Double Layer Capacitance and Relaxation in Electrolytes and Solids

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After a review of the idealizations usually made in theories of space-charge polarization in liquids and solids, published theoretical and experimental work dealing with the a.c. response of two-electrode systems is discussed and various corrections pointed out. A calculation of the equilibrium space-charge capacitance of two blocking electrodes separated by material containing mobile positive and negative charges of arbitrary valences is presented for the limit of vanishingly small applied static potential. The result of this calculation may be used to obtain the frequency dependence of diffuse layer parallel capacitance and conductance in the Debye dispersion frequency range, where the motion of charges in space charge regions leads to an admittance involving only a single time constant. Expressions given previously by Baker and Buckle for this time constant and for the low-frequency limiting capacitance are corrected, along with their conditions for the extent of the Debye dispersion range.

The relaxation time constant is $G_\infty(r-1)\tau_D/G_0$, where G_0 and G_∞ are the low- and high-frequency limiting values of the series conductance, τ_D is the dielectric relaxation time of the material containing mobile charges, $r \equiv M \coth M$, and M is the ratio of the separation between electrodes to twice the Debye length. Finally, deviations from Debye dispersion behaviour for various 1 : 1 valence theories are calculated and compared; for the two-blocking-electrodes situation, Debye behaviour and a simple equivalent circuit of frequency-independent elements extend up to nearly $\omega\tau_D \sim 1$. Beyond this range, the parallel space-charge capacitance shows $\omega^{-\frac{3}{2}}$ limiting behaviour, similar to that previously found only with partly blocking electrodes, and the equivalent series space-charge capacitance eventually decreases as $\omega^{-\frac{1}{2}}$.

The frequency response behaviour of the impedance or admittance of the space charge region near an electrode which is not entirely ohmic can yield useful information about the properties of the electrode and the material next to it. Non-ohmic behaviour can arise when an electrochemical reaction occurs at the electrode (the faradaic admittance [1]), or when some or all of the species of mobile charge carriers present are partly or completely blocked at the electrode. When complete blocking occurs at an inert electrode, only displacement current passes from the material next to the electrode into it. In the electrolyte area, a completely blocking electrode is termed ideally polarized.[2, 3] Experimental admittance results, interpreted by means of a suitable theory, allow one to decide whether a given electrode is well approximated as completely blocking or not, and can, under ideal conditions, yield information about charge carrier concentrations and mobilities and about material homogeneity for solids.

The present work is primarily concerned with inert, completely blocking electrodes. Although the main discussion will be in terms of aqueous electrolytes, the idealized situation and theories considered also apply to solids with intrinsic electronic or vacancy conductivity or with ionic conductivity,[4] and perhaps to ionic melts under some conditions. We first discuss the idealizations of the actual situation which are usually made and briefly mention principal theoretical treatments of the area.

One idealization virtually always made in theoretical treatments of the present situation is reduction to one dimensionality. Only variations of charge density, potential, field, etc. in a direction perpendicular to an electrode are assumed present. Sometimes only a single electrode is considered, but usually in steady-state a.c. theories two electrodes are present. For the one-dimensional approximation to apply, it is then necessary that the current density of the two electrodes be uniform and their currents equal. These conditions require that the electrodes be symmetrically disposed,[1] and it is usual to consider two planar identical electrodes separated by a distance l containing the medium whose properties are of interest. Finally, uniform current density requires that the smallest linear dimension of planar electrodes be large compared to l. It is conventional to apply the treatment to unit cross-section of the electrodes.

Another restriction imposed by all authors in the present field, either explicitly or implicitly, is that of taking the applied a.c. potential sufficiently small that the non-linear transport equations to be solved may be linearized to good approximation. Then, when a voltage of single frequency is applied across the electrodes, harmonics in the current above the fundamental frequency are small enough to be neglected. The analytic solution of the linearized equations leads to complex results; omission of linearization would certainly require computer analysis in order to obtain results of practical value.

In addition to taking the magnitude of the a.c. potential small compared to kT/e, where k is Boltzmann's constant, T the absolute temperature, and e the protonic charge, a.c. treatments have invariably assumed that in the absence of an a.c. signal the positive and negative charge carriers are uniformly distributed in the material between the electrodes and no static space-charge distribution is present. For the electrolyte case, this restriction means that the resulting theory should only be compared with experimental (admittance, frequency) results obtained at, or very near, the point of zero electrode charge. Although the two-electrode, diffuse-layer, space-charge problem has been solved [5-8] for applied static potentials much greater in magnitude than kT/e, the difficult combination of this solution and the steady-state a.c. problem has not been carried through thus far. The restriction to very small a.c. potentials automatically ensures that power-dissipation heating of the material between the electrodes is negligible and leads to negligible change in material properties.

All a.c. relaxation treatments published thus far deal primarily with the diffuse part of the double-layer of space charge associated with one or two blocking or partly blocking electrodes. The diffuse layer is a space-charge region where the competing effects of electric field and diffusion lead to a local charge excess of one sign. Frequently when the material between the electrodes is a solid, it is a good approximation to assume that the diffuse layer begins immediately at the electrode-solid interface.[9-11] This may also be an adequate approximation for pure fused salts with careful electrode selection and preparation. It is, however, usually not an adequate approximation in aqueous and other liquid electrolytes.[2, 12, 13] For such materials, there seems invariably to be present an inner, or Helmholtz, layer between the diffuse layer and the electrode. In the absence of specific adsorption, this compact layer is charge free and is composed of a monolayer or so of solvent molecules. It acts electrically like a pure capacitance in series with the diffuse layer and bulk material admittance. Since the Helmholtz layer is so thin, it has a high capacitance/unit area. When the electrolyte solute concentration is very low, the inner layer capacitance may be considerably larger than that of the diffuse layer near the point of electrode zero static charge. Under such conditions, the diffuse layer capacitance dominates the combination, but for most concentrations of practical interest the inner layer capacitance is smaller and dominates. This situation may make interpretation of experimental relaxation measurements uncertain, and unequivocal separation of diffuse layer and bulk admittance from the total admittance difficult.

An analogue to the inner region apparently occurs for some solid-electrode combinations. Experimentally, evidence of high-resistivity layers [14-17] or even air gaps [18] next to the electrodes has been found for a variety of experiments. The problem of a potential-independent, charge-free-layer capacitor in series with a space-charge layer has been treated [7, 19] theoretically for static applied potentials (equilibrium conditions), as has that of a potential-dependent inner layer in the electrolyte case.[12, 13]

For two-electrode a.c. space-charge polarization theories *per se*, all but one have dealt with the 1 : 1 or uni-univalent case. Although Jaffé's [5, 20] original theory was later extended by Chang and Jaffé,[21] both theories were unnecessarily approximate even in the small-signal limit considered.[4, 9] A theory without Chang and Jaffé's approximations was published by the author [4] in 1953 and was followed soon thereafter by the similar but independent analysis of Friauf.[22] This work has been extended by Beaumont and Jacobs.[10] Although Grahame [23] published a theory of the diffuse layer under equilibrium conditions for unsymmetrical valence types in 1953, it was not until 1968 that Baker and Buckle [24] independently extended the Macdonald-Friauf a.c. theory to the arbitrary valence situation. Ferry [25] has been alone in presenting a transient response and a.c. steady-state theory for a single blocking electrode. In all these theories, no explicit account of finite ion size was taken, an adequate approximation for the situations to which the theories have usually been applied.

