good accuracy, the size and shape of this arc is entirely independent of \( r_n \) when \( 0 \leq r_n < 2r_m^* \). Then the maximum value of \( -\text{Im}(Z_{1N}) \) is about \( 0.417 \pi m^{-1} \), occurring at \( \Omega \approx 2.53 \ h^{-1} \ M^{-2} \). For \( \pi_n = 1 \) and \( \pi_m \ll 1 \), this value of \( \Omega \) is about \( 10 \pi_m M^{-2} \). When appreciable portions of all three arcs can be observed and they are distinct, one may very readily derive values of the pertinent parameters in the \((0, r_n^*; \pi_m, \pi_n; 0, M)\) situation. First, \( R_{\infty} \) is found from the cusp between arcs 2 and 3. Then \( C_{\infty} \) may be obtained at high enough frequencies that some appreciable portion of arc 3 appears. The \( \Omega \) scale is then determined. Next, \( \pi_m \) may be obtained from the maximum height of arc 1. The high point on arc 2 then yields \( r_m^* \) (since \( \varepsilon_n \) and \( \varepsilon_p \) may be calculated from the value of \( \pi_m^* \)), and the \( \Omega \) value at which this maximum occurs, \( \Omega = \varepsilon_n r_m^* / 2M \), yields \( M \). If the \( \Omega \rightarrow 0 \) intercept of arc 1 can be obtained, the resulting value of \( \Omega_{DN} \) will then yield a check on the consistency of the previously found values of \( \varepsilon_n \) and \( \varepsilon_p \). Only \( \pi_z \) is missing. It will frequently be known from the physical situation being investigated; if not, an estimate may be obtained from a detailed comparison of the shape and frequency dependence of arc 1, using eqn. (4').

Finally, note that even when \( r_p = 0 \) and \( r_n \ll \infty \), there are combinations of \( \pi_m, \pi_n, \) and \( M \) values which lead to some melding of the three arcs so that the cusps between them may become less sharp and even disappear. Although the curves of Figs. 3–6 and eqn. (4') have by no means illustrated all possible circle diagram shapes inherent in the theory, they should give some idea of the variety possible. One, two, or three connected arcs of different relative sizes follow from the theory. Probably even more than three would appear if charge types with more than two different mobilities were present.

It is hoped to show in a future paper under what conditions a more accurate but still simple version of eqn. (4'), may be derived from the exact theory; to show how accurate eqn. (4') and its generalizations are for further cases of interest; and to demonstrate a wider variety of two-and-three arc shapes following from the theory. Since the present eqn. (4') holds, however, within better than one percent under many \( r_p, \pi_m, \pi_z \) conditions when \( b\Omega \ll 1 \), it may already be used for experimental analysis when \( r_p = 0 \).

In the present part of this section, we have dealt with the approximate relation \( Z_{TN} \approx Z_{1N} + Z_{2N} + Z_{3N} \), which does not involve the "interface" impedance \( Z_i \) directly. For the remainder of this paper, we shall instead pursue the more accurate and general approach of considering the exact equivalent circuit of Fig. 1 and the quantity \( Z_{1N} \), which has been given exactly in closed form\(^4\) and may be calculated without approximation for the \((r_p, r_n^*; \pi_m, \pi_n; 0, M)\) situation.

Although a detailed comparison of the present possible impedance-plane curve shapes with experimental results will not be carried out here, they do seem sufficiently variable and complex to match quite well a considerable body of experimental shapes, e.g. many of those in refs. 13–17. It should be noted that frequently only a single arc is found, often of the shape of the low-frequency arc of Fig. 3b, Fig. 4, and Fig. 5a. This important shape, which is associated with diffusion, distributed circuit elements, and a finite, distributed-element transmission line, even appears for the input impedance of a bipolar transistor\(^{18}\).
There will always be a Debye dielectric relaxation semicircle appearing at higher frequencies, but frequently either the diffusion arc size is so much larger than that of the $\Omega > 0.1$ semicircle (e.g., $\pi_m \ll 1$ for $r_p \sim 0$, $r_n \sim \infty$) that the latter is completely overwhelmed and/or measurements cannot conveniently be extended to the region where $\Omega \geq 0.1$ and the dielectric relaxation semicircle appears. Such extension is, of course, easier for a very high resistivity material where $r_D$ is large, and thus the $\omega$ for which $\Omega = 1$ occurs in the relatively low frequency range\textsuperscript{13,14}. It should be noted that for ($\sim 0$, $\sim \infty$; $\sim 1$, $\sim 1$; $0$, $M$) when $M$ is large the cusp between the two arcs (at $\text{Re}(Z_{TN}) \approx 1$) represents a wide frequency range from $\Omega \sim M^{-1}$ to $\Omega \approx 0.1$. Over this range $Z_{TN}$ varies very little and remains near unity. Although $R_N$ may be found from this region, one must go to at least $\Omega \geq 0.1$ to determine $C_N$ accurately. Finally, it should be noted that sometimes four or more connected arcs appear experimentally and $\text{Im}(Z_T)$ may even be positive\textsuperscript{16}. The latter result is often ascribed to the presence of specific ionic adsorption.

### Table 1

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#### IV. Impedance Frequency Response

Figures 7–11 show how the real and imaginary parts of $Z_{TN}$ and $Z_{IN}$ depend on frequency for various cases of interest. In addition, Table 1 gives values for pertinent circuit quantities for the various cases considered in this section. Although an $\Omega$ scale is given at the top of Figs. 7a and 8a, the main frequency variable used here is $A^{-1}$, where the diffusion related\textsuperscript{3} quantity $A$ is given by $M\Omega^2$. Note that when $M = 10^4$, the points $\Omega = 1$, $M\Omega = 1$, and $M^2\Omega = 1$ occur at $A^{-1} = 10^{-4}$, $10^{-2}$, and 1, respectively. The use of a frequency variable proportional to $\omega^{-1}$ is common in electrochemical studies and immediately shows up the presence of Warburg behavior.

Let us write a general Warburg impedance $Z_W$ as

$$Z_W = A_0(1-i)/\omega^\frac{1}{2}$$

where the constant $A_0$ will be considered in detail in Section V. Then in normalized terms one has

$$Z_{WN} = Z_W/R_\infty = A(1-i)/\Omega^\frac{1}{2}$$
where
\[ A \equiv (C_v/R_x)^4 A_0 \]
\[ = [\varepsilon (\varepsilon_{2r} + \varepsilon_{2a}) (\mu_r + \mu_a) / 8\pi l^2]^4 A_0 \]  \hspace{1cm} (7)

Now when the real part of a normalized impedance is the negative of its imaginary part and both depend on \( \Omega^{-1} \), then the impedance in question exhibits Warburg behavior. In this case, both quantities will show a slope of unity, as in Fig. 8b, when plotted versus \( A^{-1} \). On the other hand, when a capacitative reactance involves a frequency-independent capacitance, plotting versus \( A^{-1} \) will yield a straight line with a slope of two as in Fig. 7a.

Figure 7 shows results for the completely blocking case for two different \( \pi_m \) conditions. Here eqn. (3) yields
\[ Z_{TN} = (Z_{IN} + 1)/[1 + i\Omega (Z_{IN} + 1)] \]  \hspace{1cm} (8)

Now computer calculations indicate that for the equal-mobility case shown in Fig. 7a, \( C_{in} = C_{INO} = r - 1 \geq M \) within 1 percent up to \( \Omega \geq 0.3 \). Further, the Figure shows that \( \text{Re}(Z_{IN}) \approx R_{IN} \) remains very near its small limiting value\(^4\) of \( R_{INO} = (2M)^{-1} \) up to \( \Omega = 1 \). Thus, in the entire frequency range of interest, we may here take \( Z_{IN} \approx Z_{INO} \) and, further, may neglect \( R_{INO} \) and \( C_{INO}^{-1} \) compared to unity. Then (8) leads to
\[ Z_{TN} \approx \{1 - i[\Omega + (M\Omega)^{-1}]\} / (1 + \Omega^2) \]  \hspace{1cm} (9)

Clearly, for \( M\Omega \ll 1 \) \( (A^{-1} \gg 10^{-2}) \), the normalized capacitative reactance \( (\Omega C_{IN})^{-1} \approx (\Omega C_{INO})^{-1} \approx (M\Omega)^{-1} \) dominates \( Z_{TN} \). Further consideration of this case has been presented earlier\(^1-3\).

![Fig. 7. Real and imaginary parts of \( Z_{TN} \) and \( Z_{IN} \) versus \( A^{-1} = (M\Omega)^{-1} \) for \((0, 0; 1, 1; 0, 10^4)\) and \((0, 0; 10^{-4}, 1; 0, 10^4)\) situations.](image-url)
Although Fig. 7b shows that in the $\pi_m \leq 1$ case, $\text{Im}(Z_{\text{IN}})$ still dominates $Z_{\text{TN}}$ for $M \Omega \leq 1$, there is evident a transition from $C_{\text{IN}} \approx C_{\text{IN}0}$ to a smaller constant value, $C_{\text{ISN}}$, in the neighborhood of $A^{-1} \approx 4 \times 10^{-2}$. This plateau value, $C_{\text{ISN}}$, will be discussed in detail in the next section. Figure 7b also indicates that $R_{\text{IN}}$ is much larger and more frequency dependent than it is when $\pi_m = 1$. Note that although $\text{Re}(Z_{\text{TN}})$ and $R_{\text{IN}}$ show an appreciable region with a slope of unity, this does not indicate pure external Warburg behavior since the dominant normalized reactances show no such slope. Warburg behavior actually occurs here in both $\text{Re}(Z_{\text{TN}})$ and $\text{Im}(Z_{\text{TN}})$, as shown by eqn. (4') with $r_p = r_n = 0$, but its contribution to $\text{Im}(Z_{\text{TN}})$ is swamped by the reactance of $C_{\text{INO}}$ and $C_{\text{ISN}}$. Finally, note that the components of $Z_{\text{TN}}$ are essentially exactly the same for $\pi_m = 1$ and $10^{-4}$ when $\Omega \gtrsim 10^{-2}$ ($A^{-1} \leq 10^{-3}$). Thus, the mobility ratio has very little effect in this relatively high frequency region.

Next we turn to the $(0, \infty)$ case. For the $\pi_m = 1$ situation of Fig. 8a, eqn. (3) yields

$$Z_{\text{TN}} = \frac{(Z_{\text{IN}} + 2)}{1 + (i\Omega + 0.5)(Z_{\text{IN}} + 2)}$$

When $\Omega \ll 1$ and $|Z_{\text{IN}}| \ll 4$, this result reduces to

$$Z_{\text{TN}} \approx 1 + (Z_{\text{IN}}/4)$$

In the region $10^{-2} \leq A^{-1} \leq 10^{-1}$, the unity slope $-\text{Im}(Z_{\text{TN}})$ and $-\text{Im}(Z_{\text{IN}})$ lines of Fig. 8a are separated by just this factor of four.

The most interesting aspect of Fig. 8a is the Warburg behavior of $Z_{\text{IN}}$ in the region $10^{-3} \leq A^{-1} \leq 10^{-1}$. Such behavior does not show up directly here in

![Figure 8](image-url)
Re\( (Z_{TN}) \) because of the overlying effects of \( R_{EN} \) and \( R_{DN} \). It is only when these effects are eliminated by calculating \( Z_{iN} \) from (10), or minimized, by calculating it from (11), that Warburg sort of behavior shows up clearly. Relatively small deviations from exact Warburg behavior of \( Z_{iN} \) are of particular interest and will be examined in depth in Section VI.

It is especially important to note that basic Warburg behavior appears in the \( Z_{iN} \) normalized "interface" impedance, not necessarily directly in \( Z_{TN} \). If in the equal-mobilities case \( (Z_{T} - R_{N}) \) is set directly equal to a theoretical Warburg impedance in the usual way, rather than to such an impedance divided by 4, a factor of four error can occur, for example, in the calculation of the concentration of the charge involved in the Warburg behavior. Even greater errors can occur for \( \pi_{m} > 1 \), and lesser ones will appear for \( \pi_{m} < 1 \). Note that even in the present \( \pi_{m} = 1 \) case, a small difference, \( \text{Re}(Z_{iN}/4) \), between two much larger quantities must be calculated to obtain the real part of the Warburg response. Experimental errors are thus magnified and make it difficult to obtain \( Z_{iN} \) accurately from \( Z_{TN} \) when \( \pi_{m} \geq 1 \).

The situation is considerably different when \( \pi_{m} \ll 1 \), as in Fig. 8b. Here approximate Warburg response shows up in both \( Z_{TN} \) and \( Z_{iN} \) in the region 0.03 \( \leq \Lambda^{-1} \leq 10 \). Here eqn. (3) yields

\[
Z_{TN} \approx \frac{(Z_{iN} + 1)}{1 + (i\Omega + \pi_{m})(Z_{iN} + 1)}
\]

which for the present \( \pi_{m} = 10^{-4} \) and the range \( 10^{-10} \leq \Omega \leq 10^{-2} \), becomes

\[
Z_{TN} \approx Z_{iN} + 1
\]

Thus, in the \( \pi_{m} \ll 1 \) region, no error such as that of a factor of 4 just discussed for the \( \pi_{m} = 1 \) case appears when the conventional procedure is used. Incidentally, the distinction between \( Z_{iN} \) and \( (Z_{iN} + 1) \) is not visible on the present log-log plot for \( \Lambda^{-1} > 0.1 \). The final low-frequency-limiting values of \( \text{Re}(Z_{TN}) \), \( R_{DN} \), and \( \text{Re}(Z_{iN}) \), \( R_{iN,0} \), are given in Table 1.

In Fig. 9 the same case as that of Fig. 8b is considered except that \( M = 10^{2} \) rather than \( 10^{4} \). Note that the results are essentially the same near and in the low-frequency saturation region, \( \Lambda^{-1} \geq 10 \). The vestiges of Warburg behavior still appear for \( 3 < \Lambda^{-1} \leq 10 \) but do not extend very far toward higher frequencies. Here the conditions \( \Omega = 1 \), \( M\Omega = 1 \), and \( M^{2}\Omega = 1 \) occur at \( \Lambda^{-1} = 10^{-2}, 10^{-1}, \) and 1, respectively. The very high frequency \( \Lambda^{-1} < 10^{-2} \) region is shown here for completeness but will generally not be experimentally accessible since the impedance level at say \( \Lambda^{-1} \approx 10^{-3} \) or \( 10^{-4} \) is so much lower than that in the low-frequency saturation region and than \( R_{p} \). Thus, the second Warburg response region of \( Z_{iN} \), occurring at \( \Lambda^{-1} < 10^{-2} \), will not usually be measurable. This region appears for any \( \pi_{m} \) and reasonably large \( M \) for \( \Omega > 1 \) but has been omitted from the other plots for simplicity.

Finally, Figs. 10 and 11 show the curves which appear for a few related choices of \( r_{p} \) and \( r_{n} \). Note that the value \( r_{p} \) or \( r_{n} = 2 \) makes \( g_{p} \) or \( g_{n} = 2 \) rather than its unity value when \( r_{p} \) or \( r_{n} = 0 \). It is the \( g \)'s rather than the \( r \)'s which enter directly into the theory; thus \( r_{p} \) and \( r_{n} \) values which double \( g \) seem reasonable to choose for special examination. The results of Fig. 10a should be compared especially with those of 7b and 8b. Similarly, Fig. 10b should be
Fig. 9. Real and imaginary parts of $Z_{TN}$ and $Z_{in}$ versus $A^{-1}$ for $(0, \infty; 10^{-4}, 1; 0, 10^{2})$ showing the effect of a reduction in $M$.

Fig. 10. Real and imaginary parts of $Z_{TN}$ and $Z_{IN}$ versus $A^{-1}$ for $(2, 2; 10^{-4}, 1; 0, 10^{4})$ and $(0, 2; 10^{-4}, 1; 0, 10^{4})$ situations.
compared with Figs. 10a, and 8b. Note that the double hump in the \(-\text{Im}(Z_{TN})\) curve of Fig. 10b is associated with the \(Z_{2N}\) and \(Z_{1N}\) terms of eqn. (4'); thus, in this situation an impedance-plane plot would show three connected arcs, although the dielectric relaxation one will be far smaller than the other two here. The results of Fig. 11a should be compared with 10a and those of 11b with 11a, 8a, and 8b. It will be seen that the change of a single blocking parameter from 0 to 2 or 2 to \(\infty\) can make a great deal of difference in some or all of the curves. Further, no approximate Warburg regions occur here except for the \((2, \infty; 10^{-4}, 1; 0, 10^4)\) case of Fig. 11b which is clearly not too far different from \((0, \infty; 10^{-4}, 1; 0, 10^4)\) as far as \(Z_{IN}\) is concerned, although even here the normalized impedance level is higher. Here, however, \(Z_{TN}\) and \(Z_{IN}\) are again connected very closely by eqn. (10), which does not reduce to \(Z_{TN} = (Z_{IN}/4) + 1\) or \((Z_{IN} + 1)\) in the region of interest.

