

**IMPEDANCE SPECTROSCOPY AND THE DOUBLE  
LAYER IN SOLIDS AND LIQUIDS\***

J. ROSS MACDONALD, Department of Physics and Astronomy,  
University of North Carolina, Chapel Hill, North Carolina



DR. J. ROSS MACDONALD

**I. Introduction**

I have been interested in the double layer, and have worked on it off and on, for over thirty years. Therefore, it is a special pleasure and honor to be invited to speak on this topic here today.

The electrical double layer (abbreviated EDL; a list of acronyms is given at the end of this paper) present in nearly all solid and liquid materials in which charge motion and translation are possible is a complicated beast and its behavior is by no means fully understood theoretically. In its simplest form it involves a space charge region (the diffuse part of the double layer) beginning at the boundary of a conducting material and decreasing away from the boundary into the material. The charge involved may be electronic, ionic, or mixed and the resulting polarization may involve charges of a single sign or of both signs. The distributed charge in the material is balanced by an equal and opposite charge on the surface or on an electrode if one is present. One general definition of the EDL is (1), "An electrical double layer is a non-homogeneous region of finite thickness containing significant variation in charge density across its thickness which consequently produces a potential drop across this dimension; the non-homogeneity invariably arises as a consequence of the competition between entropy and energy effects in the system's attempt to minimize its free energy."

The EDL plays an important role in the electrical behavior of semiconductor and electrochemical systems. The latter can include single crystals with intrinsic disorder and/or aliovalent doping, polycrystalline or composite solid electrolytes, fused salts, aqueous solutions, colloids, membranes, and even living cells. The interface at which an

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\*Based on an address presented before "The Robert A. Welch Foundation Conferences on Chemical Research XXX. Advances in Electrochemistry," which was held in Houston, Texas, November 3-5, 1986.

EDL appears may be that between the conducting material and air or vacuum (the resulting EDL is known as a Frenkel layer in solid materials); it may be an internal interface in the material; or it may appear between the material of interest and an electrode. In this work, main emphasis will be on ionic EDL's in liquid or solid electrochemical systems with metallic electrodes, and more attention will be paid to unsupported than to supported systems.

The EDL is often studied under essentially equilibrium conditions, achieved by the use of a completely blocking (ideally polarizable) electrode. Here I shall first discuss some theoretical work on the equilibrium EDL, then consider non-equilibrium steady-state conditions. The specific steady-state situation to be discussed is that involving small-signal frequency response over a wide frequency range, with or without a time-invariant biasing potential applied. Measurements of this kind (and their analysis), on either dielectric or conductive systems, have recently (2,3) been subsumed under the general term "Impedance Spectroscopy" (IS). When measurements are not limited to equilibrium conditions, important kinetic effects may occur. Long ago, Frumkin (4) first pointed out the importance of the EDL in affecting heterogeneous electron transfer reactions. The presence of an EDL affects the reaction because the electric field conditions in the reaction region near the electrode are different than they are in the bulk of the material.

Because there have been many reviews dealing with the EDL (e.g., 1,5 (and references therein), 6 (contains a listing, often with some evaluation, of all major reviews to the date of writing), 7, 8], the present discussion is selective rather than exhaustive, dealing with a bird's-eye view of a few specific areas and emphasizing still unsolved problems.

## II. The Equilibrium Double Layer

To begin with it is worthwhile to make some distinctions between various types of equilibrium EDL models (m): continuum (c) or discrete (d) models and primitive (p) or non-primitive (n) (civilized?) models. In recent years a primitive model has come to mean one in which the solvent molecules are replaced by a dielectric continuum with dielectric constant  $\epsilon_s$ . The ions may be treated in the continuum approximation (a continuum primitive model: cpm) or discretely (dpm). Thus the cpm is a full cm. In contra-distinction, the nm is a full dm since both solute ions and solvent molecules are treated discretely, with the molecules usually taken as having permanent dipole moments (usually of infinitesimal length: i.e. ideal point dipoles). If more than one conceptually different part of the EDL is defined, these characterizations may need to be applied separately to the individual parts, adding further complexity.

## A. Continuum Models

The earliest models of the electrochemical EDL involve several simplifying assumptions. First, a continuum approximation is made: mobile ions are taken to be of infinitesimal size and their charge is smeared out, eliminating all ionic discreteness effects. Only quantities averaged over planes parallel to the electrode thus appear. Second, the solvent is represented by a uniform dielectric constant  $\epsilon_s$ , often taken as the bulk value of the solvent material,  $\epsilon_B$ . Thus one is dealing with a cpm. Finally, the charge on the (metal) electrode, taken flat and smooth, is assumed to be confined to the electrode surface plane (ESP), a region of zero thickness. Thus the character of the electrode, assumed to be a perfect conductor, plays no role in the response. Progress in double layer theory has involved the gradual transcendence and elimination of these idealizations as more and more interactions are included in the analysis.

The prototype theory embodying the above assumptions is that of Gouy (9) and Chapman (10). A very important quantity which is often used to characterize the equilibrium EDL is the total differential capacitance of the system,  $C_T$ , usually expressed as capacitance per unit area of electrode, a practice we shall follow here by generally suppressing the distinction between total capacitance (or charge) and capacitance (or charge) per unit area, the more significant theoretical quantity. For a diffuse layer with total net charge  $Q_d$  and a total potential difference across it of  $\psi_d$ , the corresponding differential capacitance,  $C_{dl}$ , is just  $-dQ_d/d\psi_d$ . This quantity may often be determined from measurements and is easy to calculate from the Gouy-Chapman (GC) theory. Unfortunately, theory and experiment only approach good agreement in the limit of small ionic concentration.

The next major advance in the area was made by Stern (11) who took some account of finite ion size by introducing the assumption that the distance of closest approach to the electrode of the diffuse layer ions (taken of equal size, diameter  $2r_i$ ) is  $r_i$ , the distance between the centroid of ionic charge of ions nearest the electrode and the ESP. Finite ion size was, however, neglected in the rest of the diffuse layer. This model, the GCS, is perhaps most appropriate for solid electrolytes at relatively low ionic concentration. For liquid electrolytes, however, diffuse layer ions nearest the electrode are solvated (in the absence of specific adsorption), and it is thus usually assumed that there is a single layer of solvent molecules between the nearest ions and the ESP (12,13). In later work (14), it was assumed that the ESP lies somewhat inside the physical surface of the metal to account for field penetration into the electrode, adding a small additional increment ( $d_p$ ) to the effective electrical thickness of the charge-free inner layer next to the electrode. The outer Helmholtz plane (OHP) marks the boundary between this layer and the diffuse space charge region.

In the presence of specific adsorption (defined in crude terms as the existence of partly chemically bound solute ions located as close to the ESP as allowed by steric

constraints), even the completely blocking situation is more complicated. Specifically adsorbed ions have lost their solvation shells in the direction of the electrode so that the effective distance between the ESP and the charge centroids of such ions, located at the inner Helmholtz plane (IHP), is  $d_p + r_i$ . The situation is shown diagrammatically in Fig. 1 and with pertinent quantities defined in Fig. 2 (see Refs. 5 and 16 for justification and more detailed discussion of the EDL model implied by this figure). In Fig. 2 the  $\epsilon$ 's are local dielectric constants (generally much smaller than  $\epsilon_B$  because interactions in these planar regions are quite different from ordinary bulk-material interactions); the  $\sigma$ 's are charges per unit area; and the  $\psi$ 's are local potentials. It is quite clear from Figs. 1 and 2 that the EDL in liquid electrolytes is far from being just a simple two-component layer made up of the diffuse region and compensating charge on the electrode. When specifically adsorbed ions are of appreciably different sizes than solvent molecules, the model must be made even more complex (5).

### 1. No Specific Adsorption

#### a. Early Work

In the absence of adsorption the GCS model predicts that the total differential capacitance,  $C_T$ , is related to the inner layer capacitance,  $C_H$ , and the diffuse layer differential capacitance,  $C_d$ , through the equation

$$C_T^{-1} = C_H^{-1} + C_{dl}^{-1}, \quad (1)$$

where  $\gamma$  may be taken zero and  $C_H = C_\beta$  in Fig. 2 for this situation. Thus if  $C_T$  is derived from quasi-equilibrium measurements and  $C_d$  is calculated from an appropriate theory,  $C_H$  may be obtained. Note that in the present situation  $C_H$  should be concentration independent. No geometric capacitance,  $C_g$ , need appear in Eq. (1) because we are concerned only with single-electrode effects here. Now modern analysis of the electrochemical EDL may be said to have its inception and underpinning with the work of D.C. Grahame, especially his careful and accurate measurements on NaF in an aqueous solvent for a range of temperatures, applied potentials, and electrode charge (17,18). NaF is particularly appropriate because it shows less specific adsorption on anodic polarization than most other solutes. Grahame used ordinary GC diffuse layer theory and Eq. (1) to derive  $C_H$  as a function of the above variables; some of his results are presented in Fig. 3. It is particularly noteworthy that  $C_H$  is very far from being independent of electrode charge,  $\sigma_m (= -\sigma_d)$ , and temperature. It is the detailed structure of  $C_H$  which leads to much of the interest and challenge in understanding the equilibrium EDL.