I shall compare some of the above theories, pointing out deficiencies in them where appropriate; show how some of the earlier 1 : 1 and arbitrary valence results can be corrected and obtained in a simpler way than heretofore; present the first two-blocking-electrode equilibrium theory of the diffuse double layer with arbitrary valences; and extend the earlier 1 : 1 space-charge theory to show both the extent of the single-time-constant Debye dispersion region and deviations from such simple behaviour.

An arbitrary value of the ratio $M \equiv l/2L_D$ is assumed. Here L_D is the Debye length for the unperturbed bulk material; it is defined later in terms of material parameters. For ordinary values of l and concentrations used in most electrolyte experiments, M is very large compared to unity. Since this will not necessarily be the case for highly resistive solids and liquids and for very weak electrolytes, the various new treatments herein are not restricted to the usual condition $M \gg 1$ but allow extrapolation to $M = 0$; for $M \ll 1$, no space-charge can occur.

INITIAL CONSIDERATION OF THE ARBITRARY VALENCE SITUATION

Only Baker and Buckle [24] (denoted B & B hereafter) have given an analysis of the two-blocking-electrode a.c. space-charge polarization situation for arbitrary valences. They applied their treatment to aqueous electrolytes and ionic melts. Since this is also the latest contribution, I provide a few missing comparisons between their work and that of others, and show how some of their results may be improved. Therefore, I shall discuss: (*a*) the unnecessary complication of B & B's approach and a much simpler method of obtaining a more general version of their final results; (*b*) the contrast between a specialization and a generalization involved in the ref. (24) situation over those situations previously considered by others; (*c*) an implicit simplification in one of B & B's final results which makes it applicable only when the two blocking electrodes considered are many Debye lengths apart, leading to essentially independent conditions at these electrodes; (*d*) an unnecessary lower limit condition and an over-simplified and unnecessarily stringent upper limit condition for the frequency range over which B & B expect their simplified final results to apply; (*e*) a misleading expression given in ref. (24) for the Nernst-Einstein relation, inappropriate in the arbitrary valence case considered there; and (*f*) the specific dependence of some of the results on normalized frequency, and the dependence of the basic time constant involved in simple Debye frequency response behaviour upon the valence numbers of the positive and negative charge carriers, z_p and z_n, respectively.

Baker and Buckle's aim was to supply a more general treatment of space charge polarization in fully dissociated liquid electrolytes than previous theories for solids and aqueous electrolytes. However, the previous theories which they cite for solids [4, 20,22] are also applicable for electrolytes (and vice versa), since the mathematics for the idealized situation usually considered is the same for liquids and solids. In addition, although B & B mention that their treatment avoids the use of restrictive relations between phenomenological constants appearing in the earlier work, [4, 20, 22] the actual restrictive relations meant are not stated. In fact, the earlier work cited applies for any degree of ionization of the charge carriers; B & B's is restricted to full dissociation. Their approach is indeed more general than previous work on the two-electrode situation in generalizing from 1 : 1 or $z : z$ valent electrolytes to the arbitrary $z_p : z_n$ situation. Here z_p and z_n (denoted μ and ν, respectively, by B & B) are positive integers. The B & B analysis is rendered considerably more complex than necessary by their repeating nearly 30 complicated equations essentially taken from earlier small-signal a.c. analyses [4, 22] with minor modifications incorporated to account for arbitrary valences.

The motivation of B & B's work was apparently to generalize earlier two-electrode calculations to the arbitrary valence situation; yet they make no comparison of their results with those obtained earlier by Grahame [23] for one-electrode, arbitrary valence situations or with earlier two-electrode calculations for the 1 : 1 valence condition.[4] B & B's discussion includes graphs plotted from their analytical results for special values of the parameters involved. The values selected implicitly require that $z_n = z_p$. There is no discussion of any features of the results dependent on z_p and z_n being unequal.

After introducing several approximations into their general results, B & B finally obtain simplified expressions for the low-frequency limiting a.c. capacitance/unit area of their system, C_0, and the high-frequency limiting conductance/unit area, G_∞, which applies e.g., at frequencies too high for space charge to build up appreciably at the electrodes. The quantities C_0 and G_∞ may be combined to define the single time constant $\tau \equiv C_0/G_\infty$. Since from B & B's treatment, as in the corresponding 1 : 1 valence case, only a single time constant appears at frequencies for which $\omega\tau \ll B$, the frequency response exhibited in this frequency range by the parallel capacitance and conductance is of the simple Debye type. Here the quantity B (discussed later) is usually much greater than unity.[4, 24] Although B & B ascribe the first appearance of such a time constant and Debye behaviour for a system of the present type to the paper of Friauf,[22] both results were discussed in earlier papers, [4, 26] and one [26] specifically points out such Debye behaviour in its title. Since Debye dispersion is defined by a single time constant, only that time constant, or here C_0 and G_∞, is needed to specify fully the frequency response of the normalized capacitance and conductance of the system in the Debye dispersion range.

APPROXIMATE CALCULATION OF C_0

Grahame [23] has treated the electrolyte diffuse layer for a $z_p : z_n$ electrolyte in the static (equilibrium) one-electrode situation. His solution for charge and capacitance applies for a constant potential ψ_0 applied across the diffuse layer—from the outer Helmholtz plane to the bulk of the solution. Let us normalize all potentials with kT/e. Then, we may write $\Psi_0 \equiv e\psi_0/kT$; Grahame's solution is not restricted to $|\Psi_0| \ll 1$. Now linearized a.c. treatments [1, 4, 20-22, 24, 25] are restricted to peak a.c. applied voltages appreciably less than kT/e in magnitude. For the idealized cases usually treated the differential (or integral) capacitance calculated for an equilibrium situation in the limit $\Psi \to 0$ must equal the total a.c. capacitance C_0 in the zero-frequency limit for vanishingly small a.c. signals. Independent a.c.[4] and static [6, 7] treatments yield such agreement for the 1 : 1 valent, two-electrode situation. Baker and Buckle, however, set a lower limit condition of $\omega \gg 10^{-4}$ on the radial frequency ω of their simplified final results; this condition is unnecessary and is even inconsistent with B & B's own identification of C_0 as the low-frequency limiting capacitance.

Our problem is to obtain adequate expressions for C_0 and G_∞ for the $z_p : z_n$, two-electrode, fully-dissociated, unit-area situation in the low-voltage limit. Rather than having to re-solve the complicated a.c. problem as did B & B, we need only use the result of a much simpler $\Psi_0 \to 0$ static solution. It might be expected that this approach would not be valid because the space charge capacitances localized near the left and right electrodes might be unequal for a $z_p : z_n$ electrolyte when $z_p \neq z_n$. Fortunately, Grahame [23] found that in the $\Psi \to 0$ limit his one-electrode capacitances were the same for electrolytes of the $z_p : z_n$ type and those with z_n for the positive charge valence number, z_p for the negative charge number.

Let p_0 and n_0 be the (homogeneous) equilibrium charge concentrations in the electrolyte in the absence of any static electric field. Overall charge neutrality, dictated by the blocking electrodes, then requires that $z_p p_0 = z_n n_0$. The quantity G_∞ is unaffected by space charge and is given by the ohmic expression, $G_\infty = (e/l)[\mu_n z_n n_0 + \mu_p z_p p_0]$. Here μ_n and μ_p are the mobilities of the negative and positive charge carriers. This result was obtained by B & B. It may be written in the equivalent symmetrical form $G_\infty = (e/2l)(z_n n_0 + z_p p_0)(\mu_n + \mu_p)$.