Solution of eqn. (3) for \(Z_{IN}\) yields

\[
Z_{IN} = \frac{Z_{TN}}{1 - (i\Omega + G_{DN})Z_{TN}} - R_{EN} \tag{14}
\]

When \(i\Omega\) may be neglected, this result reduces to

\[
Z_{IN} \approx R_{EN}^2[Z_{TN} - 1][1 - G_{DN}R_{EN}(Z_{TN} - 1)] = R_{EN}(Z_{TN} - 1)[1 - G_{DN}Z_{TN}] \tag{15}
\]

In the \(\Lambda^{-1} \gg 10^{-1}\) region, where \(Z_{TN} \approx R_{DN}\), the denominator is nearly zero; thus again in the \((2, \infty; 10^{-4}, 1; 0, 10^4)\) situation calculation of Warburg response from experimental \(Z_{T}\) results involves the small difference between two much larger quantities and will be difficult to obtain adequately. The present results allow us to
conclude that for $M \gtrsim 10^2$ Warburg response will only be seen or be readily calculable when $r_p \ll 2$, $r_n \gg 2$, and most readily when $\pi_m \ll 1$. Of course one must also include the symmetry-related situation $r_p \gg 2$, $r_n \ll 2$, and $\pi_m \gg 1$.

V. FREQUENCY RESPONSE OF THE ADMITTANCE COMPONENTS

Equation (3) may be readily inverted to yield a connection between $Y_{VN}$ and the elements of $Z_{mN}$. Let $R_{SN} = R_{IN} + R_{EN}$, the total normalized series resistance in the bottom branch of Fig. 1a. Further, let $\tau_{SN} = R_s C_i / \tau_D = R_{SN} C_{iN}$. Then $D_{SN} = D_S = \Omega \tau_{SN} = \omega R_s C_i = Q_s^{-1} = \tan \delta_s$, where $D_s$ is the dissipation factor and $Q_s$ the quality factor for this branch. Similarly, we may define $\tau_{EN} = R_{EN} C_{iN}$ and $D_E = \Omega \tau_{FN}$. With these definitions eqn. (3) leads immediately to the important equations

$$C_{PN} = 1 + \frac{C_{IN}}{1 + (\Omega \tau_{SN})^2} = 1 + \frac{C_{IN}}{1 + D_s^2}$$  \hspace{1cm} (16)

and

$$G_{PN} = G_{DN} + \frac{\Omega^2 \tau_{EN} \tau_{SN} G_{EN}}{1 + (\Omega \tau_{SN})^2} = G_{DN} + \frac{D_E D_S G_{EN}}{1 + D_s^2}$$  \hspace{1cm} (17)

These equations, together with the frequency responses of $R_{IN}$ and $C_{iN}$, yield those of $C_{PN}$ and $G_{PN}$ in complete generality. For $\Omega \rightarrow 0$, $C_{PN} \rightarrow C_{PN0} = 1 + C_{iNO}$ and $G_{PN} \rightarrow G_{PN0} = G_{DN}$. Note that we are here dealing with the components of the total admittance, not that after the effect of $R_\infty$ or $R_D$ and $R_E$ is somehow subtracted out.

Figure 12 shows how $C_{PN}$ depends on $\Omega$ for various values of $M$ in the $\pi_m = \pi_n = 1$ case. The curves of Fig. 12a follow nearly exactly from eqns. (16) and (17) with $C_{IN} = C_{iNO} = M - 1$, $R_{IN} = R_{INO} = (2M)^{-1}$ and $\tau_{SN} = (R_{INO} + R_{EN}) C_{iNO} = R_{EN} \times C_{iNO} = \tau_{EN}$. Thus, one has simple Debye response here with the only significant frequency response arising from those $\Omega$'s which appear overtly in (16) and (17). Incidentally, curves such as the $M = 10^3$ ones of Fig. 12a and 12b have been ob-
served\textsuperscript{11} for F-centered KBr. One like that of Fig. 12a was indeed measured with completely blocking electrodes, while electrodes which were incompletely blocking to electrons yielded curves like those of 12b.

Figure 13 shows the frequency dependence of $G_{PN}$ and $C_{PN}$ when $r_p = r_n \equiv r_e$. In this equal-discharge case, eqn. (1) yields $C_{IN0} = \frac{(r - 1)}{g_e^2} \approx M / g_e^2$, where $g_e \equiv 1 + (r_e/2)$. For the present $\pi_m = \pi_z = 1$ situation, the corresponding $R_{IN0}$ is approximately $g_e^2 / 2M$ and $R_{EN} = g_e$. These results, used in (16) and (17) with $C_{IN} = C_{IN0}$ and $R_{IN} = R_{IN0}$, again yield the curves of Fig. 13. Note that the $\Omega \to 0$ value of $G_{PN}$ is here $G_{PN} = r_e/(2 + r_e)$. The low-frequency saturation value of $C_{PN}$ is here reached for $\Omega \leq [g_e/10(r - 1)]$.

![Figure 13](image-url)

**Fig. 13.** Normalized frequency response of $G_{PN}$ and $C_{PN}$ for the $(r_e, r_e; 1, 1; 0, 10^4)$ situation.

Figure 14a shows some dependence on $\pi_m$ and $\pi_z$ for the completely blocking situation. Detailed calculations based on the earlier theoretical results\textsuperscript{4} show that the plateau value of $C_{IN}$, $C_{PSN}$, is given in the present $\pi_m \ll 1$ situation by

$$C_{IN} \simeq \frac{(it_m m_p / \Omega f_1 f_2)}{[M \delta_p^2 - 1]} \simeq M \delta_p^2 - 1$$

where the quantities $t_2$, $m_p$, $f_1$, and $f_2$ are defined in the earlier work. The corresponding plateau value of $C_{PN}$, $C_{PSN}$, is, from (16), essentially $M \delta_p^2$ since $D_s \ll 1$ in the $C_{PN} \approx C_{PSN}$ plateau region. This region is limited approximately by $10^{\pi_m} \lesssim \Omega \lesssim [10M \delta_p^2]^{-1}$ for $M \gtrsim 10^2$. Thus no such region appears unless $\pi_m \lesssim [10^2 M \delta_p^2]^{-1}$. Incidentally, $C_{IN}$ remains at its plateau value over the larger range $10^{\pi_m} \lesssim \Omega \lesssim 0.1$. Note that $M \delta_p^2 = M 2^3 \approx 7071$ for $\pi_z = 1$ and $M 5^4 \approx 4472$ for $\pi_z = 4$, the two $\pi_z$ values of Fig. 14a. Finally, the region where $C_{PN}$ has essentially reached its low-frequency-limiting value $C_{PN0}$ is given approximately by whichever of the following two conditions yields the minimum $\Omega$: $\Omega \lesssim (10M)^{-1}$ and $\Omega(\pi - 1) \ll 1$. Here $a \equiv (\delta_p / \delta_p + (\delta_n / \delta_n))$, and for $\pi_z = 1$, $a = b$. The last $\Omega$-condition above may be expressed more explicitly as $\Omega(a - 1) \lesssim 2.5 \times 10^{-4}$. For $\pi_m = 10^{-6}$ and $\pi_z = 1$,
\[ a = b \approx 2.5 \times 10^5, \text{ yielding } \Omega \leq 10^{-9} \text{ in the present case.} \]

It is interesting to note that curves of very similar shape to the \( \pi_z = 1 \) curves of Fig. 14a were obtained long ago\(^{19} \) for a \((0, 0; \infty, 1; 0, M)\) situation, one with charge of only one sign mobile but free to recombine with fixed charge of opposite sign. This is an idealization of conditions which might occur in a solid. Such generation-recombination essentially mobilizes the fixed charge\(^{19,20} \), and the time constant ratio \( \xi^{-1} = \tau_D/\tau_r \) of the earlier work\(^{19} \) there plays the role of the present \( \pi_m \) mobility ratio. Here \( \tau_r \) is a recombination time constant involving the bimolecular recombination rate constant \( k_2 \). Since \((0, 0; \infty, 1; 0, M)\) and \((0, 0; 0, 1; 0, M)\) situations lead to the same \( Z_{TN} \), we may now consider the latter situation with recombination, since it closer corresponds to the present \((0, 0; \pi_m, 1; 0, M)\) situation with \( \pi_m \ll 1 \) and no recombination. The early work\(^{19} \) indicates that the rise from \( C_{PSN} \) toward \( C_{PNO} \) begins at \( \Omega = \Omega_m \approx 10 \xi^{-1} \), while Fig. 14a shows the start at \( \Omega = \Omega_m \approx 10 \pi_m \). When \( \Omega_m \gg \Omega_r \), or \( \pi_m \gg \xi^{-1} \), the rise associated with motion of the lower mobility charge carrier occurs at a much higher frequency than that arising from recombination, and the presence or absence of the latter doesn’t affect the frequency region where \( C_{PN} \) rises from \( C_{PSN} \) to \( C_{PNO} \). On the other hand, when \( \Omega_m \ll \Omega_r \) and \( \pi_m \ll \xi^{-1} \), the recombination rise appears at the higher frequency, and it then doesn’t matter how small the actual \( \pi_m \) is. Incidentally, for any substantial plateau to be possible it is necessary that \( \Omega \), as well as \( \Omega_m \) be appreciably less than \( M^{-1} \). This requirement leads to \( \xi \gg M \), or \( \tau_r \gg M \tau_D \).

Since there will usually either be some small residual true mobility for the less mobile charge and/or some recombination when \( \pi_m = 0 \) (this zero-mobility condition is never actually reached in solids at non-zero temperature), one should not\(^{21} \) expect to find experimentally a curve corresponding all the way down to \( \Omega = 0 \) to that for \( \pi_m = 0 \) of Fig. 14a. At sufficiently low frequencies for non-zero temperature there will always be a transition from \( C_{PSN} \) to the larger \( C_{PNO} \). This
transition frequency may, however, be too low to determine conveniently experi-
mentally. The above results justify the neglect of intrinsic recombination in the
present theoretical analysis, although it should not be forgotten that non-zero re-
combination ($\tau_r < \infty$) affects the magnitudes of the equilibrium concentrations $n_i$ and $p_i$ directly in the present intrinsic conduction case. Thus, the presence of recombination
also affects the value of $M$ directly. As far as the normalized frequency response
of $Z_{TN}$ is concerned, however, recombination can be approximately accounted for by
choosing and interpreting $\pi_m$ properly. It is the effective mobility ratio that counts,
that arising from both true mobility and from recombination. For practical purposes,
the present $\pi_m$ may thus be considered to represent the effective mobility ratio for
any $r_p$, $r_n$ situation. It will thus be the true $\pi_m$ when $\pi_m \gg \xi^{-1}$ and will be $\xi^{-1}$
when $\pi_m \ll \xi^{-1}$.

Before we leave the situation of only charge of a single sign mobile, it is in-
structive to compare the results of Beaumont and Jacobs, who considered the
idealized ($\pi$, $\rho$; $\infty$, 1; 0, $M$) situation without recombination [equivalent for $Z_{TN}$
to ($\rho$, $-\pi$; 1, 0; $M$) without recombination]. For the equivalent case, only the mobile
positive charges discharge (with $r_n = \rho$), and no $r_n$ need be specified since the negative
charges are taken immobile and homogeneously distributed. Beaumont and Jacobs'
results for $Z_{TN}$ turn out to be exactly the same as those which follow from the
present treatment for ($r_p$, $r_e$; $\pi_m$, $\pi_n$; 0, $M$) with $\pi_m = 0$ or $\infty$ and $\pi_n = 1$.

The ($r_p$, $r_e$; 0, $\pi_n$; 0, $M$) situation leads, for example, to $C_{PN0} = C_{PSN} \equiv$

$$g_e^{-2} M \delta_p^4 + (1 - g_e^{-2})$$

(19) But, as eqn. (2) shows,

$$M \delta_p^4 = \frac{l \delta_p^4}{2 L_D} = \frac{l}{2 L_{DP}} = M_p$$

where $L_{DP} = L_D / \delta_p^4$ is the Debye length which applies when only the positive carrier
is mobile, the situation actually considered. In this case, Beaumont and Jacobs' results
lead to $C_{PN0} = (M/2 \pi)^2/[1 + (\rho/2)]^2$, in essential agreement with the present expression
when $\pi_n = 1$. Further, their frequency response is of course the same as that found
here.

The equivalence of these results again follows from the fact that it doesn't
matter what boundary condition parameter one assigns to a charge carrier which is
immobile. Thus, the $g_e$ appearing in $C_{PSN}$ is actually $g_0$ in the $0 \leq \pi_m \ll M^{-1}$
case, and the value of $r_n$ is immaterial. Further, eqn. (19) shows that in the present
treatment it is unnecessary to deal with two separate Debye lengths, one defined
where there is only one species of mobile carrier present and the other for two.

The effect on formulas involving the Debye length of a shift from both positive
and negative charge carriers mobile to only one type mobile occurs automatically
here.

Figure 14b shows how $C_{PN}$ depends on $\pi_n$ for the $(0, \infty)$ discharge situation.
On this scale the change from $\pi_n = 1$ to $\pi_n = 3$ is quite small. Incidentally, the
$\pi_n = 3^{-1}$ curve lies so close to that for $\pi_n = 3$ that it cannot be shown separately on
this plot. Although $\pi_m$ has no effect on $C_{PN0}$ it does of course affect $C_{PN}$ at
non-zero $\Omega$. Thus, it is possible to compensate the effect of $\pi_n \neq 1$ to large degree
by choice of $\pi_m$, except in the neighborhood of low-frequency saturation. For
example, the choice $\pi_m = 1.15$, $\pi_n = 3$, makes the resulting $C_{PN}$ and $G_{PN}$ curves lie
almost exactly on those for $\pi_m = 1$, $\pi_n = 1$ except for the saturation region, $\Omega \lesssim 10$
$\pi_m M^{-2}$. To illustrate, at $\Omega = 10^{-4}$, the $(0, \infty; \pi_m, \pi_n; 0, 10^3)$ case leads to the following
values of $C_{P_N}$ for $(\pi_m, \pi_f) = (1, 3^{-1}), (1, 3), (1, 1), \text{ and } (1.15, 3)$ respectively: 698.1, 695.4, 616.2, and 616.3. Corresponding values of $G_{P_N}$ are 0.9218, 0.9196, 0.9308, and 0.9300. This possible compensation effect requires one to be especially careful in deriving values of $\pi_m$ and $\pi_f$ from experiment in the rather unusual case where both ratios are initially unknown.

Figure 15 shows important results for $G_{P_N}$ and $C_{P_N}$ in the variable $\pi_m$ discharge case. Notice that the $C_{P_N}$ curves show portions with slopes of $-2$, $-1.5$, and $-0.5$. The somewhat odd looking values of $\pi_m$ used here result in $G_{PNO} = G_{DN} = e^{-\pi_m} = (1 + \pi_m^{-1})^{-1}$ yielding particularly simple values. The $C_{P_N}$ curves for $\pi_m > 9$ appearing in Fig. 15b are here included largely for completeness. As $\pi_m$ increases, the resistance $R_E$ in series with $Z_f$ increase while $R_D$, in parallel with the $Z_f$, $R_E$ branch, decreases toward $R_\infty$. When $\pi_m = 999$, for example, $R_{DN} \approx 1.001$ and $R_{EN} = 10^3$. At $\Omega = 10^{-9}$, $R_{IN} \approx 134$ and $(\Omega C_{IN})^{-1} \approx 186$. Thus, as mentioned earlier, when $\pi_m > 1$, it will be difficult to obtain the components of $Z_{IN}$ accurately.