Some of Grahame's NaF  $C_T$  data are presented in Fig. 4. The dashed line shows a fit using GC diffuse layer theory alone. It is clear that it is inadequate and

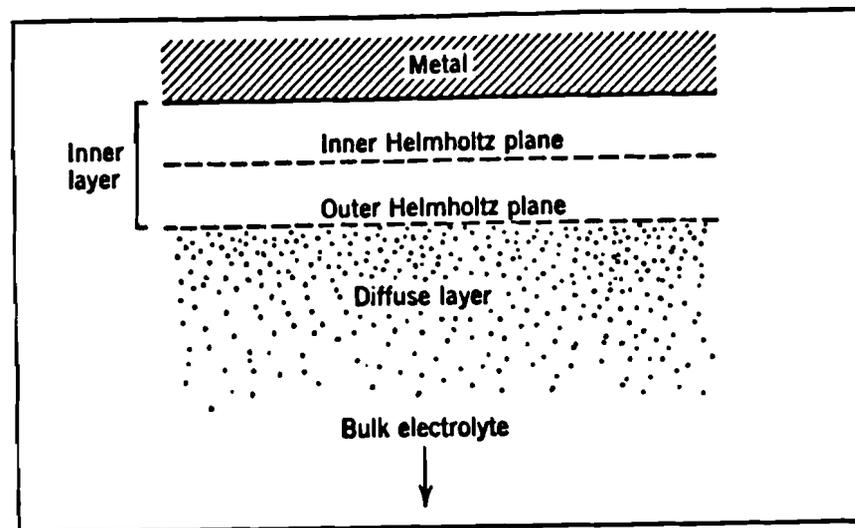


FIGURE 1

Schematic representation of the EDL (Reprinted by permission of John Wiley & Sons, Inc., copyright © 1967, 6; 15).

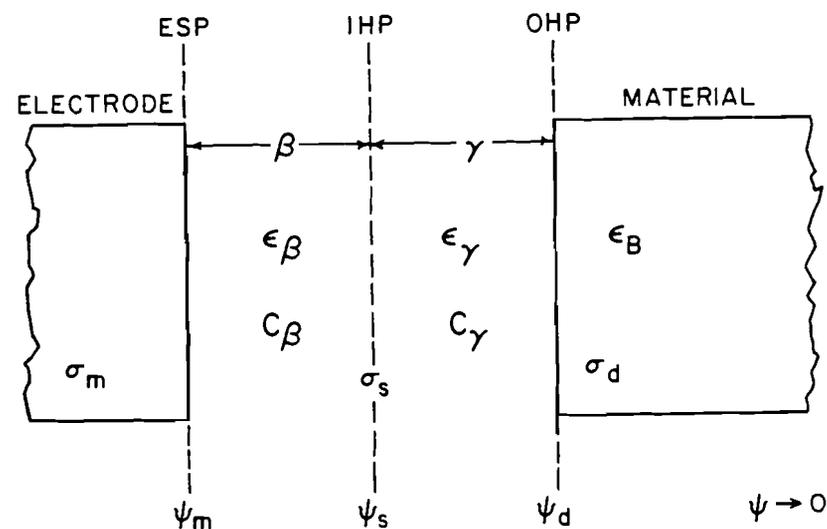


FIGURE 2

Definitions of various quantities in electrode-interphase region of the EDL (5,16).

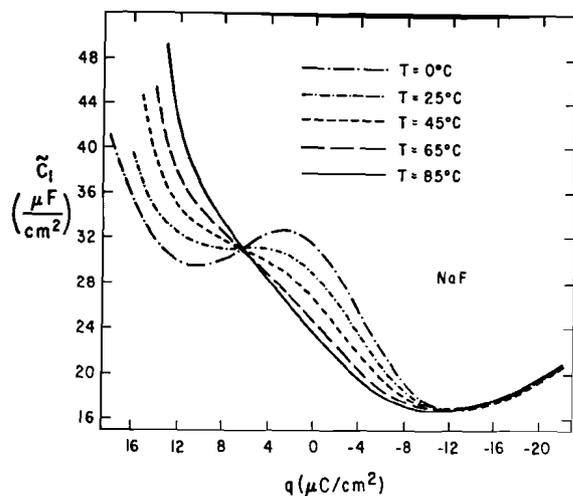


FIGURE 3

Differential capacitance of the inner layer,  $\tilde{C}_1 \equiv C_H$ , vs. electrode charge ( $q = \sigma_m$ ) (Reprinted with permission, 5; 14). Data calculated by Grahame (17,18) from his experimental results using a dropping mercury electrode and assuming no specific adsorption.

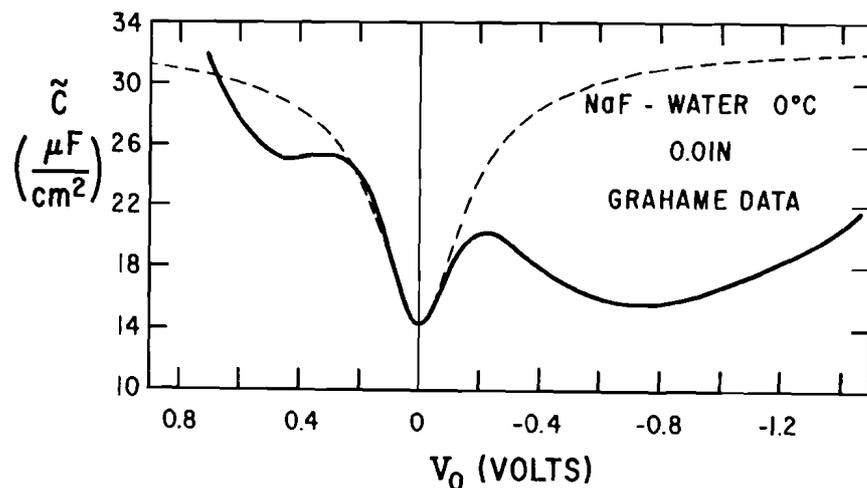


FIGURE 4

Total differential capacitance of the EDL,  $\tilde{C} \equiv C_T$ , vs. applied p.d.,  $V_0 \equiv \psi_m$ , based on data of Grahame (18) and showing diffuse layer fit (dotted line).

thus the effects of an inner (or compact) charge-free region must not be neglected. The first full analysis of the Grahame  $C_T$  data was produced by the present author (13) and was later improved and extended (14). The first treatment was carried out completely in the spirit of the continuum approximation and involved the assumption of dielectric saturation in both the diffuse layer and the inner monolayer of water molecules next to the electrode. In addition, compression of this monolayer under the high electric field in the inner region was included as well. Such electrostriction leads to a dependence of inner layer solvent number density on  $\sigma_m$ . A defect of this kind of approach, however, beyond its neglect of discreteness effects, is the presence of several semi-macroscopic parameters, applied to a microscopic situation, along with the necessity of determining some parameter values from the data themselves rather than from other independent measurements. Nevertheless, good fitting results were obtained using physically reasonable parameter values, shedding some light on inner layer behavior. The separate effects of dielectric saturation and layer compression are illustrated in Fig. 5, as well as the overall fit obtained for cathodic polarization when both effects are present.

The approach of Ref. 13 was improved in various ways in Ref. 14 and fitting carried out for a variety of temperatures. An important improvement over the earlier phenomenological calculations of inner-layer dielectric saturation was the treatment of the dielectric behavior of the inner layer in a somewhat more discrete fashion by approximating the water molecules as point dipoles able to rotate continuously under the influence of the effective electric field. But only average dipole behavior was treated, still a cm. In addition, imaging of dipoles in the electrode (single imaging) or in the electrode and the diffuse layer (infinite imaging, also called conductive-conductive imaging) was considered, as well as the presence of a "natural" field causing the dipoles to line up more in one direction than others even in the absence of applied fields (i.e. at the ECM potential,  $\psi_m = V_0 = 0$ , the point of zero electrode charge, PZC). Some possible sources of this field have been discussed in Refs. 6 and 14, and the presence of such a natural field or potential has often been independently suggested since the earlier work (e.g., 19,20).

A weakness in the Ref. 14 inner layer model is its neglect of dipole-dipole interactions; in addition, the assumption of arbitrary dipole orientations may be less realistic in some real situations than the assumption that only a few orientations are possible. These matters will be discussed further below. In spite of the model's apparent weaknesses, it yielded excellent agreement with Grahame's data, better overall than that of any later treatments. Results are presented in Figs. 6 and 7; here curves for different concentrations have been successively displaced for clarity of presentation. The effects of some of the main physical processes included in the model are summarized in Fig. 8. The discrepancies apparent at appreciable positive potential