A good first approximation for C_0 may be obtained from Grahame's general $z_p : z_n$ differential capacitance result. We write $C_0 = C_1/2$, where C_1 is the one-electrode differential capacitance obtained from the Grahame static solution when $\Psi \to 0$. Since the two electrodes each have a capacitance approximately equal to C_1 localized near it, the series combination C_0 is $C_1/2$. We define the average valence number $\bar{z}$ as $(z_p + z_n)/2$. Then denoting the C_0 determined from Grahame's results as C_{0G}, we find

$$C_{0G} = [e^2 \varepsilon \bar{z}(z_n n_0 + z_p p_0)/16\pi kT]^{\frac{1}{2}}, \tag{1}$$

where ε is the dielectric constant of the electrolyte.

Baker and Buckle give an expression for C_0, C_{0B}, which involves μ_p/D_p and μ_n/D_n and thus does not employ the general Nernst-Einstein relation connecting μ_i and D_i (i = n or p).[27] Here D_i is the diffusion coefficient for the ith type of charge carrier. The general relation will be used here since for all situations where it is likely to fail for ions the simple transport equations used in the rest of the theory will fail as well. The only version of the Nernst-Einstein relation appearing in B & B's paper, $\mu/D = e/kT$, which followed their expression for C_0, is pertinent only for the 1 : 1 valence case; it was used by B & B, without specification of the valence situation considered, to show agreement of their expression for C_0 with the expression for the low-potential limit of the Gouy capacitance.

The location in the text of the B & B expression for μ/D and the fact that their only literature citation to the Nernst-Einstein relation does not give the general $z_p : z_n$ valence relation explicitly may give the impression that their relation is that appropriate in general to reduce their expression for C_0 to the usual form, which involves neither μ_i nor D_i; it is not. For arbitrary valences the correct expression is $\mu_i/D_i = z_i e/kT$. When this relation is employed in B & B's C_0 expression,

$$C_{0B} = [\{ez_p p_0 \varepsilon/16\pi\}\{(\mu_p/D_p)+(\mu_n/D_n)\}], \tag{2}$$

one obtains C_{0G} on using the neutrality condition. Unfortunately, reduction to a form like that of C_{0G} is not carried out by B & B, and the impression may be given that both valence numbers are not involved symmetrically in the expression for C_0. The agreement of C_{0B}, using the proper Nernst-Einstein relation, with C_{0G} shows the essential independent-electrode character of the B & B result.

IMPROVED CALCULATION OF C_0

A more general expression for C_0 than C_{0G} or C_{0B} may be obtained as follows. The C_{0B} result implicitly takes the space-charge capacitances near the two electrodes as independent and uncoupled. This is a good approximation when the normalized length $L \equiv l/L_D \gtrsim 5$ or 6, where L_D is the Debye length, defined below. It is not a good approximation when there are only two or three or less Debye lengths between the electrodes. To obtain C_0 for arbitrary L, we may either generalize Grahame's treatment to two electrodes or our previous 1 : 1, two-electrode, static treatments [6, 7] to the $z_p : z_n$ situation. Although the expression could be written down directly by combining previous results, we derive it, both because no such general derivation has been given previously and as further direct proof that an equilibrium calculation of C_0 must yield agreement with the low-frequency limiting result of an a.c. treatment.

The net charge density in the electrolyte is $\rho = e(z_p p - z_n n)$. Let ψ_d be the value of ψ for which $\rho = 0$. For the present situation, with $\psi = \psi_0$ applied at the left electrode and ψ zero at the right, $\psi_d = \psi_0/2$. Now we define $\phi \equiv \psi - \psi_d$. At equilibrium, $n = n_0 \exp(z_n\Phi)$ and $p = p_0 \exp(-z_p\Phi)$, where $\Phi = e\phi/kT$. We next normalize the electric field $\mathscr{E}$: $E \equiv eL_D\mathscr{E}/kT$. Finally, we define the value of E at $\Psi = \Psi_d$ as E_d. Since charge neutrality is maintained globally but not locally between the electrodes when $|\Psi_0| > 0$, integration of Poisson's equation over the space between the electrodes shows that $E_L = E_R$, where E_L and E_R are the fields at the left and right electrodes. The Poisson-Boltzmann equation in the present one-dimensional approximation may now be written in the normalized form

$$\begin{aligned}\frac{d^2\Phi}{dX^2} &= \tfrac{1}{2}\frac{d}{d\Phi}\left[\frac{d\Phi}{dX}\right]^2 = \tfrac{1}{2}\frac{dE^2}{d\Phi} = -(4\pi\rho/\varepsilon)(eL_D^2/kT)\\ &= (4\pi e^2L_D^2/\varepsilon kT)[z_n n_0 e^{z_n\Phi} - z_p p_0\, e^{-z_p\Phi}],\end{aligned} \tag{3}$$

where $X \equiv x/L_D$, $E \equiv -d\Phi/dX$, and neither μ_n nor μ_p is assumed identically zero. Here x is the distance measured from the left electrode. Integration from $\Phi = 0$ to Φ yields

$$E^2 = E_d^2 + (8\pi e^2L_D^2/\varepsilon kT)[n_0(e^{z_n\Phi}-1)+p_0(e^{-z_p\Phi}-1)], \tag{4}$$

Next, we need to calculate E_d. This we do only for $|\psi_0| \ll 1$; expansion to second order of the exponentials in (4) then yields

$$E^2 \cong E_d^2 + (4\pi e^2L_D^2/\varepsilon kT)(z_n^2 n_0 + z_p^2 p_0)\Phi^2. \tag{5}$$

This equation and all those below which involve C_0, Ψ_0, and/or Φ hold only for $|\Psi_0| \ll 1$. Now $(z_n^2 n_0 + z_p^2 p_0) = 2z_p p_0[(z_n+z_p)/2] = 2\bar{z}z_p p_0 = \bar{z}(z_p p_0 + z_n n_0)$.

Further, integration of $E \equiv -(\mathrm{d}\Phi/\mathrm{d}X)$ for $X = 0$ to $X = L$ and $\Phi = -\Psi_0/2$ to $\Psi_0/2$ yields

$$L \cong \int_{-\Psi_0/2}^{\Psi_0/2} \frac{\mathrm{d}\Phi}{[E_d^2 + (4\pi e^2 L_\mathrm{D}^2 \bar{z}/\varepsilon kT)(z_p p_0 + z_n n_0)\Phi^2]^{\frac{1}{2}}}. \tag{6}$$

We now take [4]

$$L_\mathrm{D}^2 \equiv [\varepsilon kT/4\pi e^2 \bar{z}(z_p p_0 + z_n n_0)], \tag{7}$$

a choice we show below to be consistent. Eqn (6) then leads to

$$L \cong 2 \sinh^{-1} (\Psi_0/2E_d). \tag{8}$$

It follows that

$$E_\mathrm{d} = (\Psi_0/2) \operatorname{cosech} (L/2), \tag{9}$$

equivalent to an earlier 1 :1 valence result [6, 7] except for the more general expression for L_D here in L. Now when $L/2 \ll 1$, eqn (9) leads to $\mathscr{E}_\mathrm{d} \cong \psi_0/l$, a correct and necessary result in this extreme where $\mathscr{E}$ must be independent of x. Next we define $M \equiv L/2$, formally in agreement with the definition used earlier.[4, 6, 7] Now eqn (5) may be written

$$E^2 \cong (\Psi_0/2)^2 \operatorname{cosech}^2 M + \Phi^2. \tag{5'}$$

Since $\Phi = \Psi_0/2$ at the left electrode, we finally obtain

$$E_\mathrm{L} = E_\mathrm{R} \cong (\Psi_0/2) \operatorname{cotanh} M. \tag{10}$$

Alternatively, the substitution of eqn (7) in eqn (3) leads, for $|\Phi| \ll 1$, to $\mathrm{d}^2\Phi/\mathrm{d}X^2 \cong \Phi$. For the present situation, the solution of this equation is $\Phi \cong E_\mathrm{d} \sinh (M - X)$, showing that the choice of L_D yields the proper dependence of Φ on $X \equiv x/L_\mathrm{D}$. It follows that $E \cong E_\mathrm{d} \cosh (M - X)$, in agreement with (9) and (10) for $X = 0$ and L.