Let us now consider how the various types of curves of Fig. 15 may be explained. To do so, we need further information concerning $R_{IN}(\Omega)$ and $C_{IN}(\Omega)$. These quantities show approximate Warburg response in part of the $\Omega$ region and thus are approximately proportional to $\Omega^{-\frac{1}{2}}$ in this region. One way of showing such response is to plot the normalized quantities $C_{ID} \equiv A(C_{IN}/C_{INO})$ and $R_{ID} \equiv A(R_{IN}/R_{INO})$ versus $\Omega$, as in Fig. 16. Those curves with slope 0.5 in Fig. 16a represent constant $C_{IN}$ regions, that on the left for $C_{IN} \approx C_{INO}$ and that on the right for $C_{IN} \approx C_{ISN}$, as will become clearer later. Similarly, the lines with slope 0.5 in Fig. 16b represent $R_{IN} \approx R_{INO}$ regions while $R_{IN}$ decreases as $\Omega^{-2}$ for the $\pi_m \approx 1$ lines with slope $-1.5$.

The regions with essentially zero slope in Fig. 16 are those where $Z_{IN} \approx Z_{WN}$. A more exact approximation for $Z_{IN}$ in these regions will be considered in the next
Fig. 16. Normalized frequency dependence of the normalized quantities $C_{in}/A(C_{in}/C_{in0})$ and $R_{in}/A(R_{in}/R_{in0})$ for the $(0, \infty; \pi_m; 0, 10^4)$ situation.

section. Low-frequency saturation clearly occurs when $\Omega \lesssim 10\pi_m M^{-2}$. Thus, approximate Warburg response is well started by $\Omega \gtrsim 10^2 \pi_m M^{-2}$. Figure 16 shows that for $\pi_m \ll 1$ it is over by $\Omega \sim \pi_m$. These results also indicate that no such response occurs unless $M \gtrsim 10$, so that the Warburg range is non-zero. We shall generally consider only $M \gtrsim 10^2$ from now on. Because the range of $\pi_z$ is physically limited, the above Warburg range is still adequate for any experimental $\pi_z$ not just the $\pi_z = 1$ of Fig. 16, and the inequalities that limit it need not involve $\pi_z$.

In the Warburg range of $Z_{in}$, we have approximately,

$$Z_{in} \approx Z_{WN} = R_{WN} + (i\Omega C_{WSN})^{-1} \tag{20}$$

where

$$R_{WSN} = A/\Omega^{3/2} \tag{21}$$

and

$$C_{WSN} = (A\Omega^{3})^{-1} \tag{22}$$
Similarly, we may write
\[ Y_{in} \approx Y_{wn} = Z_{wn}^{-1} = G_{wpn} + i\Omega C_{wpn} \] (23)
where
\[ G_{wpn} \equiv \Omega^{1/2}A \] (24)
and
\[ C_{wpn} \equiv (2A\Omega^{1})^{-1} \] (25)
Now when \( C_{in} \) is replaced by \( C_{wsn} \) and \( R_{in} \) by \( R_{wsn} \) in eqns. (16) and (17) one obtains
\[ C_{pn} \approx 1 + \frac{(A\Omega^{1})^{-1}}{1 + [1 + \Omega^{1}(R_{en}/A)]^{2}} \] (26)
and
\[ G_{pn} \approx G_{dn} + \frac{(\Omega^{1}/A)[1 + \Omega^{2}(R_{en}/A)]}{1 + [1 + \Omega^{2}(R_{en}/A)]^{2}} \] (27)

Since \( (\Omega^{1}R_{en}/A) = R_{en}/R_{wsn} \leq R_{en}/R_{in} \) here, we need to consider the two cases: (A) \( (R_{en}/R_{in}) \ll 1 \), and (B) \( (R_{en}/R_{in}) \gg 1 \).

In case (A) we have
\[ C_{pn} \approx 1 + (A\Omega^{1})^{-1/2} \approx 1 + C_{wpn} \approx 1 + (C_{in}/2) \] (28)
and
\[ G_{pn} \approx G_{dn} + (\Omega^{1}/A)/2 = G_{dn} + G_{wpn} \] (29)
These equations lead to the important slope \( \pm 0.5 \) regions of Figs. 15a and 15b which there occur for \( \pi_{m} \leq 10^{-4} \), the value of \( M^{-1} \).

Low-frequency saturation is approached when \( \Omega \leq 10 \pi_{m}M^{-2} \), and \( C_{pn} \) approaches the plateau value \( C_{psn} = 1 + C_{isn} \approx M\delta_{p}^{1} \) when \( \Omega > \pi_{m} \). Figure 15b shows that this \( r_{p} = r_{n} = 0, \pi_{m} < M^{-1} \) plateau is also reached for \( \pi_{m} < M^{-1} \) even in the \( r_{p} = 0, r_{n} = \infty \) discharge situation. As pointed out earlier, this plateau is reached when the mobility of the discharging carrier (here \( \mu_{n} \)) is sufficiently low and the frequency sufficiently high that the discharging carrier has insufficient time to discharge and is essentially immobile; it then acts as though it were completely blocked. If we take the necessary condition as \( \Omega > 10\pi_{m} \), then the actual radial frequency corresponding to the choice of the equality sign is

\[ \omega = \omega_{b} = 10 \mu_{n}/\mu_{n} C_{g} R_{x}, \]
\[ = (4\pi e/\epsilon)(10 z_{p} p_{i} \mu_{n})(1 + \pi_{m}) \]
\[ \geq 40 \pi e z_{p} p_{i} \mu_{n}/\epsilon \] (30)
where the last equation follows on using \( \pi_{m} \ll 1 \). As before, the plateau region gives way to a simple Debye dispersion region proportional to \( \Omega^{-2} \) when \( \Omega > (M\delta_{p}^{1})^{-1} \).

The various regions which appear when \( \pi_{m} \ll 1 \) and especially when \( \pi_{m}M \ll 1 \) as well are described for \( C_{pn} \) and \( C_{in} \) in Table 2. Although the \( \Omega \)-values chosen to divide the various regions are somewhat approximate, they are quite adequate for usual situations. In the \( (r_{p}, r_{n}, \pi_{m}, \pi_{z}, 0, M) \) situation with \( 0 \ll \pi_{m} \ll 1 \) the
### TABLE 2

**RESPONSE REGIONS FOR $C_{PN}$ AND $C_{m}$ WHEN $\pi_m \ll 1$**

<table>
<thead>
<tr>
<th>Region</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description:</td>
<td>Low-frequency-limiting saturation</td>
<td>Approximate $Z_{TN}$, $Y_{TN}$ Warburg response</td>
<td>Double-layer plateau</td>
<td>External transition</td>
<td>Dielectric relaxation</td>
</tr>
<tr>
<td>$C_{PN}$ (Case A)</td>
<td>$C_{PN0}$</td>
<td>$C_{PN0} &gt; C_{PN} &gt; C_{WN} &gt; C_{PSN}$</td>
<td>$C_{PSN}$</td>
<td>$&lt; C_{PSN}$</td>
<td>$C_m$</td>
</tr>
<tr>
<td>$C_{IN}$</td>
<td>$C_{IN0}$</td>
<td>$C_{IN0} &gt; C_{IN} &gt; C_{WS} &gt; C_{SN}$</td>
<td>$C_{SN}$</td>
<td>$&lt; C_{SN}$</td>
<td></td>
</tr>
<tr>
<td>$\Omega$ range</td>
<td>$0 \leq \Omega \leq 10 \pi_m M^{-2}$</td>
<td>$40 \pi_m M^{-2} \leq \Omega &lt; \pi_m$</td>
<td>$10 \pi_m \leq \Omega \leq (10 M \delta_k^a)^{-1}$</td>
<td>$(M \delta_k^a)^{-1} \leq \Omega \leq 0.1$</td>
<td>$0.1 \leq \Omega &lt; \infty$</td>
</tr>
<tr>
<td>$\Omega$ division points</td>
<td>$10 \pi_m M^{-2}$</td>
<td>$\pi_m$</td>
<td></td>
<td>$(M \delta_k^a)^{-1}$</td>
<td>0.1</td>
</tr>
</tbody>
</table>
appropriate expression for \( C_{\text{IN}} \) is \( g_p^{-2}[M\delta_p^+ - 1] \); \( G_{\text{EN}} \approx [1 + (r_p/2)]^{-1} + \pi_m[1 + (r_n/2)]^{-1} \); and \( G_{\text{DN}} \approx [1 + (2/r_p)]^{-1} + \pi_m[1 + (2/r_n)]^{-1} \). Thus, when \( r_p = 0 \), \( R_{\text{DN}} = \pi_m^{-1}[1 + (2/r_n)] \) and may be neglected for sufficiently small \( \pi_m \). In addition, \( R_{\text{IN}} \) will be appreciably less than unity in the plateau region and may be neglected compared to \( R_{\text{EN}} \). When \( r_p = 0 \), Fig. 17 then shows the approximate equivalent circuit of the overall system. Of course when \( \pi_m \ll r_p \ll \pi_m^{-1} \), the \( R_x \) in Fig. 17 must be replaced by \( R_x \approx [1 + (r_p/2)] R_x \) and the resistance \( R_D \approx [1 + (2/r_p)] R_x \) must be connected in parallel with \( C_g \).

![Fig. 17. Approximate equivalent circuit in the plateau region (Regions C and D of Table 2).](image)

In order to find under what conditions \( (R_{\text{EN}}/R_{\text{IN}}) \) is smaller or greater than unity, we require an expression for the normalized Warburg parameter \( A \). In the approximate Warburg region, the exact expression for \( Z_{\text{IN}} \), given earlier, may be simplified under the overlapping conditions \( M \gg 1 \), \( 10 \leq M^2 b\Omega \), \( (a - 1)\Omega \ll 1 \), \( \Omega[b(a - 1)] \ll 1 \), \( (b\Omega)^2 \ll \delta_n \delta_p [(g_p - g_n)/g_p g_n]^2 \), and \( b\Omega \ll \delta_n \delta_p (g_p - g_n)^2/g_p M \). Note that for \( r_p = 0 \), \( r_n = \infty \) the last two conditions reduce to \( (b\Omega)^2 \ll \delta_n \delta_p = \pi_m \), and \( b\Omega \ll \infty \). The condition \( 10 \leq M^2 b\Omega \) leads to \( \Omega \geq 10 M^{-2}(2 + \pi_z + \pi_m^{-1})/(2 + \pi_m + \pi_m^{-1}) \) when the exact relations \((\epsilon_0\epsilon_p)^{-1} = (2 + \pi_m + \pi_m^{-1})\) and \((\delta_n \delta_p)^{-1} = (2 + \pi_z + \pi_m^{-1})\) are used. For \( \pi_z = 1 \), this reduces to \( \Omega \geq 40 M^{-2}\pi_m \), \( 10 M^{-2} \), and \( 40 (M^2\pi_m)^{-1} \) for \( \pi_m \ll 1 \), \( \pi_m = 1 \), and \( \pi_m \gg 1 \), respectively. When \( M^2 b\Omega < 10 \), one approaches the low-frequency saturation region.

The result of the \( Z_{\text{IN}} \) simplification yields \( Z_{\text{IN}} \approx Z_{\text{WN}} \) together with the following expression for \( A \),

\[
A \equiv [MG_{\text{pn}}(2\epsilon_n\epsilon_p \delta_n \delta_p)]^{-1}
\]

(31)

applying for \( r_p, r_n, \pi_m, \pi_z; 0, M \). Here

\[
G_{\text{pn}} \equiv [(g_p - g_n)/g_p g_n]^2
\]

(32)

The symmetric function \( G_{\text{pn}} \) is unity for \( r_p = 0 \), \( r_n = \infty \) and, in the \( r_p = 0 \), \( r_n < \infty \) case, decreases only slowly as \( r_n \) decreases. For example for \( r_n = 200 \), \( G_{\text{pn}} \approx 0.99 \). Since \( G_{\text{pn}} \) is symmetric in \( n \) and \( p \), so also is \( A \).

Now since \( (R_{\text{EN}}/R_{\text{IN}}) \approx \Omega^{1/2}/AG_{\text{EN}} \) in the Warburg region, we find

\[
R_{\text{EN}}/R_{\text{IN}} \approx M\Omega^{1/2}G_{\text{pn}}(g_p g_n/g_s)[(2\epsilon_n\epsilon_p \delta_n \delta_p)]^{1/2}
\]

(33)

Now for \( r_p = 0 \), \( r_n = \infty \), this result reduces to

\[
R_{\text{EN}}/R_{\text{IN}} \approx M\Omega^{1/2}[2\epsilon_n \epsilon_p \delta_n \delta_p]^{1/2}
\]

\[
= M[\pi_m \Omega]^{1/2}[2\delta_n \delta_p]^{1/2}
\]

\[
= M[\pi_m \Omega]^{1/2}[1 + 0.5(\pi_z + \pi_m^{-1})]^{1/2}
\]

(34)
Again since the range of $\pi_z$ is limited, the $\pi_z$ terms in the last expression may be neglected for most purposes. At the large-$\Omega$ edge of the Warburg region where $\Omega = \pi_m$ when $\pi_m \ll 1$, $(R_{EN}/R_{IN}) \sim M\pi_m$. Thus, in order for case (A) to hold in Region B of Table 2 we must have $\Omega \ll (M^2\pi_m)^{-1}$ and $M\pi_m \ll 1$. It is, of course, essentially just the $M\pi_m \ll 1$ condition that ensures that Region C, the plateau of Table 2, is appreciable. When $M\pi_m \simeq 1$, Fig. 15b shows no plateau.

Before considering case (B), let us first examine the intermediate $(0, \infty ; 1, 1; 0, M)$ situation. Here $(R_{EN}/R_{IN}) = M(\Omega/2)^{1/2}$ and low-frequency saturation occurs near $\Omega = 10M^{-2}$. Thus the $(R_{EN}/R_{IN}) = 1$ condition is almost within Region A of Table 2. In this region, of course $Z_{IN} \neq Z_{WN}$, however. Figures 15b and 16a show that for $Z_{IN} \approx Z_{WN}$ in the present situation, we must have $\Omega \gtrsim 32M^{-2}$. At this point $(R_{EN}/R_{IN}) = 4$. The denominator of eqns. (25) and (26) is then 26, sufficiently large that explicit external Warburg behavior, as in Region B of Table 2, does not appear. We will thus next consider the limiting $(R_{EN}/R_{IN}) \gg 1$ situation. Now consider case (B), where eqn. (34) yields $\Omega > (M^2\pi_m)^{-1}$, consistent with the general simplification condition $\Omega > 10(bM^2)^{-1}$, which itself allows case (B) behavior even for $\pi_m$ as small as $10^{-2}$ when $\Omega \gtrsim 10^{-4}$ in the present $M = 10^4$ case. Now eqns. (26) and (27) lead to

$$C_{PN} \simeq 1 + (\Omega^2 R_{EN}^2/\lambda)^{-1}$$

and

$$G_{PN} \simeq G_{DN} + G_{EN} = 1$$

On using the earlier expression for $\lambda$, eqn. (35) becomes, for $(r_p, r_n; \pi_m, \pi_z; 0, M)$,

$$C_{PN} \simeq 1 + [\Omega^2 M \{(g_p-g_n)/g_n\}^2 (2\pi_0 \pi_p \pi_n)^{1/2}]^{-1}$$

As mentioned earlier, equations such as (37) also hold in the extrinsic conduction situation when the $\varepsilon$'s and $\delta$'s are suitably redefined. When $r_p=0$ and $r_n=\infty$, eqn. (37) reduces to

$$C_{PN} \simeq 1 + [2^{1/2} \Omega^{-1/4} \pi_n^{1/4} /M (2\pi_0 \pi_p \pi_n)^{1/2}]$$

and for $\pi_z=1$ as well to

$$C_{PN} \simeq 1 + [2^{1/2} \Omega^{-1/4} \pi_n^{1/4} /M]$$

This result describes those curves of Fig. 15b which show a slope of $-1.5$. In the $\pi_z=\pi_n=1$ case,

$$C_{PN} \simeq 1 + (2^{1/2} \pi_0)^{-1}$$

To illustrate the size of the second term in (38), take $(R_{EN}/R_{IN}) = 10$ and use this value in (34) and the result in (38). At this point, where $\Omega = 100 \pi_0^{1/2} /2\pi_0 \pi_n \pi_n M^2$, $C_{PN} \simeq 1 + 2\pi_0 \pi_n \pi_n \pi_p 10^{-3} M^2$.

For $\pi_z=1$ and $\pi_m \gg 1$, this equation yields $C_{PN} \simeq 1 + (M^2/2000)$, which can still be considerably larger than the plateau value, $M\delta_p^2$, for large $M$.