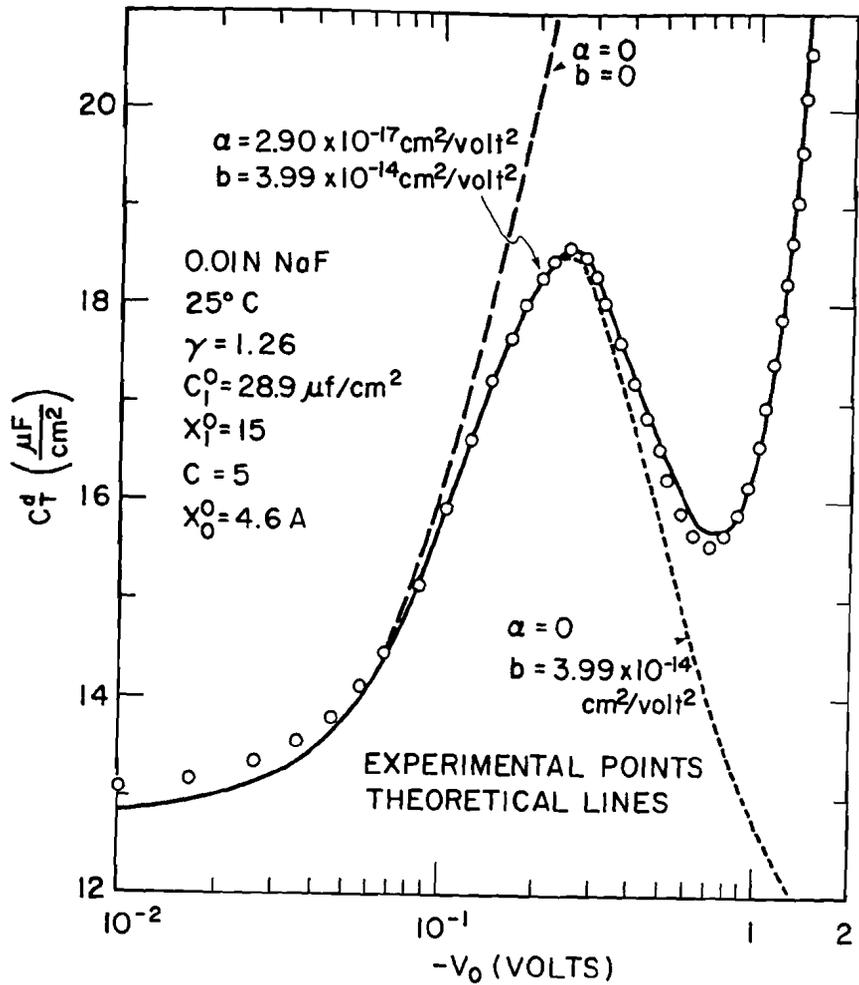


FIGURE 5

Comparison of Grahame 25°C NaF  $C_d^T \equiv C_T$  results with continuum theory, showing effect of no compression and no dielectric saturation ( $\alpha = b = 0$ ), no compression ( $\alpha = 0$ ), and saturation and compression both present (13).

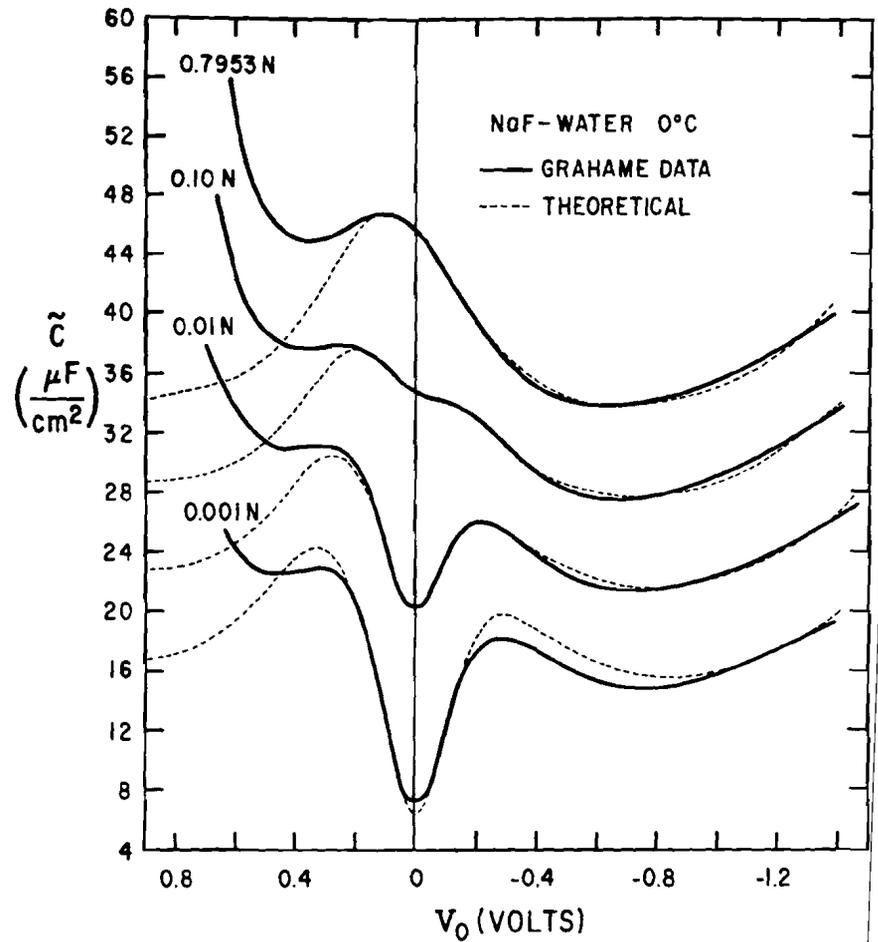


FIGURE 6

Comparison of Grahame 0°C  $C_T$  results with continuum theory (Reprinted with permission, 5; 14).

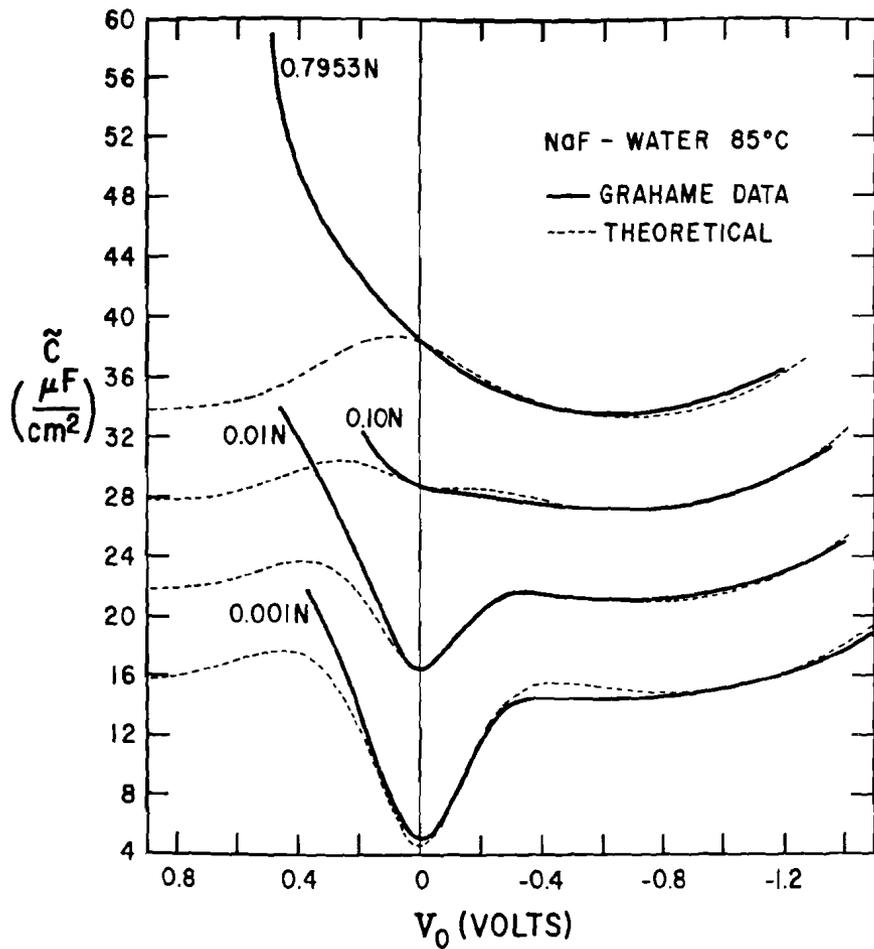
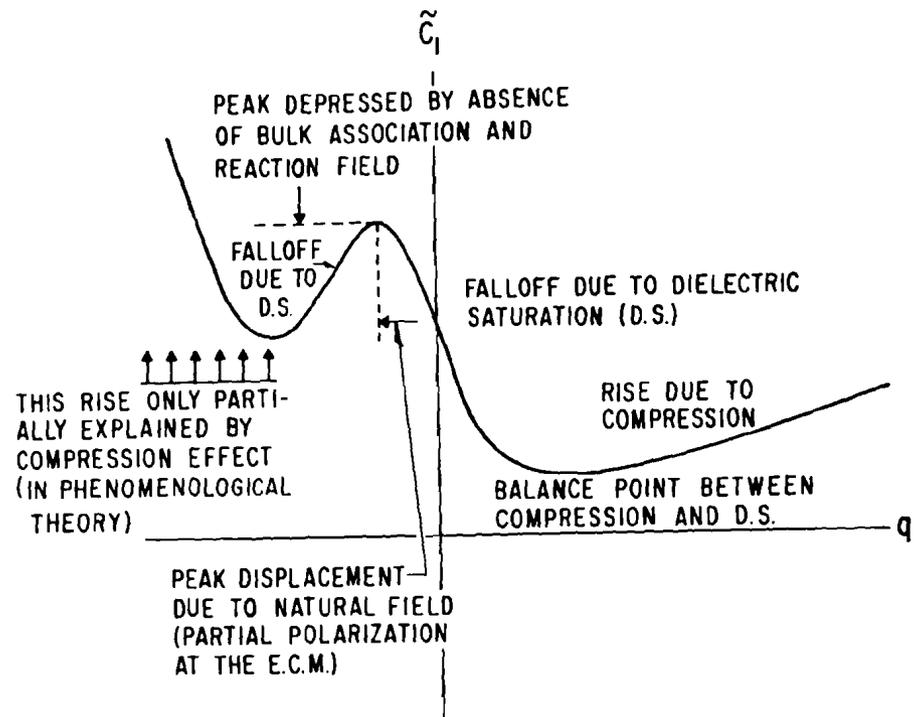


FIGURE 7

Comparison of Grahame 85°C  $C_T$  results with continuum theory (Reprinted with permission, 5; 14).



### PHENOMENA INFLUENCING DIFFERENTIAL CAPACITANCE

FIGURE 8

Summary of main phenomena influencing  $C_T$  in the continuum theory (1).

differences (p.d.'s) may arise from the presence of specific adsorption of F ions, behavior not included in the theory.