It remains to calculate the differential capacitance per unit area, $C_0 \equiv (\varepsilon/4\pi)(\mathrm{d}\mathscr{E}_\mathrm{L}/\mathrm{d}\psi_0) = (\varepsilon/4\pi L_\mathrm{D})(\mathrm{d}E_\mathrm{L}/\mathrm{d}\Psi_0)$. The result is

$$C_0 = (\varepsilon/8\pi L_\mathrm{D}) \operatorname{cotanh} M = C_\mathrm{g} M \operatorname{cotanh} M = rC_\mathrm{g}, \tag{11}$$

where $C_\mathrm{g} \equiv \varepsilon/4\pi l$, the geometrical capacitance of the two unit-area electrodes separated by a material of dielectric constant ε, and

$$r \equiv (l/2L_\mathrm{D}) \operatorname{cotanh} (l/2L_\mathrm{D}) \equiv M \operatorname{cotanh} M. \tag{12}$$

As eqn (11) shows, C_g is the limiting value of C_0 when $l \ll L_\mathrm{D}$, as it must be. The space-charge component of C_0 is $C_0 - C_\mathrm{g}$. These results are in agreement with earlier ones [4, 6, 7] for which $z_\mathrm{p} = z_\mathrm{n} = 1$. For comparison with $C_{0\mathrm{G}}$ and $C_{0\mathrm{B}}$, C_0 may be written as

$$C_0 = [e^2 \varepsilon \bar{z}(z_\mathrm{n} n_0 + z_\mathrm{p} p_0) \operatorname{cotanh}^2 M/16\pi kT]^{\frac{1}{2}}. \tag{13}$$

Thus, $(C_0/C_{0\mathrm{G}}) \cong \operatorname{cotanh} M$ and when $M \gtrsim 3$, $C_0 \cong C_{0\mathrm{G}} = C_{0\mathrm{B}}$. The present result for C_0 is more general than the original $C_{0\mathrm{B}}$ of eqn (2) because of the cotanh M factor; it also explicitly exhibits necessary symmetry in z_n and z_p.

The Grahame and B & B results for C_0 include only the decoupled space-charge contributions, which do not involve l or L, while eqn (13) gives the proper total limiting capacitance between electrodes of unit area. The independence of l exhibited by the single-electrode Grahame C_0 result is proper; on the other hand, when C_0 represents the low-frequency limiting capacitance between two electrodes separated by a distance l, C_0 must depend on l. Incidentally, since the author's original 1 : 1 valence treatment [4] yielded an expression for $C_0 - C_\mathrm{g}$ (termed C_0 there) equal to the present $C_\mathrm{g}(M \operatorname{cotanh} M - 1)$ when the pertinent L_D is used in M, one would expect that B & B's treatment, depending directly as it does on the earlier work, should also yield this result. No comparison of this type was made by B & B. The difference in results arises because of simplifying approximations introduced by them. Although the condition $l \gg L_D$ is implicit in their simplifications, it is not mentioned by them, and they do not specifically identify a Debye length.

In their simplifications B & B replaced hyperbolic functions of their $\alpha^{\pm}$ eigenvalues (denoted $\rho^{\pm}$ in the earlier work [4]) by $\frac{1}{2}$ exp $(l\alpha_{\pm}/2)$. Their justification was first that mod $(\alpha^{+}) \gg 1$, although this is not the case for all possible values of the parameters entering the expression for α^{+}. Now α^{-} is proportional to $\sqrt{\omega}$ for sufficiently small ω, provided μ_p is not zero. In order to justify the replacement of cosh $(l\alpha^{-}/2)$ and sinh $(l\alpha^{-}/2)$ by $\frac{1}{2}$ exp $(l\alpha^{-}/2)$, B & B had to specify the conditions $\omega \gg 10^{-4}$, $(l/2) \gtrsim 1$ cm, and $D_p \leqslant 10^{-3}$ cm^2/s. These specific conditions are unnecessary in general and are a result of their particular simplification. They apparently did not recognize that in the $\omega \to 0$ limit when $\alpha^{-} \to 0$ all terms in the admittance involving α^{-} disappear. Thus, there is no problem in taking the $\omega \to 0$ limit to obtain such a quantity as C_0. Further, the above condition on α^{+} is the place in B & B's work where the requirement $l \gg L_D$ actually implicitly enters. In previous work,[4] this restriction was not introduced in obtaining relatively simple exact expressions for parallel capacitance and conductance and for C_0. It is not required for such simplification of B & B's exact results either. Finally, in related work of Beaumont and Jacobs [10] the condition $l \gg L_D$ was explicitly introduced before the limit $\omega \to 0$, yet no difficulty in passing to this limit was encountered.

When the condition $|\Psi_0| \ll 1$ is not imposed, the calculation of C_0 is difficult and can generally only be carried out numerically. In this case, $\Psi_d \neq \Psi_0/2$. Further, it is most unlikely that the capacitances localized near the electrodes are equal in this situation as they are here.

DEBYE DISPERSION REGION

The complete admittance/unit area Y_p of the present system may be written in the form $Y_p = G_p + i\omega(C_g + C_p)$, where G_p and C_p arise from the ionic charge carriers and C_g is associated with the polarization of the solvent.[4] This expression shows that G_p and $(C_g + C_p) \equiv C_{pT}$ are in parallel electrically. C_p and C_g will generally show different frequency behaviour: C_g should be independent of frequency up to quite high frequencies while C_p depends on ionic mobility and thus will begin to decrease with increasing frequency at much lower frequencies than does C_g.

In the frequency range, if any, for which single-time-constant simple Debye dispersion is a good approximation, G_p and C_p may usually be written as $G_p/G_\infty \cong (\omega\tau_m)^2/[1+(\omega\tau_m)^2]$ and $C_p/(C_0 - C_p) \cong [1+(\omega\tau_m)^2]^{-1}$. The time constant τ_m, not necessarily equal to the $\tau \equiv C_0/G_\infty$ already defined, is the single time constant which governs the dispersion. It may be found approximately as follows. We convert the frequency-dependent, parallel quantities G_p and C_p to the related series quantities G_s and C_s by means of the relations $C_s \equiv [1+(\omega\tau_m)^2]$ and $G_s \equiv [1+(\omega\tau_m)^{-2}]G_p$. These expressions for G_p and C_p then lead to the frequency-independent results $G_s = G_\infty$ and $C_s = (C_0 - C_g)$. These two quantities in series define the time constant [4, 26] $\tau_m \equiv C_s/G_s = (C_0 - C_g)/G_\infty$; it is only equal to τ when C_g is negligible compared to C_0. Clearly, the appropriate equivalent circuit in the Debye dispersion range is [4] C_g in parallel with the series combination of the frequency-independent elements $(C_0 - C_g)$ and G_∞. A slight modification of these results, important for $M \lesssim 100$, is discussed in the next section.