In case (B), where Warburg behavior of $Z_{IN}$ requires $\Omega \gtrsim 40(M^2\pi_m)^{-1}$, and $C_{IN}$ approaches low-frequency saturation for $\Omega \lesssim 10(M^2\pi_m)^{-1}$ when $\pi_m \gg 1$, the curves of Fig. 15b show that $C_{PN} \to C_{PNO}$ in this case when $\Omega < 10(M^2\pi_m)^{-1}$. The
initial decrease of $C_{PN}$ below $C_{PN0}$ thus arises here both from the decrease of $C_{IN}$ and from an increase in the denominator of (26).

When the expression for $A$ of eqn. (31) is converted to one for $A_0$ through using eqn. (7), one obtains in the present two-electrode situation

$$A_0 = \left[ \left( \frac{e^2}{2} kT \right) \left( G_{pn}/2 \right) \left( z_n n_i + z_p p_i \right) \times \left\{ \left[ (z_p D_p)^{-1} + (z_n D_n)^{-1} \right] \left[ z_p^{-1} + z_n^{-1} \right] \right\} \right]^{-1}$$

where mobilities have been converted to diffusion coefficients through the relation $D_i = (kT/\varepsilon z_i) \mu_i$. This result for $A_0$ will be considered in more detail in the next section and compared to earlier expressions for the Warburg parameter. It simplifies for $(0, \infty; \pi_m, 1; 0, M)$ and $z_p = z_n = \infty$ to

$$A_0 = \left[ \left( \frac{e^2}{2} \varepsilon \sigma^2 / kT \right) \left( D_p^{-1} + D_n^{-1} \right)^{-1} \right]$$

where $n_i = p_i = \varepsilon \sigma$ has been used, a condition following from $\pi = 1$. Since $A_0$ is independent of $l$ and thus intensive, $Z_w$ is also intensive as it should be.

The unnormalized form of eqn. (28), applying in the case (A) Warburg region, is just

$$C_p \approx C_g + (2\omega^2 A_0)^{-1}$$

Similarly, the case (B) result given in eqn. (35) becomes

$$C_p \approx C_g + (A_0/R_{EN}^2 \omega^2)$$

In the $z_p = z_n = 1$, $(0, \infty; \pi_m, 1; 0, M)$ case, this result reduces to

$$C_p \approx C_g + (A_0 \varepsilon^2 / R_{EN}^2 \omega^2)$$

$$= C_g + (2\varepsilon \sigma^2 / l^2) \left[ \mu_p (D_p/D_n)^4 (D_p + D_n)^4 \right] \omega^{-\frac{1}{2}}$$

Although the Warburg $(C_p - C_g)$ of eqn. (44) is intensive, the $(C_p - C_g)$ of eqn. (46) is certainly not.

For this same $r_p = 0$, $r_n = \infty$ situation, Friauf obtained the expression (rewritten in the present notation)

$$C_p = (2\varepsilon \sigma^2 / l^2) \left[ \mu_p (D_n/D_p)^4 (D_p + D_n)^4 \right] \omega^{-\frac{1}{2}}$$

Except for the absence of $C_g$ and the subscript transformation $n \rightarrow p$ and $p \rightarrow n$, the results are the same. In addition, however, Friauf gives no range of $\omega$ defining the region of applicability of this result. The $n$-$p$ transformation is just that where changes $(0, \infty; \pi_m, 1; 0, M)$ to $(\infty, 0; \pi_m, 1; 0, M)$ or its equivalent, $(0, \infty; \pi_m^{-1}, 1; 0, M)$. Thus Friauf's result applies not, as he states, for $(0, \infty)$ but for $(\infty, 0)$ boundary conditions. When $\pi_m$ is appreciably different from unity, Friauf's result, when incorrectly applied to the $(0, \infty)$ case, leads to $C_p$ values which will differ very significantly from the correct values since the ratio of his result to the correct one is, on neglecting $C_g$, just $\pi_m^2$.

Figure 15b shows that $\Omega \leq 10^{-3}$ is necessary for very much case (B) behavior to appear. Therefore, for case (B) we may write $(\pi_m M^2)^{-1} \ll \Omega \leq 10^{-3}$. Thus here $\pi_m M^2 \geq 1$, as compared to the $M \pi_m \leq 1$ condition required for case (A).

We have devoted especial attention to the curves of Fig. 15b because most experimental results yield similar sorts of curves. Figures 18 and 19 show how the $\pi_m = \pi_p = 1$ curves of Fig. 15 change when $r_p$ or $r_n$ are separately varied. The Tables in these Figures also indicate how $R_{NO}$, $R_{EN}$, and $R_{DN}$ vary. Nore from
Fig. 18. Normalized frequency response of $G_{PN}$ and $C_{PN}$ for the $(r_p, \infty; 1, 1; 0, 10^4)$ situation.

Fig. 19. Normalized frequency response of $G_{PN}$ and $C_{PN}$ for the $(0, r_n; 1, 1; 0, 10^4)$ situation.

Fig. 18b that for small $r_p$ there is still an appreciable region of approximately $-1.5$ slope present and that regions with negative slopes nearer zero appear as $r_p$ increases. On the other hand, Fig. 19 shows that a new dispersion region appears when $r_p=0$ and $r_n<\infty$. This result is consistent, of course, with the three arcs which appear in Fig. 5b for the same $(0, r_n; 1, 1; 0, 10^4)$ situation.

Some comparison of theoretical and experimental Warburg region behavior will be presented in the next Section from an electrochemical point of view. But a great deal of experimental evidence is available for solids and fused salts where $C_p$ or the apparent dielectric constant, $\epsilon_a$, shows $\omega^{-m}$ dependence over appreciable ranges with $0 \leq m \leq 2$ and especial concentrations of values around 0.5 and 1.5. Reference has already been given to the work of Friauf$^{23}$ ($m \sim 1.5$) and the author$^{11}$ ($m=1.5, 2$). In addition some of the earlier literature has been summarized else-
where\(^1\)\(^-\)\(^4\). Here only a few relatively recent experimental results will be briefly mentioned.

Some of the types of frequency response results with which we shall be concerned have been ascribed to the presence of a continuous or discrete distribution of relaxation times. While this explanation will be appropriate in some cases, a partially blocking space-charge theory\(^2\)\(^4\)\(^23\) explanation seems more likely in most cases, especially those where very high values of \(C_p\) or \(e_a\) appear at low frequencies.

Michel et al.\(^24\) have seen \(\omega^{-m}\) behavior in diverse solid materials with \(0 < m < 1.5\) and numerous results with \(m \sim 1\). Cochrane and Fletcher\(^25\) have found \(e_a\) versus frequency curves rather similar to some of those of Figs. 15b and 19b for single crystal AgI. Armstrong and Race\(^26\) have observed good \(r_p = r_a \approx 0\) type curves in liquid electrochemical situations. Allnatt and Sime\(^27\) working with single crystal NaCl, found many slopes in the range \(1.3 < m \leq 1.9\). In contrast, Lancaster\(^28\) found many slopes of \(\sim 1.5\) or less for thin films of cerous fluoride.

Some application of the results of the present theory to the experimental measurements of Mitoff and Charles\(^29\) has already been given\(^2a\)\(^30\). Although these authors question the applicability of some of the conclusions\(^31\), their reasons do not seem convincing\(^21\). Mitoff and Charles found \(m\)-values of 0.5, 1, 1.5, and 2 for a variety of solid materials. Also, Tibensky and Wintle\(^32\) found series capacitance frequency dependences with \(m \approx 0.5\) for KBr single crystals, although the conversion from measured parallel capacitance to calculated series capacitance was not carried out using one of the circuits of Fig. 1. Nevertheless, Warburg response appears and may be associated with a \(\pi_m \ll 1\) situation. Finally, Maeno\(^33\), working with pure and doped single crystals of ice, has found many \(e_a\) curves with shapes like those of Figs. 15b and 19b. Both \(m \sim 0.5\) and \(m \sim 1.5\) values appear. He also gives impedance-plane results consistent with those of Fig. 3b. Although the data indicate the high probability of an incompletely blocking space-charge situation, Maeno suggests a distribution of relaxation times explanation.

Incidentally, for simplicity I have presented no discussion of the many different doping and electrode situations applicable for the various experiments mentioned above. Both essentially blocking and non-blocking (e.g., \(r_p \sim 0\), \(r_a \sim \infty\)) electrodes were used. Not all the materials measured were in an intrinsic conduction temperature region but many were. It is hoped to compare intrinsic-extrinsic conduction theoretical predictions\(^4\) and appropriate experimental results, with especial emphasis on temperature dependence, in a later paper\(^5\).

VI. DETAILED CONSIDERATION OF APPROXIMATE WARBURG RESPONSE

A. Analysis

In this Section, we shall be particularly concerned with the region showing approximate Warburg response of \(Z_{IN}\). As we have seen, strong external Warburg response only appears for \(\pi_m \ll M^{-1}\) and leads to Region B of Table 2. But Fig. 16 shows that approximate Warburg response appears in \(Z_{IN}\) in certain frequency regions for all \(\pi_m\). Thus, to the degree that experimental accuracy allows \(Z_t\) to be obtained adequately from \(Z_p\). Warburg response can be derived from even the \(m = 1.5\) regions of case (B) of the last Section, where \(\pi_m\) may appreciably exceed unity.

As an extreme example, consider the \((0, \infty; 999, 1; 0, 10^4)\) curve of Fig. 15b.
at $\Omega = 10^{-9}$, where the overall dissipation factor, $D_T \equiv G_{PN}/\Omega C_{PN} = -\text{Re}(Z_{TN})/\text{Im}(Z_{TN})$, is about 7085. Now although Seitz et al. have described a technique which allows measurement of $C_p$ and $G_p$ with reasonable accuracy up to $D_T$ values of about $10^4$, the main difficulty arises here in the calculation of $C_i$ and $R_i$ from $C_p$ and $G_p$ measurements. Assume that $C_g$ and $R_{\infty}$ can be obtained from $\Omega \geq 0.1$ measurements and $G_0$ from measurements in the low-frequency saturation region, $\Omega \leq b^{-1} M^{-2}$. Then at a given $\omega$ value of interest, $\Omega$, $C_{PN}$, $G_{PN}$, $G_{DN}$, and $G_{EN}$ may be calculated. The solution of eqns. (16) and (17) for $C_{IN}$ and $R_{IN}$ yields

$$C_{IN} = (C_{PN} - 1) + \frac{[(G_{PN} - G_{DN})^2/\Omega^2(C_{PN} - 1)]}{(G_{PN} - G_{DN})^2 + (G_{PN} - G_{DN})^2}$$

and

$$R_{IN} = \frac{[(G_{PN} - G_{DN})/(\Omega^2(C_{PN} - 1)^2 + (G_{PN} - G_{DN})^2)]}{-R_{EN}}$$

For the $(0, \infty; 999, 1; 0, 10^4)$ situation, the terms involving $(G_{PN} - G_{DN})$ dominate. But here $G_{PN} \approx G_{DN} \approx 1$, and $(G_{PN} - G_{DN}) \approx 8.59 \times 10^{-4}$. The problem is thus evident: $G_{PN}$ and $G_{DN}$ must be known to one part in $10^4$ or better to achieve even moderate accuracy in $C_{IN}$ and $R_{IN}$. Of course when $\pi_m$ is appreciably smaller, this problem is much less severe.

Some comparison has already been given of the present expression for the Warburg parameter $A_o$, which applies for a binary system without a supporting indifferent electrolyte, with the conventional expression. In the usual derivation of $A_o$, electroneutrality is assumed everywhere, implicitly or explicitly arising from the presence of a supporting electrolyte whose ions are taken to be completely blocked. Then the contributions to $A_o$ are, for example, from the diffusion of oxidizing and reducing species in the neighborhood of the working electrode. The situation is considerably different in the present work. Here in the $r_p=0$, $r_n=\infty$ case, for example, charges are coupled through Poisson's equation; charge of one sign is completely blocked; and only that of opposite sign reacts at the electrode. Further, we have considered the situation of two identical electrodes. Thus, in the simplest case the charged state of the reacting species is created by charge transfer at one electrode and destroyed at the other. These processes are reversed when the polarities of the electrodes reverse.

It is believed that the physical situation described above and analyzed earlier is a plausible one for the unsupported binary electrolyte and for the two carrier intrinsic conduction situation in solids. Some modification is necessary to pass from the present assumption of two identical, plane-parallel electrodes, usual for experiments with solids, to that of a small working electrode and a large indifferent counter electrode, common for work with liquid electrolytes. To good approximation, it seems plausible to pass from two identical electrodes each of area $\sigma$ to a single working electrode of area $\sigma$ by dividing intensive impedance components, associated with processes at the electrodes, by two. Thus, in the present situation, where only specific quantities are considered, $Z_W \equiv 0.5^{(1)}Z_W$, where the superscripts indicate one or two electrodes. It follows that $(1)^{(1)}A_o \approx 0.5^{(1)}A_o$. Non-intensive quantities such as $C_g$ and $R_{\infty}$ cannot be treated in this way, of course. For the actual single working electrode situation used in an experiment, $C_g$ and $R_{\infty}$ should either be calculated accurately or, preferably, directly measured in the region where they dominate, $\Omega > 0.1$. 

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The above prescriptions may be adequate when $Z_T - R_n \cong Z_w$ to good approximation, but they are impractical to apply accurately in the present binary case where $Z_T$ and $Z_i$ may be made up of both intensive and extensive circuit elements mixed together in complicated fashion. In a recent preliminary note\textsuperscript{35}, comparison of $A_0$'s was made for a single working electrode situation. Here such comparison will be made for two identical electrodes by using $(^{(2)}A_0 = 2^{(1)}A_0$, where $(^{(1)}A_0$ is the conventional result. We may then continue to deal directly with the unmodified two-electrode theoretical circuit elements $C_e$, $R_F$, $R_R$, and $Z_t$.

The conventional supported result for oxidizing and reducing species with concentration $c_O$ and $c_R$, diffusion coefficients $D_O$ and $D_R$, and stoichiometric factors $v_O$ and $v_R$ may be written in the two-electrode case as\textsuperscript{36,37}

$$A_0 = \left[ \left( \frac{n^2 e^2}{2 kT} \right) \left( \frac{v_O^2}{c_O D_O} + \frac{v_R^2}{c_R D_R} \right) \right]^{-1} $$

where $n$ is here the number of electrons participating in the reaction. This result may be compared to that of eqn. (42) for $z_p$ and $z_n$ arbitrary in the $(r_{m}, r_{n}, \pi_{m}, \pi_{z}; 0, M)$ situation. The explicit result for $(0, \infty; \pi_{m}, 1; 0, M)$ and $z^* = z_n = z_e$ has already been given in eqn. (43).

Although eqns. (43) and (50) are still notably different in ways readily amenable to experimental verification, in the special situation where $z^e = (n/\nu) = (n/v_k)^2$, $D_O = D_R = D_1 = D_p$, and $c_O = c_R = c_p$, the equations yield the same result. It is this result which is, in fact, most often used to analyze experimental measurements, probably because of lack of separate information on $D_n$, $D_p$, etc. Although the $n$, $p$, and $c_i$ quantities in the present treatment are equilibrium bulk values, as are $c_O$ and $c_R$, the diffusion coefficients $D_n$ and $D_p$ refer to charged species in the present binary case while the question of the charge states of the possibly many species considered in the conventional supported case\textsuperscript{36} does not enter the derivation explicitly except through the presence of $n$. Comparison between the present result for $A_0$ and a more pertinent generalization of the conventional result will be carried out later in this Section.

Let us now consider a somewhat better approximation for $Z_i$ than the $Z_w$ employed in the last Section. Let $c \equiv (\delta_n/\epsilon_n) - (\delta_p/\epsilon_p)$. Next apply the inequalities $M > 1$, $\Omega \geq (10/hM^2)$, $\Omega |a - 1| \ll 1$, $\Omega |c| \ll 1$, and $\Omega |c| \ll (g_p - g_n)/g_n$ to simplify the complete expression for $Z_{in}$ given earlier\textsuperscript{4}. The result of very considerable manipulation can be written as

$$Y_{in} \cong G_{wpn} \left[ \frac{(1 - \delta_1 - \delta_2) + i(1 + \delta_2 + \delta_3)}{(1 + \alpha_1) + i\alpha_2} \right] $$

where

$$\delta_1 \equiv (2/h\Omega M^2)$$

$$\delta_2 \equiv \Omega (r - 1) G_{EN}^2 G_{pn}^{-1} / g_e \epsilon_p \epsilon_n$$

$$\delta_3 \equiv \Omega (M/g_e) G_{EN}^2 G_{pn}^{-1} (2 + \pi_m + \pi_m^{-1})$$

$$\alpha_1 \equiv g_n^{-1} (\delta_1^{-1} - 1)$$

$$\alpha_2 \equiv (2\Omega h M^2)$$
and

\[ \alpha_2 \equiv g_s^{-1} \left[ \delta_1^{-1} + \Omega(a - 1)(r - 1) \right] \]  

(56)

Here,

\[ H_{pn} \equiv \frac{\left(g_n^2 - g_p\right)}{\left(g_p - g_n\right)^2} \]  

(57)

When \( g_p \) or \( g_n \) is infinite, \( H_{pn} \) reduces to \( \delta_n^2 \) or \( \delta_p^2 \), respectively. For \( r_p = 0, r_n \gg 1, \pi_n \ll 1, \) and \( \pi_x = 1, H_{pn} \cong 0.25 \).