#### b. Dipoles in the Inner Layer and the Cooper-Harrison "Catastrophe"

There have been many treatments of the inner region of the EDL which approximate it as a single layer of solvent molecules whose electrical effects are modelled by point dipoles with  $n$  orientational states allowed. We have already discussed the early  $n = \infty$  case (14), one which led to very good agreement with experiment over wide ranges of concentrations, temperatures, and applied potentials. At about the same time Watts-Tobin (21) independently treated the  $n = 2$  situation, although his comparisons with experiment were far less extensive. In addition,  $n = 3$  (22) (with the effect of surrounding dipoles replaced by a mean field) and  $n = 4$  (23) state models have been investigated. We shall not discuss these and other dipole models in depth because this has recently been done by Marshall and Conway (24), and by Marshall (25) in great detail.

One of the major problems in many of these studies, besides that of determining the most appropriate value of  $n$  to use, is how to take dipole-dipole interactions properly into account. One approach, an extension of the  $n = \infty$  theory discussed above, includes both induced and permanent dipole moments (no explicit dielectric constant introduced) and treats interactions approximately but self-consistently by means of a modified cutoff disk method (to be discussed below for the specific adsorption case), including some dipole imaging (6, 26, 27). Mean field and other approximate statistical mechanical treatments of interaction have been used by some, but Schmickler (28), in connection with a recent investigation of models with different  $n$ 's and of a cluster model, concluded that "the strength of the dipole-dipole interaction precludes the use of simple approximations like the mean field approximation" (29). Further, he found, on the basis of an approximate Monte Carlo treatment of a monolayer of point dipoles, that the  $n = \infty$  model with exact dipole interactions for nearest neighbors and mean field interactions beyond, was much superior to those with  $n = 3$  and  $n = \infty$  with more approximate interaction relations (29).

In 1975 Cooper and Harrison (30) pointed out that the  $n = 2$  dipole model could lead to non-physical negative differential capacitance values for reasonable values of the relevant parameters of the model. Much attention has been directed since then at this Cooper-Harrison catastrophe (CHC, 31), and numerous papers have been devoted to discussing and even explaining it. It has been ascribed, for example, not to an incorrect method of calculation but instead to the approximation of real molecules as point dipoles (28). Another recent paper concludes that the CHC is avoided if the dipole-dipole coordination number is greater than 14.5 (32)! Nevertheless, the CHC is a non-problem, a pseudo catastrophe arising from an error in elementary

electrostatics. Again we need not discuss the matter in detail because that has recently been done, for various values of  $n$ , by Marshall and Conway (24). Here it is sufficient to summarize and extend their conclusions somewhat.

These authors have pointed out that the CHC disappears, for all the models considered, when (i) calculations ensure the continuity of dielectric displacement across the electrode/inner-layer interface; when (ii) dielectric displacement continuity is maintained across the inner-layer/solution interface; and when (iii) continuity of the potential is ensured between the inner layer and the solution. Although Marshall and Conway point out that the  $n = \infty$  treatment of Macdonald and Barlow (14) does not involve a CHC because the proper continuities are maintained, they did not mention that this was also the case in even the 1954 phenomenological treatment of the EDL by the present author (13). The matter may be closed, hopefully for good, with the following quotation from the Marshall thesis (25, p. 27), "The importance acquired in the literature by the catastrophe since publication of ref. 16 [the present Ref. 30] suggests that Cooper and Harrison and subsequent authors were unaware of the purport of the earlier work of Macdonald and Barlow (14)."

#### 2. Specific Adsorption

Consider Fig. 2 once more. Since the use of a dielectric constant (a semi-macroscopic concept) at all in a microscopic region is a considerable approximation, it is usually scarcely worthwhile to distinguish between the quantities  $\epsilon_\beta$  and  $\epsilon_\gamma$  of Fig. 2. If one does not and takes their common value as  $\epsilon_A$ , then  $C_\beta = \epsilon_A/4\pi\beta$  and  $C_\gamma = \epsilon_A/4\pi\gamma$ . Although these quantities should depend somewhat on  $\sigma_m$ , they are often taken independent of it in specific adsorption calculations. Even when they are dependent on  $\sigma_m$ , however, if they are taken as differential capacitances it turns out that a fully self consistent expression for the total differential capacitance associated with the Fig. 2 model is possible (16). Although this treatment has been explicitly developed for the aliovalent ionic single crystal situation (e.g., for AgBr), it applies as well to the liquid electrolyte case with suitable redefinition of the quantities involved (5).

The analysis first yields the more or less conventional expression (33),

$$C_T^{-1} = C_\beta^{-1} + C_\gamma^{-1} + C_{dl}^{-1} + (C_\gamma^{-1} + C_{dl}^{-1}) (d\sigma_s/d\sigma_m), \quad (2)$$

one often presented without the  $C_{dl}^{-1}$  terms. Here  $C_{dl} \equiv -d\sigma_d/d\psi_d$ . But the ratio  $(d\sigma_s/d\sigma_m)$  may be expressed as

$$(d\sigma_s/d\sigma_m) = (C_\beta^{-1} - C_T^{-1})C_A, \quad (3)$$

where  $C_A \equiv -(d\sigma_s/d\psi)$ . The presence of the  $C_T^{-1}$  term in (3) provides a feedback factor. When Eq. (3) is substituted in (2) and the result solved for  $C_T^{-1}$ , one finds that the overall differential capacitance  $C_T$  is exactly represented by the simple electrical circuit of Fig. 9, a result necessarily contingent on the applicability of the Fig. 2 model but nevertheless not well known in the electrochemical area. When one assumes that the work of adsorption does not involve the transport of the ion to be adsorbed through the diffuse layer,  $C_A$  may be defined as  $-\sigma_s/d(\psi_s - \psi_d)$ . One then finds  $C_T^{-1} = C_B^{-1} + (C_A + C_Y)^{-1} + C_{dl}^{-1}/[1 + C_A C_Y^{-1}]$ , a result which does not lead to a simple equivalent circuit made up of capacitors in series and parallel like that of Fig. 9.

To apply the Fig. 9 circuit self-consistently, one must also use the simple equations which follow from ordinary electrostatics with continuity of dielectric displacement and relate  $\epsilon_m$ ,  $\sigma_s$ ,  $\sigma_d$  and  $\psi_m$ ,  $\psi_s$ ,  $\psi_d$  (16). In addition one must introduce an adsorption isotherm,  $\sigma_s(\psi_s)$ , which relates the amount of (average) adsorption to the (average) local potential at the IHP and so yields an expression for  $C_A(\psi_s)$ . Finally, some model of the diffuse layer must be used to provide an expression for the potential-dependent diffuse layer differential capacitance  $C_{DL}(\psi_d) \equiv C_{dl}$ . Some specific choices for these sub-models will be discussed in the next section. Note that it is unnecessary to iterate to obtain full self-consistency for the Fig. 9 circuit if one considers  $\psi_d$  as the known variable (16). It is worth emphasizing that Fig. 9 shows that it is improper to take  $C_B$  and  $C_Y$  in series electrically when  $C_A$  is non-zero, as has sometimes been suggested. The requirement of self-consistency in the present approach clearly leads to a more complex situation. When an expression for  $C_{dl}$  is available, comparison of experimental  $C_T$  data with Fig. 9 circuit predictions should allow  $C_A$  to be calculated as a function of  $\sigma_m$  or  $\sigma_s$ . Such results, in turn, may then be used to calculate the adsorption isotherm  $\sigma_s(\psi_s)$ .

### B. Discreteness and Ion Size Effects

In this section I shall discuss EDL approaches and models where the discreteness of ions and, later, solvent molecules is recognized and at least partly accounted for. In such treatments the finite size of these entities is not wholly neglected as it is in say the GC model. In the most discrete of the models to be considered, the nm, where the ions and molecules can move freely under the influence of their mutual interactions and a field arising from charge on the electrode, no explicit inner layer needs to be introduced. In the most general treatment, instead of using a separate, often ad hoc, adsorption isotherm, which may or may not be appropriate, the absence or presence of adsorption should be a consequence of the basic general equations governing the ensemble.

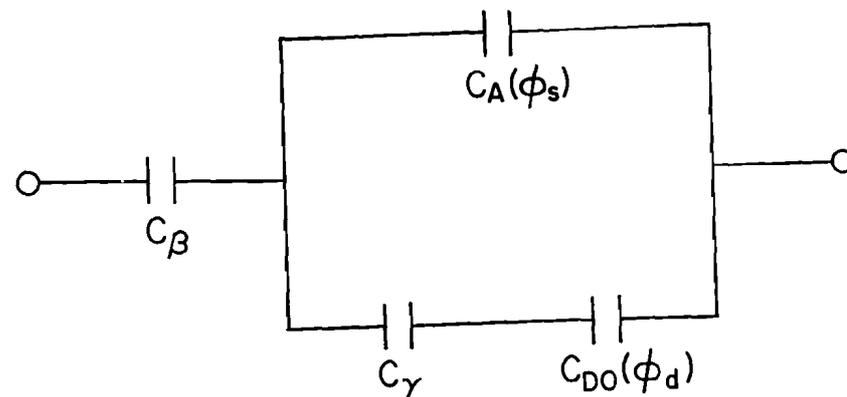


FIGURE 9

Exact equivalent circuit for  $C_T$  associated with the model of Fig. 2 (16). Here  $\phi \equiv \psi/V_T$ , where  $V_T \equiv kT/e$ , the thermal potential. In addition,  $C_{DO} \equiv C_{dl}$ .