Also, $C_g/G_\infty = \varepsilon/4\pi\sigma_\infty \equiv \tau_D$, the dielectric relaxation time for the material. Here $\sigma_\infty \equiv lG_\infty$ is the ohmic conductivity corresponding to G_∞. The dielectric relaxation time τ_D is the proper time constant of the material when there is essentially no space charge between the electrodes ($L \to 0$ or $l \ll L_D$), or at such high frequencies that space charge cannot appear. Since the present $C_0 \to C_g$ when $L \to 0$, $\tau \to \tau_D$ as it should under this condition. Further, since as shown later, the accurate C_p decreases slower than ω^{-2} for sufficiently high ω, the exact susceptance of C_s, calculated from $G_p(\omega)$ and $C_p(\omega)$, will continually increase with increasing ω, finally leaving G_∞ alone in parallel with C_g. Thus, the limiting high-frequency time constant will again be $\tau_D \equiv C_g/G_\infty$. Formally, $\tau \equiv \tau_m + \tau_D$. The time constant $\tau_m = (r-1)\tau_D$ may also be considered the motional relaxation time.[4, 26]

Next, we show how the time constants depend on z_p and z_n. For simplicity, we consider only the expression for τ rather than that for $\tau_m = [(r-1)/r]\tau$. The present results lead to

$$\tau^2 = \frac{\varepsilon(l \operatorname{cotanh} M)^2 \bar{z}}{4\pi kT(\mu_n+\mu_p)^2(z_n n_0 + z_p p_0)}, \tag{14}$$

a result which depends symmetrically on z_p and z_n, not on one or the other only as does B & B's corresponding expression. The latter involves only z_p explicitly and, as written, appears to remain unchanged for $z_n = 0$. The dependence on τ of z_p and z_n is of interest since only when $z_p \neq z_n$ does the present result differ significantly from that of previous work [4] when $M \gg 1$. There is likely to be some dependence on valence in the μ_n and μ_p of eqn (14). Simple theories of mobility yield for a univalent charge carrier $\mu_i = e\tau_{ci}/m_i$, where m_i is the mass of the particle and τ_{ci} is the mean time between collisions. Provided τ_{ci} is independent of the magnitude of the particle charge, frequently a reasonable approximation, the corresponding expression for a charge carrier of arbitrary valence number, z_i, is $\mu_i \cong z_i e\tau_{ci}/m_i \equiv a_i z_i$. If we define $\lambda \equiv z_n/z_p$ and introduce this expression for μ_i in eqn (14), then, e.g.

$$(z_p\tau)^2 = A_0(1+\lambda)/(a_p+a_n\lambda)^2, \tag{15}$$

where $A_0 \equiv (\varepsilon l^2 \operatorname{cotanh}^2 M)/16\pi kTp_0$. There is thus a substantial dependence of τ on the valence numbers and their ratios. There is also further dependence on these quantities through the appearance of M in eqn (14) and in A_0. Since cotanh M will be essentially unity for most electrolyte cases of practical interest, this dependence is usually unimportant.

Baker and Buckle [24] have explicitly neglected the geometrical capacitance C_g and have presented expressions for G_p and C_p which involve C_{0B} in place of $(C_0 - C_g)$ and τ in place of τ_m. Their results, when symmetrized, are adequate when $l \gg L_D$, since then $C_0 \gg C_g$ and $\tau_m \gg \tau_D$.

The Debye frequency range over which G_s and C_s may be well approximated by the frequency-independent quantities G_∞ and $(C_0 - C_g)$ is of importance. In the general case of arbitrary mobilities and arbitrary valence, it has not been precisely defined. B & B's restriction $\omega \gg 10^{-4}$ is inapplicable, and we may write as before $0 \leqslant \omega\tau \ll B$. Now B & B set the upper limit condition $\omega \ll \omega_0 \equiv 4\pi e\mu_p p_0/\varepsilon$. This result cannot be correct in general since it does not depend on μ_n, n_0, z_p, and z_n. Clearly, space charge effects of the present type could still occur when $\mu_p \ll \mu_n$ or when $\mu_p \to 0$, provided μ_n remained non-zero. In such cases, ω_0 would become very small or approach zero and there would be little or no Debye dispersion region at all according to the B & B criterion. Since the criterion is insufficiently general, let us symmetrize it and write $\omega_0 \to \omega_{0s} = 4\pi e(\mu_n z_n n_0 + \mu_p z_p p_0)/\varepsilon = G_\infty/C_g$. Thus the condition $\omega \ll \omega_{0s}$ becomes $\omega \ll G_\infty/C_g = \tau_D^{-1}$, or $\omega\tau_D \ll 1$, a reasonable result. Now since $\tau/\tau_D = C_0/C_g \equiv r$, the new condition may be written $0 \leqslant \omega\tau \ll r$; thus, $B = r$. When $L \to 0$, $r \to 1$ and $\tau \to \tau_D$. Although as stringent a condition as $\omega\tau \ll r$, or equivalently, $\omega\tau_D \ll 1$, was not explicitly given in the earlier work,[4] the normalized frequency $y \equiv \omega\tau_D$ was itself considered, and $\omega\tau_D \ll 1$ is an approximate minimum upper bound in the situation there treated.

DEVIATIONS FROM SIMPLE DEBYE DISPERSION BEHAVIOUR

Although the inequality $y \ll 1$ is a sufficient condition for C_s to remain essentially frequency independent in this frequency range, one may ask whether the Debye dispersion range is so limited. The earlier 1 : 1 valence results suggest that the above inequality is too stringent.[4] For the 1 : 1 case, by starting with the exact, but complex, expressions [4] for $C_p(\omega)$ and $G_p(\omega)$, these results may be written, for $\mu_n = \mu_p$ and full dissociation, as

$$C_p/(C_0 - C_g) = [\mathrm{Re}(N) - 1]/(r-1), \tag{16}$$

$$\cong [Mhy + Mg - 1]/[M-1][M^2my^2 - 2Mhy + 1],$$

$$G_p/G_\infty = -y\,\mathrm{Im}(N), \tag{17}$$

$$\cong \{M[Mm-g]y^2 - Mhy\}/[M^2my^2 - 2Mhy + 1],$$

where

$$N \equiv \frac{M[1+iy]^{\frac{3}{2}}}{\tanh\{M[1+iy]^{\frac{1}{2}}\} + iyM[1+iy]^{\frac{1}{2}}}, \tag{18}$$

$y \equiv \omega\tau_D$, and $M \equiv l/2L_D$ with L_D as given in eqn (7) for $z_p = z_n = 1$. Thus, here $M = l[2\pi e^2 n_0/\varepsilon kT]^{\frac{1}{2}}$. Further, $G_\infty = 2e\mu_n n_0/l$ in the present situation where $p_0 = n_0$. The approximate relations given above, following the separation of N into real and imaginary parts, only hold well for $\tanh M \cong 1$, say, $M \gtrsim 3$, so that $r \cong M$. In these relations, $m \equiv (1+y^2)^{\frac{1}{2}}$, $g \equiv [(m+1)/2]^{\frac{1}{2}}$ and $h = [(m-1)/2]^{\frac{1}{2}}$. Although separation can be readily carried out for $M < 3$, the general results obtained are complicated; much simpler replacements for them will be given later. Eqn (16) and (17) lead, for $M \gtrsim 3$, to $C_p/(C_0 - C_g) \to 1$ and $G_p/G_\infty \to M(M-1.5)y^2 \to 0$ for $y \to 0$, and to $C_p/(C_0 - C_g) \to [\sqrt{2}M(M-1)y^{\frac{3}{2}}]^{-1} \to 0$ and $G_p/G_\infty \to 1$ for $y \to \infty$.