Although eqn. (51) is only an approximate result for the Warburg region, it nevertheless maintains the original symmetry of \( Z_{in} \) which ensures that \( Z_{in} \) is the same for \( (r_p, r_n; \pi_m, \pi_x; 0, M) \) and for \( (r_n, r_p; \pi_m^{-1}, \pi_x^{-1}; 0, M) \). Note that when \( g_p \) or \( g_n \) is infinite, \( \delta_n, \alpha_1, \) and \( \alpha_2 \) are all zero. Since we require \( f_2 > (10/bM^2) \) here, eqn. (52) yields the result \( \delta_1 \approx 5^{-\frac{1}{4}} \approx 0.447 \). It will be considerably smaller away from the low-\( \Omega \) edge of the Warburg region.

Let us now introduce some new quantities and write

\[ Y_{in} \equiv G_{kn} + i\omega C_{kn} \]

\[ Y_{on} \equiv G_{opn} + i\omega C_{opn} \]

\[ Z_{in} \equiv R_{in} + (i\omega C_{in})^{-1} \]

\[ Z_{on} \equiv R_{osn} + (i\omega C_{osn})^{-1} \]

We have \( Z_{in} = Y_{in}^{-1} \) here but have not assumed \( Z_{on} = Y_{on}^{-1} \). The above exact relations lead to

\[ G_{kn} \equiv G_{wpn} + G_{opn} \]

\[ C_{kn} \equiv C_{wpn} + C_{opn} \]

\[ R_{in} \equiv R_{wn} + R_{osn} \]

\[ C_{in}^{-1} \equiv C_{wn}^{-1} + C_{osn}^{-1} \]

(62)

(63)

(64)

(65)

Although eqns. (62) through (65) are always possible when the \( \theta \) quantities are arbitrary, we shall be particularly interested here in relatively small deviations from Warburg behavior, where the second term in each equation is substantially smaller in magnitude than the first term. Further, we shall also be interested in any frequency region where the second terms are substantially independent of frequency. In this region, let us denote the constant parts of the second terms with a subscript "C". Thus for example, over a certain \( \Omega \) range \( G_{opn} \geq G_{cpn} \), a frequency-independent circuit parameter. Equivalent circuits involving the above \( \theta \)-subscript quantities will be considered in the next part of this Section. Note that eqn. (64) suggests that \( R_{os} \) (or \( R_{cs} \)) plays a role in the present unsupported case equivalent to the equilibrium charge transfer resistance \( R_0 \) appearing in the usual supported situation. A detailed comparison will be made later in this Section.

Let us now assume \( \alpha_1 \ll 1 \) and \( \alpha_2 \ll 1 \) in eqn. (51). On series inverting the denominator, retaining only first-order terms, and ignoring all small frequency-dependent product terms, one is immediately led to
\[ G_{\text{wpN}} \approx -G_{\text{wpPN}}[(\delta_1 + \delta_2) + (\tau_1 - \tau_2)] \]  
\[ C_{\text{wpN}} \approx C_{\text{wpPN}}[(\delta_2 + \delta_3) - (\tau_1 + \tau_2 + \tau_3)] \]

where

\[ \tau_3 = \frac{C_{\text{WPN}}}{H_{\text{PN}} G_{\text{PN}}(M/g_s)} \]  

The frequency-independent parts of the above expressions are, on ignoring the difference between \((r - 1)\) and \(M\),

\[ G_{\text{CPN}} \equiv -G_{\text{wpPN}} \delta_1 = -e_p e_n G_{\text{PN}} = -G_{\text{PN}}/(2 + \pi_m + \pi_m^{-1}) \]  
\[ C_{\text{CPN}} \equiv C_{\text{wpPN}}[\delta_3 - 2(g_s \delta_1) - (2 + \pi_m + \pi_m^{-1})] \]

Because of the presence in \(G_{\text{wpN}}\) and \(C_{\text{wpN}}\) of somewhat compensating terms involving \(\Omega^m\) and \(\Omega^{-m}\), where \(m \neq 0\), the approximations \(G_{\text{wpN}} \approx G_{\text{CPN}}\) and \(C_{\text{wpN}} \approx C_{\text{CPN}}\) hold good over an appreciable \(\Omega\) range.

If we next write an expression for \(Z_{\text{IN}}\) from (51), now assume \(\delta_1, \delta_2,\) and \(\delta_3\) all small compared to unity, invert the denominator of \(Z_{\text{IN}}\), and again neglect all small frequency-dependent products, we obtain

\[ R_{\text{OSN}} \approx R_{\text{WSN}} \left[ \tau_1 + \tau_2 (1 + \delta_1) - \delta_2 - (\delta_3 + 2 \delta_1 \delta_2)(1 - g_s^{-1}) \right] \]  
\[ C_{\text{OSN}} \approx C_{\text{WSN}} \left[ \tau_1 (1 - g_s^{-1}) \right]^{-1} \]

The corresponding frequency-independent quantities are

\[ R_{\text{CSN}} \equiv R_{\text{WSN}} [2(g_s \delta_1)^{-1} - (\delta_3 + 2 \delta_1 \delta_2)(1 - g_s^{-1}) + g_s^{-1} \delta_1 \Omega(a - 1)(r - 1)] \]

\[ = (g_s G_{\text{PN}} e_n e_p)^{-1} - \left( \frac{r - 1}{M^2} \right) \left( \frac{G_{\text{PN}}}{\delta a \delta p} \right) \]

\[ \times \left[ (e_n e_p)^{-1} \left( H_{\text{PN}} (1 - g_s^{-1}) - \left( \frac{2 G_{\text{EN}}^2}{G_{\text{PN}} g_s} \right) \right) + \left( \frac{1 - a}{g_s} \right) \right] \]

\[ \approx (G_{\text{PN}} e_n e_p)^{-1} [g_s^{-1} - (H_{\text{PN}}/M \delta a \delta p)] \]  
\[ C_{\text{CSN}} \equiv C_{\text{WSN}} [\delta_1 (1 - g_s^{-1})]^{-1} \]

where \(g_s^{-1}\) has been neglected compared to terms of order unity in the last forms of eqn. (70) and in eqns. (73) and (74). These simplified results will be used as the definitions of the constant quantities from here on. Note that the larger of the two contributions to \(C_{\text{IN0}}\) when \(r_p\) and \(r_s\) are appreciably different is just \((\delta_s \delta_p M^2 G_{\text{PN}}/3)\); thus, \(C_{\text{CSN}}\) as given above is then appreciably larger than \(C_{\text{IN0}}\). Table 3 shows how the various frequency-independent elements depend on several quantities of interest for \((0, r_n; \pi_m, \pi_n, 0, M)\) with \(\pi_m \approx 1\).

Using the properties of the Warburg impedance, one may readily derive the exact equation

\[ Y_{\text{WN}} Z_{\text{IN}} + Y_{\text{IN}} Z_{\text{WN}} + Z_{\text{IN}} Y_{\text{IN}} = 0 \]  

(75)
TABLE 3

DEPENDENCE OF NORMALIZED, FREQUENCY-INDEPENDENT CIRCUIT ELEMENTS ON VARIOUS QUANTITIES FOR \((0, r_m, \pi_m, \pi_n, 0, M)\) WITH \(\pi_m \ll 1\), AND SEVERAL \((M/r_n)\) SITUATIONS

<table>
<thead>
<tr>
<th>(Y) (M/r_n)</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
<th>(D)</th>
<th>(E)</th>
<th>(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_{CSN}) (\geq 1)</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(\geq 1)</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(C_{CPN}) (\leq 1)</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(\geq 1)</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(G_{CPN}) Any</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>(C_{CSN}) Any</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

When the last term can be neglected, the result yields the approximate relations

\[
C_{\theta PN} \approx -2A^2G_{\theta PN} \quad (76)
\]

and

\[
R_{\theta SN} \approx -2A^2C_{\theta PN} \quad (77)
\]

Here, of course, \(2A^2 = (G_{WPN}C_{WSN})^{-1} = R_{WSN}/C_{WPN}\). Equations (76) and (77) are satisfied exactly by the final forms of the constant quantities, those where the subscript transformation \(\theta \rightarrow C\) is made. These results suggest that examination of the ratios

\[
U_1 = -\left(\frac{G_{\theta PN}}{G_{WPN}}\right)/(C_{\theta SN}^{-1}/C_{WSN}^{-1}) \quad (78)
\]

and

\[
U_2 = -\left(\frac{C_{\theta PN}}{C_{WPN}}\right)/(R_{\theta SN}/R_{WSN}) \quad (79)
\]

which both should be near unity over an appreciable \(\Omega\) range, should be of some interest.

It is of especial interest to point out that eqns. (70) and (73) show that \(C_{\theta PN}\) and \(R_{\theta SN}\) are both zero when

\[
H_{\theta}\left(\delta_\theta^\delta_\theta\right)^{-1} = (M/g_\theta) \quad (80)
\]

We may thus expect that \(C_{\theta PN}\) and \(R_{\theta SN}\) will also be zero near this value. In the \(r_\theta = 0, r_\pi \gg 1\) situation with \(\pi_m \ll 1\), this condition becomes approximately

\[
\delta_\pi^\delta_\pi = \pi_\pi^{-1} = (M/g_\pi) \approx (2M/r_n) \quad (81)
\]

Therefore, when \(r_n \approx 2\pi_n M\), one may expect \(C_{\theta PN}\) and \(R_{\theta SN}\) to pass through zero. Although this zero point, where \(C_{KN} = C_{WPN}\) and \(R_{IN} = R_{WSN}\), yields perfect Warburg response for \(C_{KN}\) and \(R_{IN}\) to the degree that \(C_{\theta PN} \approx C_{CPN}\) and \(R_{\theta SN} \approx R_{CSN}\), \(Z_{IN}\) is not exactly equal to \(Z_{WN}\) here since the small quantities \(G_{\theta PN}\) and \(C_{\theta PN}^{-1}\) are not exactly zero as well. At \(r_n \approx 2\pi_n M\), \(Z_{IN}\) will, however, be closest to showing perfect Warburg response. It is interesting that such maximal Warburg response does not
occur at \( r_n = \infty \), where one would expect an infinite electrode reaction rate, but at a finite value of \( r_n \).

Next, the apparent intensive-extensive character of \( G_{cp} \), \( C_{cs}^{-1} \), \( R_{cs} \), and \( C_{cp} \) needs examination. Since \( G_{wp} \) and \( C_{ws} \) are intensive, eqns. (69) and (74) show that \( G_{cp} \propto G_{aw} \propto l^{-1} \) and \( C_{cs}^{-1} \propto (M^2C_g)^{-1} \propto l^{-1} \). These quantities are thus clearly not intensive, but it will shortly be shown that they make no significant contribution to \( G_{pN} \) and \( C_{iN} \) in the Warburg region when \( \eta_m \ll 1 \); thus their failure to be intensive is not important here.

On the other hand, \( C_{cp} \) and \( R_{cs} \) do play important roles. Because of eqn. (77), we need examine only \( C_{cp} \) for dependence on \( l \). When \( g_e = \infty \), eqn. (70) shows that \( C_{cp} \propto MC_v \) a properly intensive quantity. The second part of \( C_{cp} \), dominant when \( (M/g_s) \gg 1 \), is proportional to \( M^2C_g G_{pN}/g_s \), however. If \( r_p \) and \( r_n \) are themselves independent of \( l \), as was tacitly assumed in the preliminary note on this work\(^{35} \), then this second part is proportional to \( l \) and is therefore strongly extensive.

The normalized Chang–Jaffé boundary parameters \( r_p \) and \( r_n \) require further consideration, however. They have been introduced into the theory\(^4 \) through relations such as

\[
I_p(l) = (e\xi_p)(r_pD_p/l)[p(l) - p_e(l)]
\]

and

\[
I_n(0) = (e\xi_n)(r_nD_n/l)[n(0) - n_e(0)]
\]

Here \( I_p(l) \) is the conduction current of positively charged carriers at the right electrode; \( I_n(0) \) is that associated with negative carriers at the left electrode; \( p(l) \) and \( n(0) \) are boundary charge concentrations; and the subscript “e” denotes equilibrium values. In the present a.c. solution for the intrinsic-conduction case of no static fields within the material, \( p_e = p_i \), \( n_e = n_i \), and eqns. (82) and (83) reduce to the a.c.-only results\(^4 \)

\[
I_p(l) = (e\xi_p)(D_p/l)r_p
\]

and

\[
I_n(0) = (e\xi_n)(D_n/l)r_n
\]

where the effective rate constants are

\[\xi_p \equiv (D_p/l)r_p\]

and

\[\xi_n \equiv (D_n/l)r_n\]

Each \( \xi \) can be separately associated with a thermally activated rate process involving a symmetric free energy barrier to charge transfer at the electrode\(^{22, 23} \). Under these conditions, \( \xi_p \) and \( \xi_n \) are never actually either zero or infinite, but their possible range is such that the \( r \)'s may be well approximated by either zero or infinity. Note that we have followed Beaumont and Jacobs\(^{22} \) rather than Friauf\(^{23} \) in writing \( r_p \) and \( r_n \) rather than \( 2r_p \) and \( 2r_n \) in (82) and (83). Thus the present \( r_p \) and \( r_n \) are twice Friauf’s \( r_p \) and \( r_n \) and agree with Beaumont and Jacobs’ equivalent parameter \( \rho \) as well as the original Chang–Jaffé parameters. The present usage is slightly unfortunate, however, since it leads to definitions such as \( g_p = 1 + (r_p/2) \) rather than the simpler \( g_p = 1 + r_p \), but it has been widely enough used that it does not seem
worthwhile to redefine \( r_p \) and \( r_n \) at this stage.

Now since \( \xi_p \) and \( \xi_n \) are clearly intensive quantities, eqns. (86) and (87) show that \( r_p \) and \( r_n \) are extensive! The virtue of using \( r_p \) and \( r_n \) in normalized solutions of the general \((r_p, r_n; \pi_m, \pi_n; 0, M)\) situation is, however, that they are dimensionless and no separate knowledge of \( l, D_m \) and \( D_p \) values is required for a normalized solution. Now it is clear that while \( M/r_n \) and \( M/r_p \) are purely intensive, quantities such as \( M/g_s \), \( G_{pn} \), and \( H_{pn} \), which involve \( g_n \) and \( g_p \), contain parts independent of \( l \) as well as parts directly involving \( l \). Thus, even the introduction of eqns. (86) and (87) into the full expression for \( Z_i \) will not make it entirely intensive. It is thus not a pure interface impedance under all conditions.

Let us next consider, however, the usual situation of interest when electrode charge transfer occurs, that where \( \varepsilon_p r_p \) or \( \varepsilon_p r_n \) is much greater than unity. Then \( G_{pn} \approx 1, g_s \approx 0.5(\varepsilon_p r_p + \varepsilon_p r_n) \gg 1, \) \( H_{pn} \approx g_s^2/(g_p - g_n)^2 = \left(\left(\delta_n r_p + \delta_p r_n\right)/\left(r_p - r_n\right)\right)^2 \), and eqn. (80) becomes

\[
(\varepsilon_p r_p + \varepsilon_p r_n)\left(\delta_n r_p + \delta_p r_n\right)/\left(r_p - r_n\right)^2 \approx 2M\delta_n \delta_p
\]

(88)

For arbitrary \( \pi_m \) and \( r_p \sim 0, r_n \gg 1 \), for example, this zero condition becomes

\[
(\varepsilon_p r_p + \varepsilon_p r_n) \approx 2M\pi_x
\]

(89)
in agreement with (81) when \( \pi_m \ll 1 \). Note that eqn. (88) is entirely intensive when eqns. (86) and (87) are used for \( r_p \) and \( r_n \).