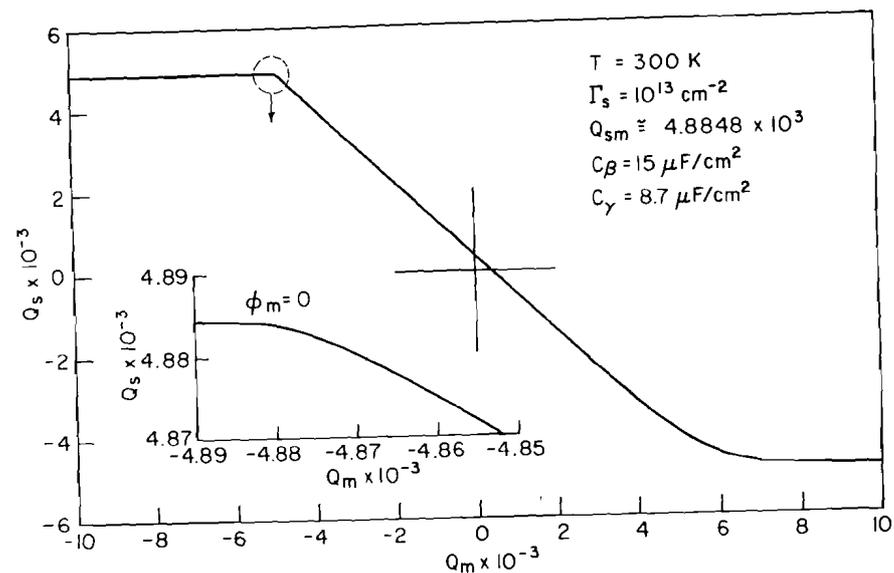


FIGURE 10

Adsorption isotherm for the 1gm;  $Q_s$  and  $Q_m$  are normalized adsorbed charge and charge on the electrode, respectively (16).

### 1. Three-dimensional Lattice-Gas Model

One approximate way to take some account of finite ion size is to require that mobile charges only occupy sites of a three-dimensional lattice whose lattice parameter is determined by the effective diameter (6, p. 97) of the ions (usually taken the same for cations and anions). Such lattice gas models (lgm) have proved useful for liquids even though they involve more order than actually present. Intuitively, one might expect the lattice to approximate the close packing of ions which tends to occur near the electrode in liquid electrolytes at high applied fields and to have little or no effect far from the electrode where charge density is low.

A lgm has been developed and applied primarily to aliovalent alkali halide single crystals (16), a situation for which the lattice assumption is fully warranted. It involved "noninteracting" lattice gas statistics for the mobile charges. Thus the only interactions between them arise from the constraint that they can only occupy available sites. Each site is therefore either "empty" (filled with a solvent molecule) or is occupied by a positive or negative entity. Except for this constraint, this lgm is essentially a cm since it involved  $\epsilon_B$ , rather than the discrete electrical effects of the individual solvent molecules, except in the inner region (see Fig. 2 and 9). It can be applied as an approximate model for the EDL even for liquid electrolytes and includes the possibility of specific adsorption arising as an integral part of the analysis. For comparison, note that the GC theory is that of an ideal gas model (igm), one involving non-interacting charge carriers of infinitesimal size.

It is interesting to note that the lattice gas statistics of the above treatment lead to an expression for average ionic concentration as a function of the average potential at the point in question which may be identified as a three-dimensional Langmuir isotherm (16). In addition, the analysis assumes that there are a limited number of single-occupancy surface lattice sites available for ions (specific adsorption sites in the liquid electrolyte situation). Then free energy minimization yields an adsorption isotherm of exactly the form of the usual two-dimensional Langmuir isotherm. Under reasonable conditions the dependence of  $\alpha_s$  on  $\psi_s$  is of the tanh form, essentially the same form as the polarization charge of the two-state model of point dipoles in the inner layer (24). Thus the possibility of confusion should not be overlooked. When the lgm results are used to quantify the elements in the Fig. 9 circuit,  $C_T$  may be readily calculated. Thus far, however, calculations and results have been presented (16) which are most appropriate for the single crystal case rather than for aqueous electrolytes. It is worth mentioning, however, that without the separate introduction of a natural field, adsorption is not zero at the PZC and a large region is found where  $\alpha_s$  depends linearly on  $\alpha_m$ , as illustrated in Fig. 10.

### 2. Specific Adsorption and the Modified Cutoff Disk Method

Thus far we have considered  $\psi_s$ , the potential which is associated with specific adsorption at the IHP, to be an averaged, local potential. But it has long been recognized (e.g., 34,35) that the actual potential which "produces" adsorption is that at the adsorption position in the absence of the adion itself, a micropotential. A great deal of effort has been devoted to calculations of such quantities as the micropotential, which are associated with charge discreteness, and the area was reviewed through 1966 in Ref. 6. More recent work, particularly on specific adsorption, has been recently discussed by Marshall (25). When the micropotential, rather than the average potential, is used in an adsorption isotherm such as that discussed above, more realistic results will be obtained. One approximate method of micropotential calculation is the use of the Grahame cutoff disk model (gcdm,36). Charge adsorbed in the IHP is taken averaged, and a disk of radius  $r_0$ , centered at the adsorption position, is taken free of charge, with  $r_0$  determined by charge conservation. The potential at the center of the disk, an approximation for the micropotential, is then relatively readily calculated, even in the presence of single or infinite imaging.

In the more accurate modified cutoff disk method (mcdm,6,27), the radius of the disk,  $r_b$ , is taken to be a more complicated function of adion number density than in the Grahame case. This allows the approach to yield virtually exact micropotential estimates in the two limiting occupancy regions: that where the adions are sufficiently close to each other that Coulomb repulsion ensures that they lie on a hexagonal array, and that where they are so far away from each other on the average that they may be taken as moving independently and are randomly ordered. Thus tedious lattice sum calculations are avoided.

Results for the normalized mcdm radius,  $R_b \equiv r_b/\beta$ , vs. the normalized hexagonal array nearest neighbor distance,  $R_1 \equiv r_1/\beta$ , are presented in Fig. 11 for a particular situation. Since no accurate values of  $R_b$  are available in the transition region, several empirical bridging curves are shown; of these curves  $b$  is probably most appropriate. Future Monte Carlo studies should allow this part of the curve to be well determined. Note that  $R_b$  is temperature dependent; in particular, the  $R_1$  values where the transition region begins and ends depend directly on temperature. The dashed line in the figure, the normalized Grahame prediction, is clearly much less accurate over the available occupancy region than is that of the mcdm. In recent work on the depolarization of adions arising from their neighbors in a plane (37), the gcdm and lattice sum calculations were separately employed to calculate the micropotential instead of using the simpler mcdm approach.

A serious, largely unsolved problem with usual micropotential calculations in the liquid electrolyte area, including those discussed above, is that it is likely to be a poor approximation to represent the solvent molecules in the neighborhood of adions by

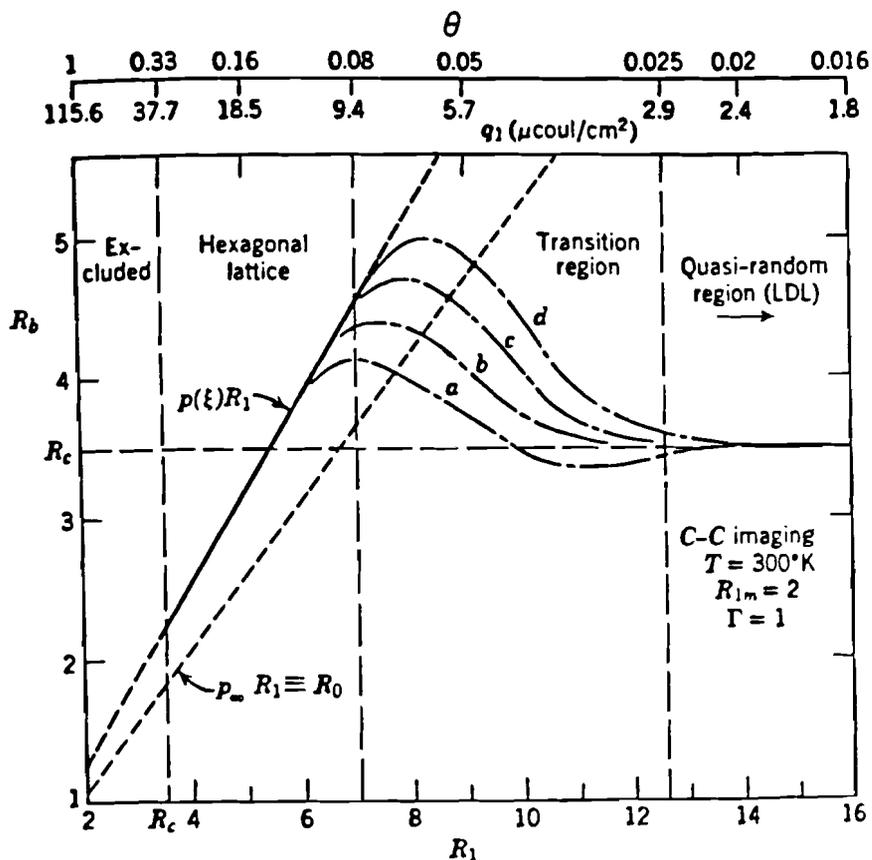


FIGURE 11

Normalized disk radius,  $R_b$ , vs. normalized hexagonal lattice spacing,  $R_1$ , for the modified cutoff disk method. Quantities normalized with the distance  $\beta$  (Reprinted by permission of John Wiley & Sons, Inc., copyright © 1967, 6).

just a small field-independent dielectric constant, as above, or even by one which decreases with increasing field. The discrete effects and interactions of both adions and solvent molecules in the inner layer should be simultaneously accounted for, with the molecules at least replaced by hard spheres with permanent embedded point dipoles. An approximate mean field calculation of these effects has been carried out recently by Marshall (25), but the results are unsatisfactory, probably in part because of the inadequacy of the mean field approach. Alternatively, some recent work (38,39) on adsorption isotherms has considered dipole effects and adion interactions more from a continuum standpoint. Incidentally, when the adsorption capacitance  $C_A$  is defined as  $-\sigma_s/d\psi_i$ , where  $\psi_i$ , the micropotential, is used in place of the average potential  $\psi_s$ , the simple Fig. 9 circuit for  $C_T$  still applies, with an effective  $C_A$ , when the micropotential parameter  $\lambda$  (6) is taken charge independent.