The above expressions for C_p/C_g and C_p/C_∞ also apply, with a slight reinterpretation, when $\mu_p = 0$, $\mu_n \neq 0$ (or $\mu_n = 0$, $\mu_p \neq 0$) as well. It is only necessary to replace the M in eqn (18) by $M/\sqrt{2}$, and note that $G_\infty = e\mu_n n_0/l$ (or $e\mu_p p_0/l$) in this case. Thus, e.g., results obtained for $M = 10$ for $\mu_p = \mu_n$ are equally applicable for $\mu_p = 0$, $\mu_n \neq 0$ with $M = 10\sqrt{2}$.

To assess the applicability of the Debye-dispersion condition $y \ll 1$ and examine the adequacy of the single-time-constant Debye relaxation approximation, we can convert the exact $C_p/(C_0 - C_g)$ and G_p/G_∞ expressions of eqn (16) and (17) to their corresponding series representations and examine the departures of the resulting $C_s/(C_0 - C_g)$ and G_s/G_∞ from unity for various M and y values. The exact relations applicable when C_p and G_p are frequency dependent are $C_s \equiv [1 + (\omega C_p/G_p)^{-2}]C_p$ and $G_s \equiv [1 + (\omega C_p/G_p)^2]G_p$. I have used these relations and eqn (18) to obtain accurate values for $C_p/(C_0 - C_g)$, $C_s/(C_0 - C_g)$, G_p/G_∞ and G_s/G_∞ for comparison with the explicit relations given herein and to assess the adequacy for these quantities of the Debye approximations which involve only $\omega\tau_m \equiv (r-1)y$. Again, for $M \gtrsim 3$, one obtains

$$C_s/(C_0 - C_g) \cong [M^2m - 2Mg + 1]/[M-1][Mhy + Mg - 1], \tag{19}$$

$$G_s/G_\infty \cong [M(Mm - 2g)y + y]/[M(Mm-g)y - Mh]. \tag{20}$$

For $y \to 0$, $C_s/(C_0 - C_g) \to 1$ and $G_s/G_\infty \to G_0/G_\infty$, where $G_0 \leqslant G_\infty$. For arbitrary M this ratio is given by

$$G_0/G_\infty = [r-1]^2/[(3r/2)(r-1) - (M^2/2)]. \tag{21}$$

It goes to 5/6 as $M \to 0$, reaches 0.953 by $M = 10$, and rapidly approaches unity as M further increases.[4] In the opposite extreme of y (for $M \gtrsim 3$), as $y \to \infty$, $G_s/G_\infty \to 1$

and $C_s/(C_0-C_g)\to\sqrt{2M/(M-1)y}$. Thus, for usual M values, $G_s \cong G_\infty$ over the entire range of y.

Some of the results of the accurate calculations are shown in fig. 1. The curves of the figure show that the condition $y \ll 1$ for C_s to remain constant is considerably too stringent.[4] In fact, for $M \geqslant 10$, C_s is constant within 1 % to about $y \simeq 0.3$ and to within 10 % up to $y \simeq 1$. For $M < 10$, the range of frequency independence is even greater.

The computer results show that for $0 \leqslant y \lesssim 0.3$ the following simple approximations are highly accurate for any M:

$$C_p/(C_0-C_g) \cong Z^2/(1+Z^2), \tag{22}$$

$$C_s/(C_0-C_g) \cong 1, \tag{23}$$

$$G_p/G_\infty \cong (G_0/G_\infty)/(1+Z^2), \tag{24}$$

$$G_s/G_\infty \cong (G_0/G_\infty), \tag{25}$$

where the quality factor Z is

$$Z \equiv \omega C_p/G_p \cong (G_0/G_\infty)/(r-1)y. \tag{26}$$

These results differ from those discussed in the last section only by the presence of (G_0/G_∞). The appropriate time constant is thus $(G_\infty/G_0)(r-1)\tau_D$. The equivalent circuit applicable in the range $0 \leqslant y \leqslant 0.3$ is C_g in parallel with the series combination of (C_0-C_g) and G_0. The transition from $G_s \cong G_0$ to $G_s \cong G_\infty$ occurs almost entirely in the range $y > 0.3$.

The present results show that for the 1 : 1 valence case the $y \ll 1$ condition, which should apply for any valence number ratio, is considerably too stringent. Although detailed calculations would be required to show the precise frequency limits for applicability of the Debye dispersion approximation in the situation of unequal valence numbers, the present results make it highly probable that even in this case the $y \ll 1$ condition will still be unnecessarily restrictive.

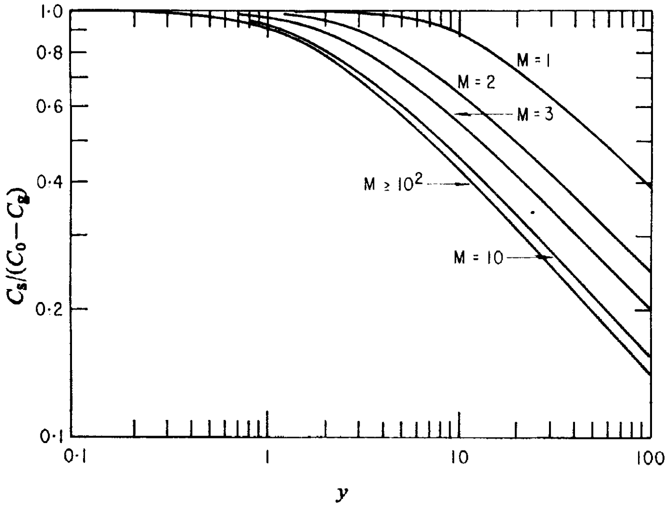

FIG. 1.—Dependence for $z_n = z_p = 1$ and $\mu_n = \mu_p$ of normalized series space charge capacitance on normalized frequency, $y \equiv \omega\tau_D$, for several values of $M \equiv l/2L_D$.