Now for the present \( g_s \gg 1, \) arbitrary \( \pi_m \) situation, \( R_{CS} \) becomes

\[
R_{CS} \approx \frac{(\varepsilon_p r_p)}{\left(2\varepsilon_p r_p + \varepsilon_p r_n\right) - \left(M\delta_n \delta_p\right)^{-1} \left(\delta_n r_p + \delta_p r_n\right)/\left(r_p - r_n\right)^2} R_x
\]

(90)

Let us now examine the case where the clearly intensive negative part of this expression is negligible compared to the positive part. Then on using

\[
(R_{CS}/\varepsilon_p r_p) = (2l/e)[(\mu_p + \mu_n)/(\mu_p H_n)](z_n n_i + z_p p_i)^{-1}
\]

(91)

and eqns. (86) and (87), one finds that

\[
R_{CS} \approx \frac{4kT/e^2}{(z_n n_i + z_p p_i)\varepsilon_p r_p^{z_n} \varepsilon_p r_n^{z_p}}
\]

(92)

This entirely intensive result holds, provided the positive part of \( R_{CS} \) remains dominant, for any \( \pi_m \) and either \( r_n \gg 1, 0 \ll r_p \ll r_n \) or \( r_p \gg 1, 0 \ll r_p \ll r_n \). Note that its calculation requires values of \( z_n \) and \( z_p \) not just their ratio, \( \pi_x \). Further, this expression for \( R_{CS} \) has been derived for a two-electrode situation; it must be halved when only a single working electrode is considered.

Equations (82)-(85) are similar to those used in conventional supported electrolyte theory; thus a comparison of effective rate constants is of interest. Note that in the region around equilibrium, where the present linearized results particularly apply, quantities such as the \( p_i \) and \( n_i \) of eqns. (84) and (85) are directly proportional to the amplitude of the applied a.c. potential, in consonance with supported case results.

In the conventional analysis, it is somewhat unusual to consider together both positive and negative charged entities which can react simultaneously at the
electrode. But this is the general situation considered here when both \( r_p \) and \( r_n \) are non-zero. The usual expression for \( R_0 \) for a single charge carrier reacting at an electrode may be written \(^{39}\)

\[
R_0 = (kT/e)\left(\frac{i_0}{n_0}\right)
\]

where \( i_0 \) is the apparent exchange current density. In the present case, we must introduce such a current for each reacting entity. Since the overall currents are in parallel and are assumed non-interacting, the effective \( R_0 \) may be written for the case of two identical electrodes as

\[
R_0 = (2kT/e)\left[\left(\frac{z_p}{n_p}i_{0p}\right) + \left(\frac{z_n}{n_n}i_{0n}\right)\right]^{-1}
\]

Now in the present case of zero direct current, \( i_{0p} \), for example, may be expressed as \(^{40,41}\)

\[
\frac{z_p}{n_p}i_{0p} = \frac{z_p}{n_p}k_pe_k, \quad \text{where} \quad k_p \text{ is the apparent standard heterogeneous rate constant for the positive charges, and the effective concentration } c_{pe} \text{ is often given by } c_{0p}^4c_0^{1-x}. \text{ Here } c_0 \text{ and } c_n \text{ are, as before, bulk concentrations of the oxidizing and reducing species and } x \text{ is the transfer coefficient. We may now write}
\]

\[
R_0 = (2kT/e^2)\left[\frac{z_p^2}{n_p}k_pe_k + \frac{z_n^2}{n_n}c_{pe}\right]^{-1}
\]

The predictions of eqn. (94) are different in general from those of eqns. (73) and (92) for the coupled-case \( R_{cs} \). For example, the present unsupported treatment involves the ratio of the mobilities of the charged particles, while the extended conventional result does not. This difference between \( R_{cs} \) and \( R_0 \) certainly arises from the strong coupling between charges of opposite sign in the unsupported situation.

When eqns. (92) and (94) are set equal and \( z_p^2i_{pt} = z_n^2i_{nt} \) is used, one finds

\[
\left(\frac{z_p^2}{n_p}k_pe_k + \frac{z_n^2}{n_n}c_{pe}\right) = \left(\frac{z_p}{n_p}k_pe_k + \frac{z_n}{n_n}c_{pe}\right)
\]

Now when \( \xi_p \) and \( k_p \) are both zero, (95) leads to

\[
\xi_n = (c_{pe}/n_0)e_p^{-2}k_n
\]

This result applies in the general \((0, r_n; \pi_m, \pi_z; 0, M)\) case with \( r_n \gg 1 \). When \( \pi_m \ll 1, e_p^{-2} \) in (96) is essentially unity. We then see that when \( c_{ne} = n_1 \) as well, \( \xi_n = k_n \). A result analogous to (96) can be derived in the \( r_p > 0, r_n = 0 \) case. Finally, it should be noted that the comparisons represented by eqns. (95) and (96) only turn out so simple when the negative second term in \( R_{cs} \) is negligible. There is clearly a contribution to \( R_{cs} \) in the present work which does not appear in the analogous \( R_0 \) of the unsupported case. Again, this term probably arises because of charge coupling effects in the unsupported case. Since it involves a negative resistance, the electrode is more open (less blocking) when \( r_n = \infty \) and this term is dominant than it is when eqn. (80) holds, \( g_0 \ll \infty \), and \( R_{cs} = 0 \).

Finally, when \( k_p \) and \( k_n \) are both non-zero, we may patch together an expression for the appropriate \( A_0 \) in this generalized supported case for comparison with the unsupported result of eqn. (42). Let us consider the situation where there is a large reservoir of neutral forms of the mobile positive and negative ions at (and in) the electrodes. The neutral concentrations will be taken large enough to be essentially invariant: small a.c. perturbations change these concentrations only negligibly, and they will not contribute significantly to the expression for \( A_0 \) in the supported case\(^{42}\). Take \( p_l \) and \( n_l \) as usual as the concentrations of the two ionic species in the bulk of the electrolyte or solid material. Then the two conventional contributions to the Warburg admittance arising from these charges are uncoupled and add directly. For the two-electrode case, the expression
then seems appropriate. Here \( u_0(x) \) is the unit step function: \( u_0(x < 0) = 0; \ u_0(x > 0) = 1 \).

The introduction of this function is probably an approximation (associated with the assumption of no coupling at all), but it is needed, just as is the function \( G_{pn} \), which appears in eqns. (31) and (42) for \( A \) and \( A_0 \) and in all unsimplified expressions such as eqns. (69), (70), (73) and (74). When \( r_p = r_n \), \( G_{pn} = 0 \), so \( A \) and \( A_0 \) go to infinity in this completely blocking case.

The present supported \( A_0 \) is still quite different, however, from the unsupported case result of eqn. (42). There, when one \( D \) is much smaller than the other, that one dominates the expression for \( A_0 \). Here, when \( z_p D_p^2 u_0(k_p) \gg z_n D_n^2 u_0(k_n) \), for example, only the larger \( D \) is important in \( A_0 \). Even when \( z_n = z_p = z_o \), \( n_i = n_p = o_n \), \( D_p = D_n = D_o \), and \( k_p \ k_n > 0 \), the unsupported result is, from eqn. (43),

\[
A_0 \approx 2e^2 kT/e^2 z_c D_o \]

while the result following from eqn. (97) is one fourth of this \( A_0 \). The differences between the unsupported and supported results again arise from the charge coupling present in the unsupported case and perhaps also from some possible inappropriateness of eqn. (97). It does, however, seem very reasonable that the magnitude of the Warburg impedance be appreciably higher, as above, in the unsupported than in the supported situation. Finally, although the present theory and results have been here applied primarily in an electrochemical context, they also apply to solids as well. Impurity ions and various charged defects in crystals may be the dominant charge carriers, and electrode kinetics may involve injection and annihilation of defects as well as electron (and hole) transfer and chemical reactions at the electrodes.

**B. Approximate equivalent circuits**

Figure 20a shows the conventional equivalent circuit usually employed over the entire frequency region for both supported and unsupported electrolyte situations. The \( Z_W \) here is usually taken to involve the \( A_0 \) of eqn. (50), rewritten for a single working electrode, or a simplification of it. The element \( C_d \) is the double-layer capacitance. The usual expression for \( C_d \) in the case of two identical plane-parallel electrodes is

\[
MC_d = \varepsilon/8\pi L_D \]

where \( L_D \) here involves the concentrations of all mobile charges completely blocked at the electrodes. Finally, \( R_0 \) is the equilibrium charge transfer resistance discussed in Part A of this Section; it will be zero for infinite electrode reaction rates. All quantities in this circuit are intensive except the extensive \( R_\infty \). Here the other extensive quantity, \( C_\infty \), has been omitted. Figures 20b and 20c show the limiting forms of the circuit when \( \omega \rightarrow 0 \) and \( \omega \rightarrow \infty \), respectively. Note that although the circuit is supposed to apply to a faradaic process, it does not allow a continuous current to flow as it should and as the circuits of Fig. 1 do.

Let us now consider how the circuits of Fig. 1, representing the unsupported situation, simplify for \( r_n < 1 \) when the relations of Section VI-A for \( Y_i \) and \( Z_i \) are used in the approximate Warburg region. The results thus only apply when \( r_p \neq r_n \). Figure 21a is a form of Fig. 1a in which exact Warburg elements are shown explicitly. Now consider the situation \( (0, r_n; \ \pi_m, \pi_z; \ 0, M) \) when \( \pi_m < 1 \) and \( r_n > 1 \). Then

\[
G_E \approx G_\infty, \ \ G_D = \varepsilon e_n [r_n/(r_n + 2)] G_\infty, \ \ \text{and} \ \ G_{dp} \approx G_{cp} = -\varepsilon e_n [r_n/(r_n + 2)]^2 G_\infty. \]

Since
Fig. 20. (a) Conventional electrochemical equivalent circuit; (b) low-frequency-limiting form of the circuit; (c) high-frequency-limiting form of the circuit.

Fig. 21. (a) Form of the exact equivalent circuit of Fig. 1 appropriate in the Warburg frequency response region. (b) Approximate but frequently applicable form of the circuit.

\[ \varepsilon \approx 1 \quad \text{and} \quad \varepsilon_n \approx \pi_m, \quad G_{DN} \quad \text{and} \quad |G_{D_PN}| \quad \text{are much smaller than unity.} \]

It will thus make little difference if \( G_{D_P} \) is reconnected to the right terminal of \( G_E \) rather than the left. Then \( G_D \) and \( G_{D_P} \) are in parallel, and their sum is approximately 

\[ \pi_m \left[ \frac{r_n}{(r_n+2)} \right] \left[ 1 - \frac{1}{r_n/(r_n+2)} \right] G_\infty = 2 \pi_m r_n/(r_n+2) G_\infty. \]

For \( \pi_m \ll 1 \) and \( r_n \gg 1 \), the result is completely negligible, thus justifying the absence of \( G_D \) in the conventional circuit when applied to an unsupported situation: (a) in the Warburg region only, and (b) when \( \pi_m \ll 1 \).

The result of the above manipulations is shown in Fig. 21b. Note the absence of any direct current path from electrode to electrode in this \( \Omega \) region, region B of Table 2. Under some usual conditions, we may still simplify the circuit of Fig. 21b further. The reactance of \( C_{D_P} \) is \( (\omega C_{D_P})^{-1} \equiv R_\infty/\Omega C_{D_P} \approx (\Omega C_{CPN})^{-1} R_\infty \). Taking, for example, \( \Omega = 0.1 \pi_m \) and assuming \( (g_\delta \delta_\rho g_s) \approx H_{sp} \), one finds 

\[ \Omega C_{CPN}^{-1} R_\infty \approx \frac{10g_s}{\delta_\rho g_s} \left( \pi_m M \right)^{-1} G_{pp}^{-1} R_\infty \approx \left( \pi_m M \right)^{-1} R_\infty. \]

Since \( \pi_m M \ll 1 \), this result will appreciably exceed \( R_\infty \) provided \( H_{sp} \ll (\delta_\rho g_s/M) \), making \( R_\infty \approx (\pi_m M)^{-1} \), a quite practical situation. Then, and for smaller \( \Omega \) values, it will be an adequate approximation to reconnect \( C_{D_P} \) to the right end of \( R_\infty \), and the circuit of Fig. 22a is obtained.

Another approximate equivalent circuit appropriate for \( \pi_m \ll 1 \) may be obtained by introducing the results of eqns. (64) and (65) in Fig. 1a. One then obtains the circuit of Fig. 22b. On ignoring \( R_D \approx \pi_m^{-1} R_\infty \), replacing \( R_E \approx R_\infty \) with \( R_\infty \), and ignoring \( C_{\infty S}^{-1} \) compared to \( C_{WS}^{-1} \), the circuit of Fig. 22c is obtained. This
Fig. 22. (a) A more approximate form of the circuit of Fig. 21b; (b) an alternate form of the exact equivalent circuit of Fig. 1 appropriate in the Warburg region; (c) approximate form of the (b) circuit.

circuit is probably not quite as accurate as those of Fig. 21b and 22a since $R_D$ was ignored, not "cancelled".

Comparison of the circuits of Figs. 20a, 21b, 22a, and 22b shows both similarities with and differences from the conventional circuit. In Fig. 22a, $C_g + C_{op} \approx C_{op}$ plays the role of the $C_d$ of Fig. 20a. But note that the maximum positive value of $C_{op} \approx C_{cp}$ applicable for $r_p = 0$ and $r_n = \infty$, is about $M \delta_p^2 C_g$, always less than $MC_g$. When "$C_d$" is actually determined in the unsupported case from measurements in the plateau region (region C of Table 2; see also Fig. 17), the result is not $MC_g$ anyway but is $C_{ps} \approx M \delta_p^2 C_g$, still always greater than $M \delta_p^2 C_g$. Thus $C_{op}$ is never exactly the double-layer or even the plateau capacitance. More important, eqn. (70) shows that $C_{op} \approx C_{cp}$ can go negative, and its maximum magnitude for $(M/g_s) \gg 1$ can greatly exceed $MC_g$.

Similarly, the $R_{gs}$ element of Fig. 22c may be taken to play the role of the charge transfer resistance of Fig. 20a. Note that $C_{op}$ and $R_{gs}$ are not independent, however, as shown by eqn. (77). When one is positive, the other is negative. In the $r_p = \infty$, $r_n = \infty$ case, eqn. (73) shows that $R_{gs} \approx R_{cs} = R_{csn} R_\infty$ is negative. Similarly when $(M/g_s) \gg 1$, $R_{cs}$ is positive with dominant part $(G_{psn} G_{psn} G_{psn})^{-1} R_\infty$. In the present $\pi_m \ll 1$ case, $\tilde{\sigma}_{n}^{-1} \approx \pi_m^{-1} \gg 1$; thus, this term will greatly exceed $R_\alpha$. Note that the ratio $R_{gs}/g_s$ will be very nearly intensive if $r_n \gg 2$ but will be neither purely intensive nor extensive when this condition does not hold, i.e. in the case of a very slow electrode reaction. Finally, it is important to note that $C_{op}$ and $R_{gs}$ do not
appear simultaneously in the same equivalent circuit as do the $C_d$ and $R_\theta$ of Fig. 20a.

Figure 23 shows how $R_{\text{dsn}}$ and $C_{\text{opn}}$ actually depend on $\Omega$ for the $(0, r_m; 10^{-7}, 1; 0, 10^5)$ case. These quantities were calculated essentially exactly by the computer rather than from the approximations of eqns. (67) and (71). We see that $R_{\text{dsn}}$ and $C_{\text{opn}}$ are substantially constant up to $(2\omega/\mu m)^{-1/6}$ but do not remain constant close to the lower Warburg region boundary of $40 \pi_m M^{-2}$, here at $\Omega = 4 \times 10^{-1.6}$. Figure 23a shows that $R_{\text{dsn}} \to 0$ as $\Omega > \pi_m$. Actually, in this region $R_{\text{dsn}} \approx -R_{\text{wsn}}$, so $R_{\text{sn}} = R_{\text{wsn}} + R_{\text{dsn}}$ approaches zero rapidly. For example at $\Omega = 10^{-3}$, $R_{\text{wsn}} \approx 10/2$ and $R_{\text{sn}} \approx 6.1 \times 10^{-3}$. Note that there is not much of a $C_{\text{ps}}$ plateau region here since $\pi_m M$ is not sufficiently small. There is, of course, a wider plateau for $C_{\text{in}}$, and we see in Fig. 23b $C_{\text{opn}} \to C_{\text{dsn}}$ as $\Omega \geq 10^{-8}$ or so. Since the susceptance of $C_{\text{op}}$ will be much greater than the admittance of $Z_W$ as $\Omega$ appreciably exceeds $\pi_m$, the circuit of Fig. 21b approaches the plateau circuit of Fig. 17 as it should in this plateau region. Similarly, the circuit of Fig. 22b also goes to that of Fig. 17 as $\Omega$ increases since $R_1 \to 0$ and $C_1 = (C_{\text{ws}} + C_{\text{is}}^{-1})^{-1}$ approaches $C_{\text{is}}$.