### 3. Discrete Primitive Model and Electron Overlap

In this model the ions are represented by charged hard spheres, the solvent as a medium of uniform dielectric constant  $\epsilon_s$ , and no inner layer is included. The model thus applies only to the diffuse region of the EDL and is more applicable to fused salts, and possibly solids, than to liquid electrolytes. It has been analyzed in recent years through the use of sophisticated statistical mechanics, often involving complicated, though approximate, integral equations in an attempt to account properly for ion-ion interactions. Recent reviews (8) contain summaries of the approaches and references to much of the work in the field. Unfortunately, because of the complexities of the analysis it has generally been impossible to extend results to the region of large electrode charges and applied potentials. The results of the various theories, all using  $\epsilon_s = \epsilon_B$  (taken as 78.5 for water at  $T = 298$  K), have been compared with Monte Carlo simulations of Torrie and Valleau (40,41). These comparisons show that while the gcm is relatively poor, good fitting is found for several of the statistical theories, at least over the limited range for which they yield results. Henderson (8) has pointed out, however, that the present model is mainly of theoretical interest because it is insufficiently realistic.

Recently the quantum mechanical nature of the conductive properties of the metal electrode used in EDL experiments has been recognized and taken into account explicitly (8,19,42,43). The main effect is electron spillover from the metal into the solution, with such spillover being slightly sensitive to the direction of the field in the region next to the electrode (43). Because of spillover the effective ESP lies in front of, rather than behind, the physical surface of the electrode. For the inner layer picture, such overlap thus causes the thickness correction,  $d_p$  of Section IIA, to be negative rather than positive. The theory is complicated, approximate, and involves several parameters, but its results indeed lead to better agreement with experiment than if  $d_p$  is taken zero or positive (8).

#### 4. Modified Lattice-Gas Model

A model also applicable only to the diffuse region, like that above, is obtained if we add mean field corrections to the diffuse region solution obtained from the lattice-gas model of Section IIB.1. To do so, we add pair interaction energy terms of Coulomb form to the free energy of the lattice gas system and then minimize (44-46). These terms involve a dimensionless parameter  $\alpha$  which measures the strength of the interaction. It is positive for repulsion between charges of the same sign, and its presence renders charge calculations implicit, requiring iterative solution. Fig. 12 shows results for several values of  $\alpha$  compared to both the gcm and the Monte Carlo results mentioned above. The dotted vertical line marks the limit over which the dpm discussed above has been compared for the same one molar situation. Clearly, this model has not been tested against the Monte Carlo results over much of their range. On the other hand, the present model, marked LLGM in the figure but designated mlgm hereafter, yields excellent agreement over the full available range when  $\alpha = -3$ , agreement to better than a single standard deviation of the simulation results. The mlgm is also far simpler to use than any of the free-ion statistical approaches of the dpm, yet applies even up to the saturation region. As Henderson (8) has remarked, finite-size ion packing effects become important even when the packing is only about a tenth that of a close-packed monolayer. Although the mlgm is more averaged than the dpm, it seems much superior for use in the diffuse region if one assumes that the Monte Carlo results in fact well represent the actual situation there.

The magnitude of  $\alpha$  found above is far smaller than that for full Coulomb interaction because most of the necessary Coulomb interactions have already been implicitly incorporated in the solution through the local satisfaction of Poisson's equation. The negative sign of  $\alpha$  implies, in fact, that Poisson's equation slightly overcompensates the interaction, requiring the addition of a small residual attraction between ions of like sign (44). Fits have also been carried out between the present model and Monte Carlo results for  $M = 0.1$  and  $0.01$  as well as the present  $M = 1$ . Although there are fewer simulation results available for the lower concentrations, good fits were also obtained for these molarities with  $\alpha = -3$ , independent of concentration as expected from mean field theory, but such fits required that the basic lattice spacing parameter of the model increase slightly with decreasing concentration. These results thus suggest that the approximation of a fluid situation by a lattice model is improved by an increase in lattice step size at low concentrations.

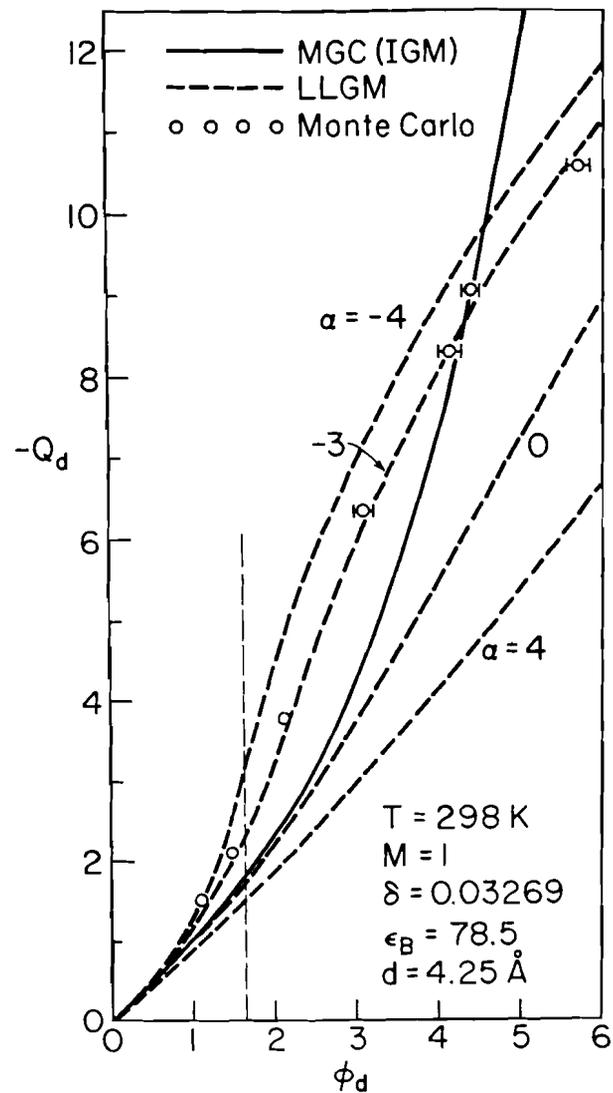


FIGURE 12

Normalized diffuse double layer charge density vs. the normalized potential difference across it (44). Potential normalized with  $V_T$ .

### 5. Non-Primitive Model

In this fully discrete model (the nm), the ions are taken as charged hard spheres and the solvent molecules also as hard spheres but with embedded permanent point dipoles. The dipoles are assumed to be fully orientatable, the  $n = \infty$  situation. No explicit inner layer region is included, or needs to be included, in this model. Unfortunately, no simulation results for this system exist, probably because of the strong interactions present which are not reduced by the factor  $1/\epsilon_s$  as they are in the pm. Although this is possibly the most realistic model thus far considered for the EDL, it is still appreciably idealized. In particular, the actual steric interactions in a real system are more complex than those represented by hard spheres; point rather than more realistic finite-length dipoles or multipoles are considered; no induced polarization of molecules and ions is included; specific adsorption is not included; and no imaging is present.

Recent work on the nm has been discussed and summarized by Henderson (8). The statistical mechanical problem presented by this model is very difficult, even when all interactions are not included and a linear approximation is employed. Even under these conditions, Henderson (8) has stated that the solution is "hopelessly implicit." Thus far, results have only been obtained for low concentrations at the PZC. These results are in good agreement with experiment at this point when a negative  $d_p$ , ascribed to electron spillover, is included. In view of the complexity of the model, its remaining idealizations, and the presence of very few disposable parameters, this is indeed a substantial achievement.

### 6. Some Layered Lattice Gas Models

The lg and mlg models are only pertinent for single crystals when there are many crystal planes contained in a Debye length,  $L_D$ . Only then is it appropriate to include the averaging over microscopic regions implicit in the use of a differential equation such as the Poisson equation, a continuum approach. Similarly, for a liquid electrolyte these models will only be reasonable approximations when  $L_D$  is much larger than the ionic diameter, or lattice spacing when the lattice gas approach is used. But this condition is not necessarily satisfied for the local Debye length in a high-field region near an electrode where a very high concentration of ions of one sign is possible. It then becomes appropriate to replace differentials by differences and differential equations by difference equations, thus taking discreteness more into account.

The above considerations led to the development of layered lattice gas models (llgm, 45,47-50) for the EDL. Again a three-dimensional lattice, lattice spacing  $a$ , is employed with its (100) plane parallel to the electrode. Then the electrical effects of each plane in the lattice parallel to the electrode are considered individually,

with appropriate electrical continuity relations maintained from plane to plane. Each plane is thus treated as a two-dimensional lattice gas, and electrical conditions in every plane are closely coupled in an overall self-consistent way to those in adjoining planes (and so to those in all planes). Let  $\Delta \equiv a/L_D$ , where  $L_D$  is the bulk Debye length. It was found that for  $\Delta > 0.01$ , significant differences began to appear between the lg and llg models. Of course as  $\Delta$  approaches zero the two models approach full equality. In actual calculations with the llgm, double, nested iterations are needed to achieve self consistency. First, iteration is needed for each individual layer to find its self-consistent average charge and potential; then an overall iteration is carried out to ensure electroneutrality for the entire system. We generally extended this iteration until the local potential for the  $i$ th. layer was less than  $10^{-6}$  of the applied electrode potential, yielding a very good approximation to electroneutrality. Incidentally, an analytic solution with no iterations necessary applies in the weak field limit.