Eqn (22) and (26) show that C_p begins to decrease when $y \simeq (G_0/G_\infty)/[10(r-1)]$ and then shows simple Debye dispersion until $y \lesssim 0.3$. Beyond this range, it eventually decreases as $\omega^{-\frac{1}{2}}$. At $y = 1$, $C_p/C_g \sim (r-1)^{-1} \sim M^{-1}$ for $M \gg 1$. But since C_p must be determined from the difference $C_p = C_{pT} - C_g$, where C_{pT} is the experimentally measured total parallel capacitance, one will then obtain C_p as the small difference between two much larger numbers. If C_p can only be accurately determined, e.g., when $C_p \gtrsim 0.01\ C_g$, then the decrease in C_p cannot be followed much past $y = 1$ if $M = 100$. The $\omega^{-\frac{3}{2}}$ limiting behaviour would scarcely be apparent under such conditions. For $M = 1$, however, where some space charge effects still exist, C_p/C_g does not reach 0.01 until $y = 17$. Fig. 1 shows that $C_s/(C_0 - C_g)$ has begun to approximate $\omega^{-\frac{1}{2}}$ behaviour by $y = 17$; thus, C_p shows $\omega^{-\frac{3}{2}}$ dependence in this range. Nevertheless, very accurate measurements of C_{pT} will be needed to make it possible to observe $\omega^{-\frac{3}{2}}$ behaviour for C_p, or $\omega^{-\frac{1}{2}}$ behaviour for C_s. Exact [14] or approximate [11, 22, 28] $\omega^{-\frac{3}{2}}$ behaviour has sometimes been observed in solids with blocking or partly blocking electrodes. Nevertheless, the above considerations indicate that present theory probably cannot explain the observed results.

In what frequency range should we expect the above effects to occur for electrolytes ? If we measure σ_∞ in mho/cm, then for an aqueous electrolyte near 25°C, $\tau_D \simeq 7 \times 10^{-12}/\sigma_\infty$ s. For 0.1 M KCl, $\sigma_\infty \sim 10^{-2}$ mho/cm, and $\tau_D \sim 7 \times 10^{-10}$ s. For $y = 1$, the corresponding frequency, $f_m \equiv (2\pi\tau_D)^{-1}$, will be $\sim 2.3 \times 10^8$ Hz, a very high value. Although other effects would probably obscure at such a high frequency the effect we here consider and prevent the $\omega^{-\frac{3}{2}}$ dependence from being observable, the situation is different for the Debye range. For the present concentration, $L_D \sim 10^{-7}$ cm. If $l = 0.2$ cm, then $r \cong M \sim 10^6$. Thus the beginning of the Debye decrease at $y \sim [10(r-1)]^{-1}$ would correspond to a frequency f_0 of about 23 Hz. Much of the Debye region would therefore occur in a readily measurable range.

For low concentrations, say 10^{-5} M KCl, $\sigma_\infty \sim 10^{-6}$ mho/cm, and $\tau_D \sim 7 \times 10^{-6}$ s. The corresponding f_m is only 2.3×10^4 Hz, still within a readily measurable range; here $L_D \sim 10^{-5}$ cm, and for $l = 0.2$ cm, $r \cong M \sim 10^4$. Here the frequency f_0 is only about 0.23 Hz. The low conductivity present at a 10^{-5} M concentration would make accurate measurements difficult, however.

The literature on double-layer relaxation in electrolytes is relatively sparse; it has recently been reviewed by Delahay [29] and de Levie.[30] For solid electrodes, appreciable dispersion often appears, perhaps arising from roughness and porosity of the electrode. Typical results are those of Jaffé and Rider [31] which show considerable variability and lack of reproducibility. Surface roughness and porosity are minimized or absent for the dropping mercury electrode, and most workers usually see no dispersion up to relatively high frequencies, 10^5-10^6 Hz or higher.

Why is not Debye dispersion usually apparent in aqueous electrolytes, e.g., 0.1 M KCl with liquid mercury electrodes? The foregoing discussion indicates that the beginning of dispersion might be expected for $f \gtrsim 23$ Hz with $l = 0.2$ cm. A larger l, as is frequently used experimentally, would decrease the Debye dispersion frequency range by increasing M, and one might thus expect to see strong dispersion at the usual measurement frequency of 10^3 Hz. As suggested by Delahay,[29] the compact, or inner, part of the double layer is probably complicating the situation. The relatively potential-independent inner layer capacitance may be considered to be approximately in series with the parallel combination of C_p and G_p and this combination itself in parallel with C_g. Except very near the point of zero surface charge and at very low ionic concentrations, we expect the inner layer capacitance to dominate the combination in most practical situations.[13] Evidently, for most experimental measurements thus far, any dispersion of C_p and G_p has negligible effect on the impedance of the overall combination.

On the other hand, appreciable dispersion does appear in fused salts using solid electrodes.[30] Since the inner region of the double layer may be absent or less dominant in such situations than in aqueous electrolytes, the present diffuse layer effects should be readily apparent if they can be adequately separated from porosity and roughness dispersion. However, it is usually difficult to obtain completely blocking electrodes for fused salts. In addition, the presence of ion pairing in fused salts indicates that dissociation is incomplete, forcing one to use the more general incomplete dissociation theory [4] for most situations of interest. Finally, lattice-like and layering structures,[32] which may be present in fused salts, would reduce the applicability of the present results to such materials.

Finally, we discuss the relation of the present frequency response theory to those of Ferry [25] and Friauf.[22] Both are concerned only with the diffuse part of the double layer, as is the present treatment. In addition, both involve only the 1 : 1 valence situation. Ferry analyzes the relaxation of the ionic atmosphere at a plane surface. Although not explicitly stated, his boundary condition at this surface must be one of complete blocking of both types of charge carriers. Further, his treatment is an entirely linear one, restricting potentials which disturb equilibrium conditions to appreciably less than $|kT/e|$. Thus, his analysis, like the present one, can only apply in the immediate neighbourhood of the point of zero electrode charge. Finally, the method of analysis is applicable only for ions of equal mobility. Ferry's result for C_p may be written in the form

$$\frac{C_p}{C_0} = \frac{1}{1+y^2} + \left[\frac{(1+y^2)^{\frac{1}{2}}+1}{2(1+y^2)}\right]^{\frac{1}{2}}. \tag{27}$$

This result follows since Ferry's θ and the present y are the same quantity. Although Ferry gave no expression for G_p, this quantity may be readily derived from his work. We find

$$\frac{G_p}{G_\infty} = M\left[\frac{y^2}{1+y^2} + y\left\{\frac{(1+y^2)^{\frac{1}{2}}-1}{2(1+y^2)}\right\}^{\frac{1}{2}}\right]. \tag{28}$$

The C_0 which appears in eqn (27) is $\varepsilon/4\pi L_D \equiv 2MC_g$, i.e., twice that found in the present treatment for $l \gg L_D$. The reason is that Ferry considers only a single electrode. The C_0 of the present two-electrode treatment is made up (for $M \gg 1$) of capacitances/unit area of $\varepsilon/4\pi L_D$ at each electrode. The series combination of the two is $C_0 = MC_g$. Also, G_p does not depend on l, since no such quantity is introduced in Ferry's treatment. We have expressed eqn (28) in terms of the usual G_∞ for easy comparison with the earlier results, but MG_∞ only involves L_D, not l. Finally, since G_p is evidently proportional to $\sqrt{y}$ for sufficiently large y, no true finite G_∞ (lim $y \rightarrow \infty$ of G_p) is obtainable from Ferry's analysis and comparison with the present results is most appropriate at the parallel equivalent circuit level.