In order to present further information on the important quantities $C_{\text{opn}},$
TABLE 4

VALUES OF CIRCUIT ELEMENTS MULTIPLIED BY \( g_s \) FOR THE \((0, r_n; 10^{-7}, 1; 0, 10^5)\) SITUATION

<table>
<thead>
<tr>
<th>( r_n )</th>
<th>Constant quantities</th>
<th>Frequency-dependent quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( g_s R_{CSN} )</td>
<td>(-g_s C_{CPN})</td>
</tr>
<tr>
<td></td>
<td>( g_s R_{CSN} )</td>
<td>(-g_s C_{CPN})</td>
</tr>
<tr>
<td>( 2 \times 10^6 )</td>
<td>(-9.000 \times 10^7)</td>
<td>(-2.250 \times 10^7)</td>
</tr>
<tr>
<td>( 2 \times 10^5 )</td>
<td>(1.001)</td>
<td>(2.502 \times 10^2)</td>
</tr>
<tr>
<td>( 2 \times 10^4 )</td>
<td>(9.002 \times 10^6)</td>
<td>(2.250 \times 10^9)</td>
</tr>
<tr>
<td>( 2 \times 10^3 )</td>
<td>(9.920 \times 10^5)</td>
<td>(2.470 \times 10^9)</td>
</tr>
<tr>
<td>200</td>
<td>(1.019 \times 10^7)</td>
<td>(2.448 \times 10^9)</td>
</tr>
<tr>
<td>20</td>
<td>(1.210 \times 10^7)</td>
<td>(2.066 \times 10^9)</td>
</tr>
</tbody>
</table>

\( C_{CPN}, \ R_{GSN}, \) and \( R_{CSN} \), Tables 4 and 5 show their variation under different conditions. Table 4 applies for the same \((0, r_n; 10^{-7}, 1; 0, 10^5)\) situation presented in Fig. 23 but extends to much smaller \( r_n \) values and thus into the very slow electrode reaction region. All element values in Table 4 are multiplied by \( g_s \) in order to remove first order variation arising from \( g_s \) changes. Here \( g_s \approx g_n = 1 + \left(\frac{r_n}{2M}\right) \) to excellent approximation. The Table gives the approximate maximum values of \( g_s R_{GSN} \) and minimum values of \(-g_s C_{CPN}\) for comparison with \( g_s R_{CSN} \) and \(-g_s C_{CPN}\). In addition the Table presents the \( \Omega \) ranges over which \( R_{GSN} \) remains within 10 percent of its maximum value and \( C_{CPN} \) remains within 10 percent of its minimum. The ranges are shown in logarithmic form as \( (\log_{10} \Omega_{\min})/(\log_{10} \Omega_{\max}) \) where \( \Omega_{\min} \) and \( \Omega_{\max} \) are the lower and upper 10 percent points.

Table 4 shows that when \( r_n \) is appreciably smaller than the \( 2M \) cross-over value, the quantities shown remain nearly constant for more than a 100-times reduction in \( r_n \). When \( (r_n/2M) \lesssim 10^{-4} \), however, such constancy disappears. Incidentally, \( (R_{GSN})_{\max} \) values occur here at \( \Omega \approx 10^{-12} (10 r_n/2M)^3 \). For \( (r_n/2M) < 0.1 \), \( (C_{CPN})_{\min} \) values appear at \( \Omega \approx 10^{-14} (r_n/2M) \). Thus at \( r_n = 2 \times 10^4 \), these \( \Omega \) values are approximately \( 3 \times 10^{-13} \) and \( 10^{-13} \). The ranges given show that in the approximate constant region \( R_{GSN} \) remains close to its maximum value for 3 or 4 decades, and \( C_{CPN} \) shows a decreasing \( \pm 10 \) percent range as \( r_n \) decreases below \( 0.2M \). Incidentally, for \((0, 2 \times 10^3; 10^{-7}, 1; 0, 10^5)\) the quantity \( U_1 \) shows a \( \pm 10 \) percent \( \log_{10} \Omega \) variation range around a value of unity of \(-14.75 \) to \(-12.7 \) and increases monotonically with \( \Omega \) in this range. On the other hand, \( U_2 \) shows a range of \(-13.9 \) to \(-12.2 \) for 10 percent variation around the value of unity and decreases monotonically with increasing \( \Omega \).

Table 5 is similar to Table 4 except that here \( (r_n/2M) \) is fixed at the value \( 10^{-2} \) and thus both \( r_n \) and \( M \) vary. In addition, although \( g_s \) is again used to multiply the resistive elements, \( M^{-1} \) is used in its place for the capacitative ones. Here we see quite good constancy of the elements shown nearly down to \( r_n = 20 \). Note that the \( \log g_s \Omega \) ranges decrease for both quantities as \( r_n \) and \( M \) decrease, but most of the decrease arises from a decrease in magnitude of the low-\( \Omega \) boundary value associated with the \( M \) reduction. Here \( (R_{GSN})_{\max} \) values occur at \( \Omega \approx 10^{-7.5} M^{-1} \) and \( (C_{CPN})_{\min} \) values at \( \Omega \approx 10^{-8} M^{-1} \). For \( (r_n/2M) = 10^{-2} \), \( R_{CSN} \) itself increases.
### TABLE 5

VALUES OF NORMALIZED CIRCUIT ELEMENTS FOR THE (0, \( r_n \); 10 \(^{-1} \), 1; 0, 50\( r_n \)) SITUATION

Ranges defined as in Table 4

<table>
<thead>
<tr>
<th>( r_n )</th>
<th>( M )</th>
<th>Constant quantities</th>
<th>Frequency-dependent quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( g \cdot R_{CSN} )</td>
<td>( -M^{-1} \cdot C_{CPN} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 9.900 \times 10^8 )</td>
<td>24.749</td>
</tr>
<tr>
<td>( 2 \times 10^5 )</td>
<td>10(^7)</td>
<td>( 9.902 \times 10^8 )</td>
<td>24.743</td>
</tr>
<tr>
<td>( 2 \times 10^4 )</td>
<td>10(^5)</td>
<td>( 9.920 \times 10^8 )</td>
<td>24.676</td>
</tr>
<tr>
<td>( 2 \times 10^3 )</td>
<td>10(^3)</td>
<td>( 1.010 \times 10^8 )</td>
<td>24.020</td>
</tr>
<tr>
<td>200</td>
<td>10(^4)</td>
<td>( 1.197 \times 10^7 )</td>
<td>18.577</td>
</tr>
<tr>
<td>20</td>
<td>10(^3)</td>
<td>( \quad )</td>
<td>( \quad )</td>
</tr>
</tbody>
</table>
here from about 99 to $1.2 \times 10^6$ as $r_n$ decreases from $2 \times 10^5$ to 20. Thus, in this entire range $R_{cs} \gg R_{\infty}$, and the reaction resistance dominates the bulk resistance. Over this same range, $C_{cp}$ remains approximately equal to $-24 \ M \ C_s$, much larger in magnitude than the corresponding double-layer capacitance.

C. Warburg data analysis

There are two principal ways Warburg-region data are usually presented either as impedance or admittance components. In the impedance case, the real and imaginary parts of $Z_T$ (or here more properly $Z_i$) are plotted versus $\omega^{-1}$ to yield approximate straight lines. In the present $\pi_m \ll 1$ case, over much of the range of interest where $Z_{TN} \approx Z_{IN} + 1$ and $Z_{IN} \gg 1$, either $Z_T$ or $Z_i$ may be used, but it is better to eliminate $R_{\infty}$ whenever possible as is usually done, either correctly or incorrectly, in electrochemical situations.

We shall use normalized variables in plotting $Z_i$ here since their use will make the results more independent of $M$ and $\pi_m$. Let the frequency variable be

$$X = 2^{2/(AM\Omega)^{-1}} = 2^{2/(MA^2)^{-1}} R_{\infty} = 2^{2/(MA)^{-1}} C_{\infty}$$

When $\pi_m \ll 1$, $\pi_\infty = 1$, and $G_{pn} \approx 1$, $X \approx \Omega (2 + \pi_m + \pi_m^{-1})^{-1} \approx (\pi_m/\Omega)^{1/2}$. Next, further normalize the impedance to $N Z_{IN}$, where

$$N \equiv (2/10MA^2)$$

The numerical values $2^2$, 2, and 10 in these quantities are arbitrary scaling factors. We may now write, on using eqn. (64) and replacing $R_{\infty}$ by $R_{\infty} N$

$$NR_{IN} \approx NR_{CSN} + (2^{1/2} X/10)$$

When $\pi_m \ll 1$, $\pi_\infty = 1$, and $G_{pn} \approx 1$, $X \approx \Omega (2 + \pi_m + \pi_m^{-1})^{-1} \approx (\pi_m/\Omega)^{1/2}$. Next, further normalize the impedance to $N Z_{IN}$, where

$$N \equiv (2/10MA^2)$$

The numerical values $2^4$, 2, and 10 in these quantities are arbitrary scaling factors. We may now write, on using eqn. (64) and replacing $R_{\infty}$ by $R_{\infty} N$

$$NR_{IN} \approx NR_{CSN} + (2^{1/2} X/10)$$

Similarly, on replacing $C_{\infty}$ by $C_{CSN}$ and using eqn. (65), we find

$$N(\Omega C_{IN})^{-1} \approx N(\Omega C_{CSN})^{-1} + (2^{1/2} X/10)$$

Figure 24 shows curves of this kind for $r_p \sim 0$, $r_n = \infty$. The points, appropriate for $\pi_m = 1$, show how little the curves change on going from $\pi_m \ll 1$ or $\pi_m \gg 1$ to $\pi_m = 1$. The slopes agree with those above, and the $X = 0$ intercept for $NR_{IN}$ is, from eqn. (100), $-0.4G_{pn} H_{pn} = -0.4\delta_p^2 = -0.1$. The actual intercept shown is slightly larger in magnitude. The capacitative reactance curve extrapolates to the origin, in agreement with eqn. (101) and with most experimental results. Note that for the present case, since $\Omega \approx \pi_m X^{-2}$, these curves where $X \leq 10$ emphasize the $\Omega$ region near $\pi_m$. They remain substantially straight lines, nevertheless, down to $X = 2$, where $\Omega \sim \pi_m/4$. Curves of this sort for series capacitance and resistance are frequently found experimentally, but usually the $R_i$ curve lies above the other (i.e. $R_\theta > 0$). Some slight evidence of $R_\theta < 0$, as in the present $r_p \sim 0$, $r_n = \infty$ case, has, however, been published.

Turning now to the admittance approach, we may rewrite eqn. (3) as

$$Y_{TN} \equiv G_{pn} + i \Omega C_{pn} = (i \Omega + G_{DN}) + (Z_{IN} + R_{EN})^{-1}$$
Fig. 24. The further normalized quantities \( N(Q_{Cn})^{-1} \) and \( NR_{in} \) versus \( X \) for the \((r\rho, \infty; \pi_{nr} = 1; 0, M)\) situation. Here \( N = (5MA^2)^{-1} \) and \( X = (2/\Omega^2)(AM)^{-1} \).

In the \( \pi_{nr} \ll 1 \) case, where \( R_{en} \ll 1 \) and \(|Z_{in}| > 1\), this equation leads, on using eqns. (58) and (63), to

\[
C_{PN} \geq 1 + C_{WPN} + C_{oPN} \tag{103}
\]

and

\[
G_{PN} \geq G_{WPN} + (G_{DN} + G_{oPN}) \tag{104}
\]

Note that eqn. (103) is more accurate than eqn. (28) of Section V which applies to the same situation. Now we have already seen that for \( \pi_{nr} \ll 1 \), \( G_{DN} + G_{oPN} \approx G_{DN} + G_{CPN} \approx 2\pi_{nr}/r_{n} \approx 0 \) for \( r_{n} \gg 1 \). Thus, \( G_{PN} \approx G_{WPN} \) here.

Now if we set \( C_{oPN} \approx C_{CPN} \) and neglect the unity term on the r.h.s. of eqn. (103), the result can be written

\[
M^{-1} C_{PN} = M^{-1} C_{CPN} + (X/2^1) = G_{PN} [H_{pn} - \delta_{n}\delta_{p}(M/g_{n})] + (X/2^1) \tag{105}
\]

On using the good approximation \( G_{PN} \approx G_{WPN} \approx \Omega C_{WPN} \), one also readily finds that eqn. (103) may be rewritten as

\[
C_{PN} \geq C_{oPN} + \Omega^{-1} G_{PN} \approx C_{CPN} + \Omega^{-1} G_{PN} \tag{106}
\]

In unnormalized form this equation becomes

\[
C_{p} \geq MG_{pn}[H_{pn} - \delta_{n}\delta_{p}(M/g_{n})]C_{2} + \omega^{-1} G_{p} \tag{107}
\]

De Levie\(^1\) and Leonova et al.\(^5\) have derived the similar result

\[
C_{p} = C_{d} + (\omega R_{p})^{-1} \tag{108}
\]

which is consistent with the conventional circuit of Fig. 20a only when \( R_{p} \approx 0 \). Again we see, however, that plotting \( C_{p} \) vs. \((\omega R_{p})^{-1}\) here does not yield \( C_{d} \) but rather \( C_{CP} \). Although the above authors required the assumption \( R_{d} \approx 0 \) to obtain eqn. (108), the similar eqn. (107) found here does not require the assumption.
$R_\infty = 0$. In fact, eqn. (77) indicates that when $C_{\alpha PN} \equiv C_{CPN} \neq 0$, $R_{\infty N} \equiv R_{CPN}$ cannot be zero either. Thus, experimental satisfaction of eqn. (107) does not necessarily indicate that $R_\alpha = 0$ and $k_\alpha$ or $k_\theta$ is infinite.

Figure 25 shows some $\pi_m \ll 1$ curves of the form of eqn. (105). They are fully consistent with it over most of the $X$ range and of the form found experimentally. For the present situation, eqn. (105) yields a $X \to 0$ intercept of $\delta_\alpha^2$. Thus the corresponding $C_p$ intercept is $M\delta_\alpha^2 C_p$, always less than $MC_p$ or $M\delta_\alpha^2 C_p$, as mentioned earlier. The insert in Fig. 25a shows the $X \leq 0.6$ region in expanded form. For $X \geq 1$, the curve is essentially independent of $\pi_m$ for $\pi_m \leq (10 M)^{-1}$.

Figure 26 is plotted for $r_\alpha \ll \infty$ and may be compared to the $r_\alpha = \infty$ results of Fig. 24. On the much extended $X$ scale used here, the dots, corresponding to the $r_\alpha = \infty$ condition, seem to lie virtually on the ideal Warburg line ($R_{\infty N} = 0$), because the resolution is less here than that of Fig. 24. Tables of pertinent values are shown on each part of Fig. 26. The specific values of $R_{CSN}$ shown in the Table of Fig. 26a apply for $\pi_m = 10^{-9}$, although the curves themselves apply for $\pi_m \leq 0.03$.

The $X \to 0$ intercepts of Fig. 26a all lie somewhat below those that follow theoretically from eqn. (100), $NR_{CSN}$. The differences arise both from inaccuracies in determining the final limiting slope graphically and probably also from the approximate character of eqn. (100). Now Fig. 26b shows no large departure from
Fig. 26. The quantities $NR_{IN}$ and $N(\Omega C_{IN})^{-1}$ versus $X$ for the $(0, r_n; \pi_m, 1; 0, 10^4)$ situation with large values of $(M/r_n)$.

the Warburg line as $r_n$ is decreased down to $\sim 200$ (where $M/g_n \approx 10^2$), while increases of $R_{CN}$ with decreasing $r_n$ move the $NR_{IN}$ line upward. Thus, when $(M/g_n > (\delta \rho \delta_n)^{-1} H_{pn}$ (equal to unity for $\pi_z = 1$), so that the $X \rightarrow 0$ intercept is positive, the $R_i$ lines will then lie above the $(\omega C_i)^{-1}$ lines, as is usually observed experimentally.