Three different llgm's have been developed. The first and simplest involved only ions in each plane, with the solvent represented by  $\epsilon_s$  in the usual pm fashion. It was found that this model could fit the Monte Carlo diffuse layer simulation results very well at all three available molarities without the need for the mean-field correction of the mlgm. Unfortunately, however, the parameters derived from the fits were somewhat anomalous (45). The second llgm model (47,48) represented an initial attempt to take the dielectric effects of the solvent molecules into account in a more realistic way. Their polarizability was represented by a small dielectric constant  $\epsilon_\infty$ , taken 6 for water, and the effect of their permanent dipole moments by an approximate continuum treatment of saturable finite-length dipoles. A statistical mechanical free energy minimization was carried out to determine the (average) occupancy of each lattice site by a positive or negative ion or by a molecule. Thus while the first llgm was primitive, the second presented a step toward a non-primitive model treatment.

Although no explicit charge-free layer of solvent molecules is necessarily present in any of the lgm's, they nevertheless inherently involve a small charge-free inner layer since the first plane of the lattice next to the electrode is a distance of  $r_i (= a/2)$ , or  $r_e \equiv r_i + d_p$ , away from the ESP. In this sense they are thus approximate theories of the entire EDL, not just the diffuse layer alone. It was found (48), however, that the second llgm nevertheless yielded appreciably too high  $C_T$  values at the PZC, as compared to experimental results (17,18), when the separation  $r_i$  was employed. Even worse results would be obtained if  $r_e$  were to be used with  $d_p$  negative because of electron spillover. On the other hand, excellent agreement with the data was found if  $d_p$  was taken as 0.29 A (with  $\epsilon_\infty = 1$ ), thus adding to the effective thickness of the inner layer. It is not entirely clear why additional thickness should be needed, but the causes are likely to be one or all of the following: intrinsic problems with the lattice gas approximation, inadequate treatment of the effects of the multipole moments of the

solvent molecules, and, most important, the presence of some solvated molecules between the ions nearest the electrode and the electrode itself.

The third 11gm (49,50) was developed to eliminate some of the approximations inherent in the second model. Solvent polarizability was handled either by the introduction of  $\epsilon_\infty$  or by the more discrete alternative of setting  $\epsilon_\infty = 1$  and taking the polarizability of the individual solvent molecules non-zero. The effects of the permanent multipole moments of the solvent molecules were approximated by actual orientatable finite-length dipoles with  $n = \infty$  and some interaction effects included, a discrete, and considerably more complicated, treatment. Again an inner region different from the rest of the material was needed for agreement with experiment at the PZC. Here, however, in keeping with the more microscopic and discrete character of the approach, we took the first layer of the 11gm as having finite-length dipoles with the bare dipole moment of water, rather than a higher value which would help account for cooperative effects and is used in the other planes to yield the proper dielectric properties of the bulk. Little difference in results was found at the PZC whether we took this first layer charge-free or allowed ions to compete with dipoles for site occupation.

One of the most interesting results of this third 11gm was that very little effective dielectric saturation is predicted as compared to more conventional treatments using continuum or point dipole approaches. In particular, it turns out that for the present finite-length dipole case it takes a field ten times or more higher to produce the same amount of saturation as that obtained with a smaller field in conventional approaches. To the degree that these results are applicable to real situations, they suggest that little dielectric saturation will occur in actual situations in the region near the electrode and that it can be completely neglected elsewhere.

Next it is of interest to present results of this treatment for the occupancy and saturation of the first layer of the full many-layer 11gm. Figure 13 shows, as a function of normalized applied potential and for two different molarities, how the occupancy of dipoles decreases and that of ions increases as the potential increases. Figure 14 shows, for a molarity of one and with a smaller permanent dipole moment than that used in Fig. 13, how the amount of saturation depends on potential for both the competing ions and the dipoles. Here  $Q_D$ , the effective normalized dipole charge, measures the effects of both orientation and dipole concentration, and  $Q_{max}$  is the maximum possible normalized charge density. For the experimental range of normalized potential, up to 10 or 20, neither the ions nor the dipoles are close to their maximum saturated values. Finally, it should be mentioned that several of the present 11g models have recently been compared (51) with a cut-off disk non-lattice-gas theory (52), a theory which attempts to unify inner layer and diffuse layer treatments. The third 11gm discussed above is more discrete and likely to be more accurate than such a

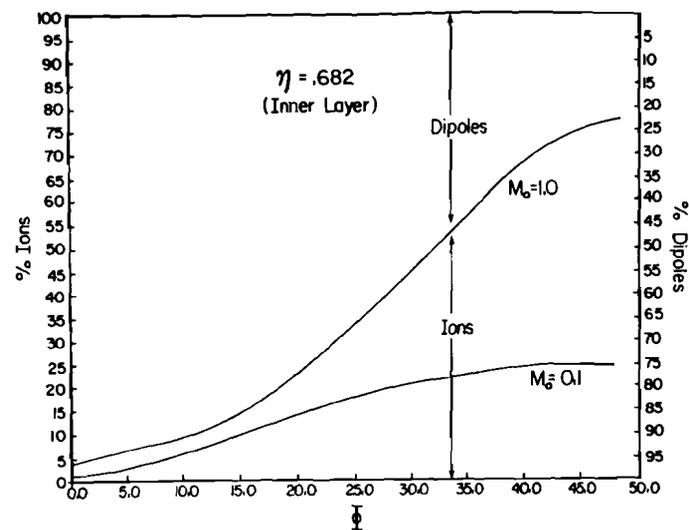


FIGURE 13

Competition for site occupancy following from the third layered lattice gas model (50).  $\phi$  is the potential difference between the electrode and infinity normalized with  $V_T$ .

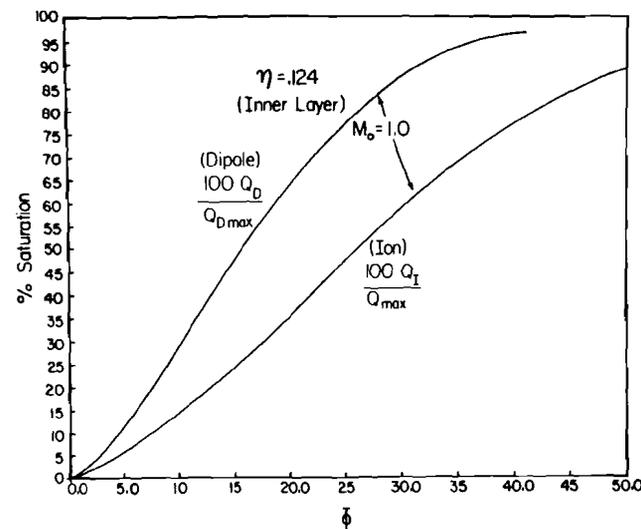


FIGURE 14

Ion and finite-length dipole saturation percentages as functions of  $\phi$  (50).

cut-off disk theory, and, in addition, it allows calculations to be made far away from the PZC, unlike the complicated integral-equation non-primitive models discussed in Section II.B.5.

### III. Impedance Spectroscopy and the Non-Equilibrium Double Layer

Here I shall discuss some aspects of the non-equilibrium steady-state response of systems containing an EDL. Although quasi-equilibrium measurements on EDL's with completely blocking electrodes yield primarily the total double layer differential capacitance,  $C_T$ , by itself, small-signal (s-s hereafter) AC measurements on EDL systems, which may or may not have blocking electrodes, yield much more information whether we like it or not, and we do like it when we can disentangle all the information available. The basic experiment is to apply a small sinusoidal potential difference to the system and measure the resulting current (or vice versa). The amplitude of the applied p.d. should preferably be less than the thermal voltage  $V_T \equiv kT/e$ . Sometimes a larger static p.d. is applied as well, but its presence greatly complicates the analysis of results, especially in unsupported situations. Measurements are carried out over as wide a frequency range as possible, often from  $10^{-4}$  Hz to  $10^6$  or  $10^7$  Hz using automatic measuring equipment, and the impedance (p.d. divided by current) or admittance (current divided by p.d.) is calculated at each frequency. Since there is generally a phase shift present between current and potential, there ratios are, by definition, complex quantities, and it is thus tautological to speak of "complex impedance" or "complex admittance" as is frequently done by many electrochemists.

Although there is nothing intrinsically new in the above approach, one that has been used in electrical engineering for seventy years or more, several new measurement and analysis elements have been added in recent years which make it far easier to carry out an experiment and to interpret its results. One such element is the development of automatic measuring equipment (3). The combination of the basic frequency response experiment and some or all of the new elements has come to be called Impedance Spectroscopy, abbreviated IS. In this section I shall first give a brief introduction to IS, with illustrations, then discuss some of its applications for solid and liquid systems. If one assumes, as I shall, that the experimental data are available, then it remains to present such data in a meaningful way and to analyze them so that maximum understanding of the material-electrode-interface response is gained.

#### A. Introduction to Impedance Spectroscopy

Only a relatively brief background on IS will be presented because a much more detailed introduction will soon be available (3). First, the word "impedance" in IS is a bit of a misnomer because in IS one deals not just with impedance but with four closely related functions which can be subsumed under the umbrella designation of

"immittances." Thus IS can also stand for Immittance Spectroscopy. The four functions are impedance,  $Z = Z' + iZ''$ ; admittance,  $Y = Z^{-1}$ ; complex dielectric constant,  $\epsilon = \epsilon' - i\epsilon'' = Y/(i\omega C_c)$ ; and complex modulus,  $M = \epsilon^{-1}$ . Here  $\omega$  is the angular frequency ( $\omega = 2\pi f$ );  $i \equiv \sqrt{-1}$ ; and  $C_c$  is the capacitance of the measuring cell in the absence of the material of interest. Although exactly the same fitting functions and mathematical models may be used for both intrinsically conducting systems and for intrinsically non-conducting dielectric systems (2), we shall only consider conducting systems here since they are more directly relevant to the response of even completely blocking EDL situations than are pure dielectric systems.