Ferry's work leads to quite different G_p/G_∞ behaviour for $y \gg 1$ than does the present analysis. Appreciable differences also appear in the capacitance comparison. For $M \gg 1$, so that C_g may be neglected compared to C_0, the present treatment leads for $y \gg 1$ to $C_p/C_0 \rightarrow (\sqrt{2}M^2)^{-1}y^{-\frac{3}{2}}$ dependence while eqn (27) leads to $C_p/C_0 \rightarrow (\sqrt{2})^{-1}$ $y^{-\frac{1}{2}}$ dependence. The situation is little different for $y \ll 1$. Although Baker and Buckle [24] have stated that Ferry's expression for C_p/C_0 resembles theirs at low frequencies, this conclusion is based on a superficial comparison. For large M, and $y \lesssim 1$, the present work leads to $C_p/C_0 \cong [1+(My)^2]^{-1}$, very different from the dependence of eqn (27). The most important difference is that Ferry's time constant is essentially τ_D, while the pertinent one in the present two-electrode situation is $M\tau_D \cong \tau$, usually a much larger quantity than τ_D. Thus, Ferry found that his dispersion occurred at a much higher frequency than he expected on the basis of experimental results.

The difference between the two treatments arises primarily because the two-electrode treatment involves a finite distance l between electrodes and also involves overall electroneutrality; in contradistinction, Ferry's model does not require electroneutrality and draws in ions from " infinity " when the electrode potential is changed. Now the present one-dimensional treatment of the two-electrode model only well approximates the experimental situation when the latter involves electrodes whose smallest linear dimension is much greater than l. Here l is taken infinite. In Ferry's case, conductance as well as capacitance is involved, and we should thus not restrict attention to a region within a few Debye lengths of the planar electrode. The conductance for a region of infinite length must be zero. It therefore appears that Ferry's non-zero result is incorrect. The apparent absence of conductance associated with the bulk of the solution is the reason why Ferry's effective time constant is essentially τ_D, not $M\tau_D$ as it should be for $y \lesssim 1$ and finite length. Even though the bulk conductance would be zero for $l = \infty$, its series combination with any conductance localized near the blocking electrode would yield zero conductance for the combination. An a.c. treatment of two electrodes, one neutral (ohmic), and one blocking, separated a finite distance l (small compared to electrode size), could be carried out along the lines of the analysis of ref. (4). Although Delahay [29] has stated that Ferry's treatment is satisfactory, this does not seem to be so for most situations of practical interest.*

Friauf considers a one-dimensional, 1 : 1 valence, two-electrode situation equivalent to that treated by the present author [4] when the electrodes are completely blocking. In addition, however, Friauf has given a result for two electrodes both blocking for ions of one sign and both non-blocking for those of the opposite sign. This is a case of particular interest and yields, according to Friauf, $C_p \propto \omega^{-\frac{3}{2}}$ and $G_p \propto G_\infty - O(\omega^{-\frac{1}{2}})$. These dependencies were obtained after some approximations which, however, do not seem to restrict the analysis to high relative frequencies. The above results are similar, nevertheless to a first approximation, to those for $y \gg 1$ of eqn (16) and (17) for the two-completely-blocking electrodes situation. In fact, Friauf's result for C_p for $\mu_n = \mu_p$, may be written as $C_p/C_0 = (\sqrt{2}M^2)^{-1}y^{-\frac{3}{2}}$, i.e., identical to the limiting form of eqn (17) when $M \gg 1$. There is thus no difference from the completely blocking result for $y \gg 1$ and $M \gg 1$. Here C_0 is taken as MC_g for easy comparison, although

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* *Note added in proof:* Buck (*J. Electroanal. Chem.*, 1969, **23,** 219) has recently provided, for two blocking electrodes (plane or spherical), a corrected version of Ferry's analysis. Besides yielding system transient response, the paper includes frequency response results which may be compared to those herein. Although Buck suggests that the impedance associated with the present problem has not been obtained previous to his work, its inverse, the admittance, has been given in closed form [4] for the plane-electrodes situation. Further, Buck's impedance equations apply only for complete dissociation, equal mobilities, and, for plane electrodes, for $M \gg 1$. The last condition was not stated explicitly. These restrictions were not made in the earlier analysis.[4] Buck states that his " treatment includes higher harmonics within the limits of linear theory", as contrasted with earlier work involving only the fundamental frequency. In fact, his treatment is, as usual, implicitly limited to applied potentials small in magnitude compared to kT/e and involves only the fundamental frequency. Although Buck treats the $z_p = z_n \equiv z$ case, he follows Baker and Buckle in quoting the Nernst-Einstein relation appropriate for $z = 1$. Finally, Buck has defined parallel and series resistances and capacitances by setting the impedances of such combinations equal to his overall system impedance. This procedure mixes the effect of the essentially frequency-independent C_g with the frequency-dependent space-charge elements. It apparently leads Buck to obtain an equivalent series resistance which decreases strongly with frequency for $y \gtrsim 1$, unlike the series resistance following from the present work which remains, for Buck's $M \gg 1$ case, frequency independent over the entire range of y. Further, Buck's equivalent series capacitance is only frequency independent up to $y \lesssim [10\,M]^{-1}$ compared to the present series capacitance which is essentially frequency independent to $y \lesssim 0.3$ or more. Besides thus dealing with series elements frequency independent over a much narrower range than found herein, Buck combines the zero-frequency values of these elements into an equivalent circuit differing from, and much less appropriate than, that discussed herein and earlier.[4]

the actual C_0 is different in the present case. These results suggest that the presence of $\omega^{-\frac{1}{2}}$ frequency response for C_p should not be used to allow one to conclude that the electrodes involved are not completely blocking.

One would not expect $\omega^{-\frac{1}{2}}$ behaviour for C_p to persist down to the zero frequency limit. Although Friauf does not give an equation for C_p for the transition region down to this limit, he does present a low-frequency limiting value for C_p of $C_g M^2/12$. For $M \gg 1$, this result is $M/12$ times larger than the present two-blocking-electrodes C_0 value of MC_g. For comparison with experiment, it would be valuable if Friauf's results for his partly blocking case were simplified, without limiting approximations, in such a way that the entire range of $C_p/(C_0 - C_g)$ were given from $\omega\tau = 0$ up to such an $\omega\tau$ that $C_p/(C_0 - C_g)$ became much smaller than unity. Debye dispersion will probably occur, as in the completely blocking case, at relative frequencies sufficiently below those where $y^{-\frac{1}{2}}$ behaviour appears.

Friauf's treatment allows arbitrary values for μ_n and μ_p. The 1 : 1 valence case with $\mu_p = 0$, $\mu_n \neq 0$ has been extended by Beaumont and Jacobs,[10] who dealt with a solid material and assumed partial blocking, or discharge, of the mobile charges at both electrodes. They found simple Debye dispersion for C_p and G_p at low normalized frequencies, with discharge merely changing the effective time constant, equal to the present τ in the completely blocking case.

Although these analyses are likely to be applicable to solids in many instances, the discharge boundary conditions assumed by Friauf and by Beaumont and Jacobs are not usually appropriate for the liquid electrolyte situation. Grahame [1] has given a treatment of the faradaic admittance in electrolytes which deals with electrochemical reactions at the electrodes and involves $\omega^{-\frac{1}{2}}$ dependence of both C_s and G_s (the Warburg impedance). Although Grahame assumed that faradaic and displacement current contributions to the total current through a partly blocking electrode were independent and that the two processes could thus be treated separately, with the results combined at the end of the calculation, Delahay [33] has shown that this assumption is invalid in general. He and his co-workers [33-37] have calculated the (small-amplitude) impedance of a single electrode in an electrolyte without *ab initio* separation of faradaic and double-layer charging processes. In addition, de Levie and Popisil [38] have summarized the results for electrode admittance in the presence of specific adsorption.

The present work has benefited greatly from many discussions with C. A. Barlow, Jr.

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