It is also worth noting that the forms of the $NR_{IN}$ and $N(\Omega C_{IN})^{-1}$ curves of Fig. 26 are very similar to those given by Vetter$^{56}$ for the components of the faradaic impedance (supported case) with diffusion and heterogeneous reaction rate control. But the present curves for $NR_{IN}$ are quite unlike those given by Vetter for the more complicated combined case of charge transfer, diffusion, and heterogeneous reaction rate control$^{55}$.

In Vetter's diffusion and heterogeneous reaction rate control case, his faradaic impedance, which essentially corresponds to the present $Z_i$, involves $Z_w$ in series
with a resistance $R_r$ and capacitance $C$, also connected in series. These elements thus correspond to the present $R_\text{os}$ and $C_\text{os}$ (see Fig. 22b). It is found\textsuperscript{55} that $R_r \propto [1 + (\omega/k)^2]^{-1}$ and $C \propto [1 + (k/\omega)^2]$, where $k$ is an effective rate constant for the reaction considered. These frequency dependences are somewhat similar to but not the same as those of $R_\text{os}$ and $C_\text{os}$ following from the present treatment. For example, in Fig. 23 $R_\text{osN}$ begins to drop off rapidly with $\Omega$ at a value of $\Omega$ related much more to $\pi_m$ than to $\xi_n$ (or $r_n$), and it goes negative to a value determined principally by $(\pi_n M)^{-1}$ before then beginning to approach zero. It should be noted, however, that for $(r_n/2M) \lesssim 10^{-2}$, as in the $r_n=200$ curves of Fig. 26, the maximum negative value is far smaller in magnitude than is $(R_\text{osN})_{\text{max}} \approx R_\text{csN}$. Similarly, $C_\text{osN}$ drops off from $\sim C_\text{csN}$ eventually as $\Omega$ increases toward $\pi_m$. As $\Omega$ decreases, on the other hand, $C_\text{osN}$ reaches a maximum nearly equal to $C_\text{csN}$ and then slowly decreases toward $C_{\text{INN}}$ rather than increasing indefinitely as does $C_r$.

It is important to emphasize, nevertheless, that it is the drop off with increasing $\Omega$ of $R_\text{osN}$ and $C_\text{osN}$ which leads to the behavior of the curves of Fig. 26 in the interesting region $5 \lesssim X \lesssim 35$. Incidentally, for the choice $\pi_m = 10^{-6}$, when $X \approx 9.8$ here, $\Omega = 10^{-9}$, and $\Omega = 10^{-10}$ for $X \approx 31$. The minima in the $N(\Omega C_{\text{IN}})^{-1}$ curves (apparent for $r_n \leq 400$) occur when $C_\text{osN} \approx C_\text{wSN}$. Since $C_\text{osN}$ decreases with increasing $\Omega$ faster than $C_{\text{wSN}}$ in this region, $C_\text{osN}$ soon dominates the series combination, and the maxima in the reactance curves occur at $C_\text{osN} \sim C_{\text{wSN}}/3$.

Alternatively, the curves of Fig. 26 may be interpreted in a simple fashion using eqn. (4'). The maxima in the curves of Fig. 26b are associated with the maximum value of $-\text{Im}(Z_{2N})$, $(\varepsilon_{\text{pN}} r_n)^{-1}$. The Warburg response of $Z_{1N}$ (not exactly $Z_W$) is in series with the parallel combination of $R_2 = (2/\varepsilon_{\text{pN}} r_n) R_\alpha$, and $C_2 = M C_g$. Note that when $R_CS$ is dominated by its positive part, as in the present situation, and $\pi_m \ll 1$, $R_{CS} \approx (2/\varepsilon_{\text{pN}} r_n^2) R_\alpha \approx (2/\varepsilon_{\text{pN}} r_n) R_\alpha = R_2$. Thus $R_2$ may be considered a pertinent equilibrium charge transfer resistance in the present unsupported case. It is interesting that in the formulation represented by eqn. (4') such a quantity appears directly in parallel with the double-layer capacitance $C_2 = M C_g$, and thus no effect of $C_2$ appears at all when $r_n = \infty$!

The close correspondence of the curves of Figs. 24 and 26, first with those that are found in the supported case for diffusion and charge transfer rate control\textsuperscript{44}, then with those for diffusion and chemical reaction rate control\textsuperscript{55} is no accident. In the $(0, r_n; \pi_m, \pi_z; 0, M)$ situation with $r_n \gg 1$, we may use eqns. (73) and (87) to allow definition of an effective rate constant, $\xi_{\text{ne}}$, which particularly covers the $R_{\text{osN}}$ region of most interest, $1 \leq R_{\text{osN}} \ll \infty$. Let us thus write in this case,

$$R_{\text{osN}} = (2D_n/IG_{\text{pa}} \varepsilon_{\text{pN}} \varepsilon_{\text{pN}})^{\xi_{\text{ne}}^{-1}}$$

where

$$\xi_{\text{ne}}^{-1} = (\varepsilon_{\text{pN}} / 2D_n) \left[ \left( \varepsilon_{\text{pN}} / \varepsilon_{\text{pN}} \right)^{2D_n} \right]^{-1} - (H_{\text{pa}}/M \delta_{\alpha} \delta_{\beta})$$

$$\geq \xi_{\text{ne}}^{-1} - (\varepsilon_{\text{pN}} L_D H_{\text{pa}}/\delta_{\alpha} \delta_{\beta} D_n)$$

A more exact expression for $\xi_{\text{ne}}$ could be formed as in eqn. (109) but with $R_{\text{osN}}$ replacing $R_{\text{osN}}$.

Now the foregoing results show that when the first term on the r.h.s. of eqn. (110) does not dominate the expression but $\xi_{\text{ne}}^{-1}$ remains $\geq 0$, $R_{\text{IN}}$ and $C_{\text{IN}}$ lead to results like those of simple charge transfer in the unsupported case. But
when the $\xi_{\text{e}}^{-1}$ term dominates, the results are like those for chemical reaction control. Evidently in the present exact treatment of the unsupported case, the two processes meld together. There is a smooth transition from apparent charge transfer control in the region $0 < (\xi_{\text{e}} / \xi_{\text{ne}}) \ll 1$ to apparent chemical reaction rate control when $(\xi_{\text{e}} / \xi_{\text{ne}}) \ll 1$. Notice that the effective rate constant $\xi_{\text{ne}}$ is more analogous to the conventional rate constant than is $\xi_{\text{m}}$ since $\xi_{\text{ne}} = \infty$ corresponds to zero electrode reaction resistance, to the degree that $R_{\text{SN}} = R_{\text{CSN}}$.

Finally, Fig. 27 shows $C_{\text{PN}}$ versus $(G_{\text{PN}} / \Omega)$ for various $r_{\text{n}}$ values. The results are in substantial agreement with eqn. (106). Here, because $(2M/r_{\text{n}}) \gg 1$ for most of the curves shown, most of the $C_{\text{CPN}}$ intercepts are negative, although positive ones would be found for $r_{\text{n}}$ values satisfying $(g_{\text{n}} H_{\text{pn}}) > (\delta_{\text{n}} \delta_{\text{p}}) M$. A specific value of $X$ is shown at the bottom of this Figure. Its size indicates that most of this plot corresponds to $\Omega$ values much less than $\pi_{\text{m}}$. These curves are also of the form of those determined experimentally except that the experimental intercept found is usually positive.

The methods of plotting experimental results described in this last Section have been quite widely used in liquid electrochemical situations but not appreciably for analysis of frequency-response data on solids. When such data indicate a $C_{\text{p}}$ slope of $m \sim 0.5$, it should be profitable to test the data against the equations of this Section and, when agreement is found, determine the values of the various parameters entering the equations. In general, comparison of experimental results with the theoretical results of the present paper should, in pertinent cases, permit the determination of values of the following physically significant parameters: $\mu_{\text{m}}$, $\mu_{\text{p}}$, $\gamma_{\text{m}}$, $\gamma_{\text{p}}$, $r_{\text{m}}$, $r_{\text{p}}$, $\xi_{\text{m}}$, $\xi_{\text{p}}$, $n_{\text{m}}$, $p_{\text{m}}$, $C_{\text{m}}$, $R_{\text{m}}$, $M$ and $\varepsilon$. Measurements at several temperatures should then allow estimates of the thermal activation energies associated with such quantities as $\xi_{\text{m}}$ and $\xi_{\text{p}}$ to be obtained.
LIST OF SYMBOLS

A. Major subscripts

i Designates an intrinsic or series "interface" quantity; also used as index with
i=n or p
n Designates quantity associated with negative mobile charged species
p Designates quantity associated with positive mobile charged species
N Normalization of impedances and resistances with $R_\infty$, of admittances and
capacitances with $G_\infty = R_\infty^{-1}$, and of capacitances with $C_g$
P A parallel quantity
S A series quantity; also indicates a plateau region quantity
T Stands for "total"
0 Designates either a static quantity or the zero-frequency limit of a frequency-
dependent quantity
$\infty$ The value of a quantity in the limit of high frequencies (i.e., $\Omega \gg 1$)

B. Major symbols in text

Numbers in parentheses indicate equations where the symbol is used or
defined.

$A = (4G_{wp}C_{ws})^{-\frac{1}{2}}$; normalized Warburg parameter; (6), (31)
$A_0$ Warburg parameter; (5), (42), (50), (97)
$C_{cp}$ Frequency-independent part of $C_{op}$
$C_{cs}$ Frequency-independent part of $C_{is}$
$C_d$ Apparent double-layer capacitance in the supported case; see Fig. 20
$C_g$ Geometric capacitance/unit area; $e/4\pi l$
$C_i$ "Interface" capacitance/unit area; the series capacitance associated with $Z_i$; (60)
$C_{is}$ "Interface" capacitance/unit area in the plateau region
$C_K (C_{wp}+C_{op})$
$C_P$ Total parallel capacitance/unit area; associated with $Y_T$; (102). Note: $C_{p0}$
$C_{ps}$ Total parallel plateau capacitance/unit area
$C_{wp}$ $(2A^2)^{-\frac{1}{2}} C_g$
$C_{ws}$ $(A^2)^{-\frac{1}{2}} C_g$
$C_{op}$ See eqns. (58), (63), and (67)
$C_{os}$ See eqns. (65) and (72)
$D_i$ Diffusion coefficient; for positive carriers $i=p$; for negative $i=n$
$G_{cp}$ Frequency-independent part of $G_{op}$
$G_D$ Frequency-independent parallel discharge conductance/unit area; see Fig. 1;
$G_D = e_n [1 + (2/r_n)]^{-1} + e_p [1 + (2/r_p)]^{-1}$
$G_E (g_{op}/g_{is}) = (G_E - G_D) = R_E^{-1}$; $G_{en} = e_n [1 + (r_n/2)]^{-1} + e_p [1 + (r_p/2)]^{-1}$; see
Fig. 1
$G_K (G_{wp} + G_{op})$
$G_P$ Total parallel conductance/unit area; associated with $Y_T$; (102).
Note: $G_{p0} = G_D$; $G_{p} = G_{p0}$
$G_{pn} [(g_p - g_n)/g_{op}]^2$
$G_{wp} \frac{\Omega^2 G_\infty}{2A}$
$G_{op}$ See eqns. (58), (62) and (66)
$G_{\infty}$ Bulk conductance/unit area; $R_{\infty}^{-1}$
$H_{pn}$ \[\frac{(g_2^2 - g_n)}{(g_p^2 - g_n)^2}\]
$L_D$ Debye length in the present intrinsic case
$M$ \((l/2L_D)\)
$N$ \((5MA^2)^{-1}\)
$R_{CS}$ Frequency-independent part of $R_{os}$
$R_D$ \(G_{D}^{-1}\)
$R_E$ Frequency-independent series resistance-unit area; $G_E^{-1}$
$R_i$ "Interface" series resistance-unit area; associated with $Z_i$; (60)
$R_s$ \((R_E + R_i)\)
$R_{WS}$ \(AR_{\infty}/\Omega^4\)
$R_0$ Equilibrium charge transfer resistance-unit area in supported case; see Fig. 20
$R_{os}$ See eqns. (64) and (71)
$R_{os}$ \(G_{os}^{-1}\)
$T$ Absolute temperature
$X$ \(2^3(AM\Omega^3)^{-1}\); (98)
$Y_T$ \(Z_T^{-1}\)
$Y_T$ Total admittance/unit area of the system; (102)
$Y_N$ \(Z_N^{-1}\)
$Y_0$ \((G_{op} + i\omega C_{op})\); (59)
$Z_i$ "Interface" impedance-unit area; (14), (60)
$Z_j$ Components of $Z_T$; $j=1,2,3$; (4')
$Z_T$ \(Y_T^{-1}\); (3)
$Z_W$ \(A_0(1-i)/\omega^3\); Warburg impedance
$Z_0$ \([R_{os} + (i\omega C_{os})^{-1}]\); (61)
$a$ \((\delta_p^2/\epsilon_p)^2 + (\delta_n^2/\epsilon_n)^2\)
$b$ \(\delta_p^2/\epsilon_p + \delta_n^2/\epsilon_n\)
$c$ \((\delta_n/\epsilon_n) - (\delta_p/\epsilon_p)\)
$e$ Protonic charge
$g_i$ \(1 + (r_i/2); i = e (r_e = r_p), n, or p\)
$g_1$ \(g_n^2 + g_p\epsilon_n\)
$g_2$ \(g_n^2 + g_p\delta_n\)
$k$ Boltzmann's constant
$k_i$ Apparent standard heterogeneous rate constants for the supported case; $i=n$ or $p$
$l$ Distance of separation of plane-parallel electrodes
$m$ Exponent in $\omega^{-m}$ response
$n$ Concentration of negative mobile charges
$p$ Concentration of positive mobile charges
$r$ \(M[\coth(M)]\)
$r_a$ Designation of common value of $r_n$ and $r_p$ when they are equal
$r_D$ Dimensionless discharge parameter for negative charges
$r_p$ Dimensionless discharge parameter for positive charges
$z_n$ Valence number for negative mobile charges
$z_p$ Valence number for positive mobile charges
$Q$ Normalized radial frequency; $\omega r_D$
$\delta_n$ \((1 + \pi_z^{-1})^{-1} \equiv z_n/(z_n + z_p)\)
The frequency response is considered of a two-electrode linearized system containing a single positively charged species and a single negatively charged species. These species may have arbitrary valences and mobilities and may individually react at the electrodes. The results follow from a detailed solution of the equations of charge motion given earlier. Normalized response is exhibited for this unsupported, intrinsic-conduction situation for a wide range of mobility ratios, valence number ratios, and reaction rate ratios. Results are given in the form of specific formulas, impedance-plane plots, and the dependences on normalized frequency of series and parallel resistive and capacitative components of the normalized total impedance of the system.

Impedance-plane plots exhibit from one to three connected arcs, depending on the specific situation. Approximate Warburg frequency response appears for the “interface” impedance over a certain frequency region when normalized reaction rate parameters differ, but it only shows up strongly in the total impedance when the mobility ratio departs appreciably from unity as well. Under such conditions, a plateau region, where the total parallel capacitance remains essentially independent of frequency over a wide frequency range, may appear at frequencies just above the Warburg region. The plateau capacitance is close to but not identical to the conventional double-layer capacitance present when both species of charge are completely blocked. In incomplete blocking cases, however, this double-layer capacitance only makes a significant appearance in the approximate equivalent circuit under slow reaction conditions; it is thus not present when one of the reaction rate constants is infinite.

In general, the system can show $\omega^{-m}$ frequency response for the parallel capacitance over a wide frequency range with $0 \leq m \leq 2$, and with the experimentally common regions where $m \geq 0$, 0.5, 1.5, and 2 especially likely. Particular attention is given to deviations from ideal Warburg behavior which lead to a combined charge-transfer and heterogeneous chemical reaction resistance. Results are
compared to those from conventional supported treatments and show both important similarities and differences. Finally, several new equivalent circuits are presented which are pertinent in various frequency ranges for the unsupported situation.

REFERENCES

39 Ref. 36, p. 154.
41 Ref. 38, p. 20.
42 Ref. 38, p. 32.
43 Ref. 38, p. 18.
44 Ref. 36, pp. 346–347.
47 Ref. 40, pp. 267, 269.
55 Ref. 36, pp. 350–352.
56 Ref. 36, p. 261.