Figure 15 shows the main elements in an IS experiment. The ideal situation, which allows estimation of the values of microscopic quantities which characterize the material-electrode system in detail, is to analyze the data by fitting them to a detailed microscopic model of the system, one which yields an explicit expression for impedance as a function of frequency and predicts the temperature dependence of all parameters present. Unfortunately, few such models are currently available, even when they are derived using continuum approximations (linear differential equations). In the absence of appropriate models one tries to make do with an equivalent electrical circuit which lumps the main physical processes occurring into macroscopic circuit elements such as capacitances, resistances and distributed circuit elements (dce's). Even then there may still remain ambiguity about the most appropriate way the elements should be connected together (3,53). Such ambiguity may often be reduced or eliminated by carrying out IS experiments on the same system at several temperatures, electrode separations, pressures, oxygen tensions, etc. This matter will be discussed further later on.

For all systems of physical interest there are two basic circuit elements which always appear. There are the high frequency limiting geometric capacitance,  $C_g$ , and the high frequency limiting resistance of the system,  $R_\infty$ , the bulk or solution resistance. They are extensive quantities and are part of the bulk response of the system as opposed to its interfacial properties. As usual, I shall ignore the distinction between such quantities and their unit area values. The product  $R_\infty C_g \equiv \tau_D$ , an intensive quantity, is just the dielectric relaxation time of the system. When neither  $C_g$  nor  $R_\infty$  is distributed, they are frequency independent and the basic equivalent circuit involving them is that shown in Fig. 16-b. The impedance  $Z_s$  represents the response of all the rest of the system and is usually the quantity of primary interest. The 16-a circuit will be discussed later.

It is worth emphasizing that  $C_g$  always spans the electrodes, as shown in the figure (54). It is improper when  $Z_s \neq 0$  to just connect  $C_g$  in parallel with  $R_\infty$ , although this has often been done and frequently makes little actual difference to the analysis. In fact,  $C_g$  is usually entirely neglected in liquid electrolyte studies since it is generally

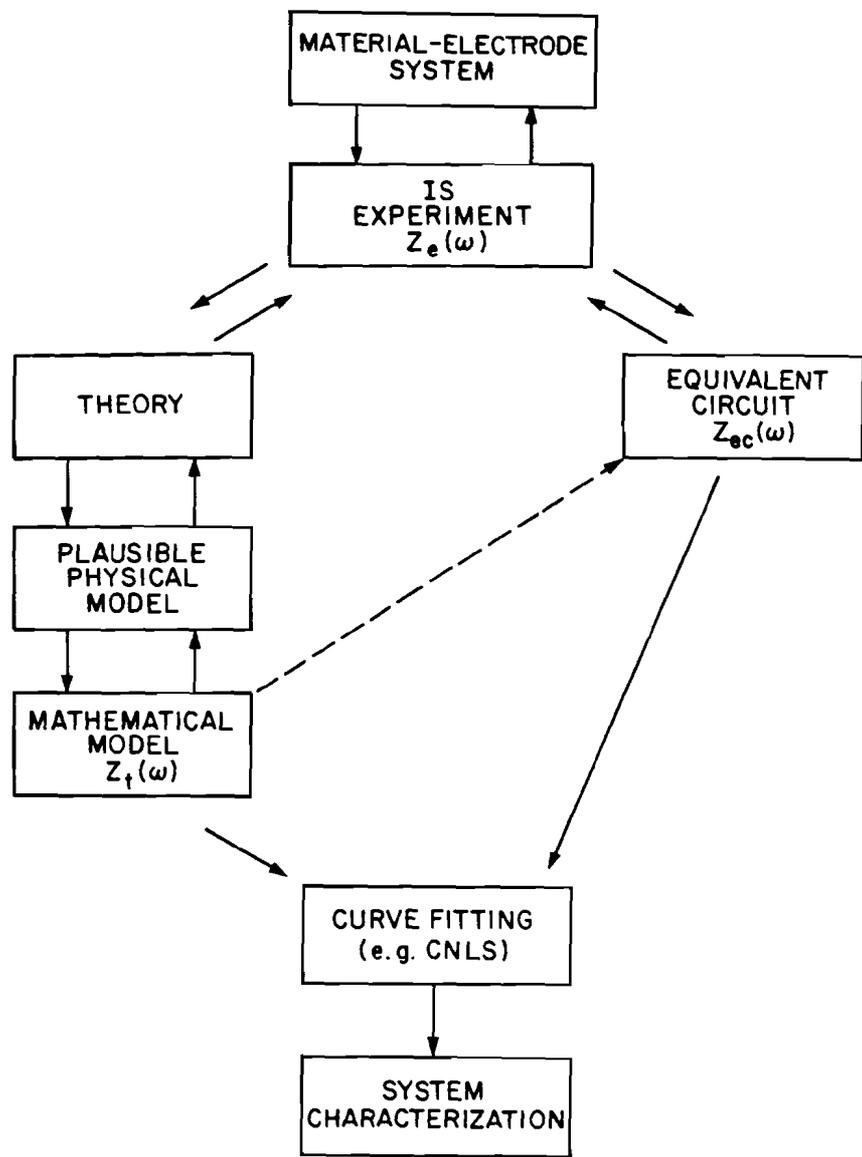


FIGURE 15

Flow diagram for the measurement and characterization of a material-electrode system (Reprinted by permission of John Wiley & Sons, Inc., copyright © 1987, 3).

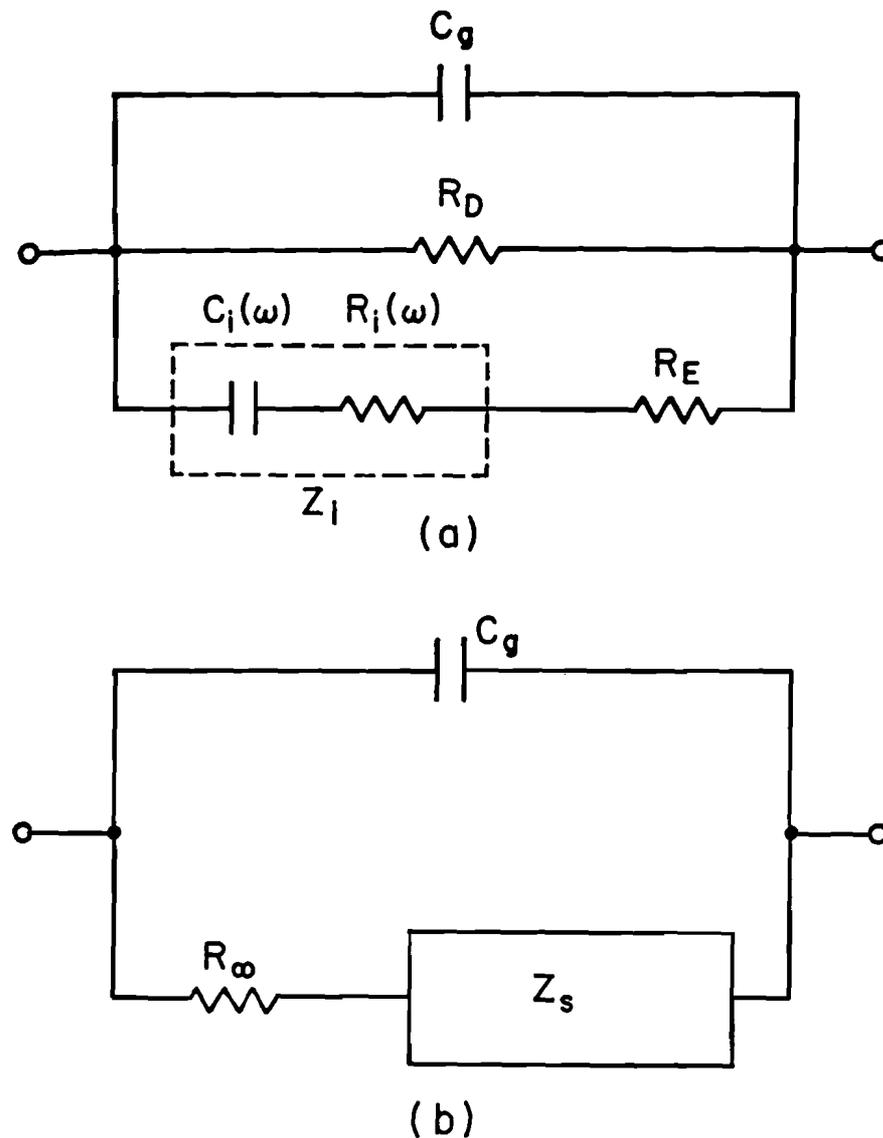


FIGURE 16

Two general equivalent circuits for the small-signal AC response of a material between two conducting electrodes (85). (a) Circuit used in early unsupported-system analysis. Here  $R_{\infty}^{-1} \approx R_D^{-1} + R_E^{-1}$ . (b) Circuit which separates out main bulk elements explicitly.

very much smaller than the double layer capacitance,  $C_{DL}$ . The  $C_T$  which is derived from quasi-equilibrium studies is actually  $C_g + C_{DL}$  when no adsorption effects occur, but it is virtually always identified as  $C_{DL}$ . In IS studies it proves important, however, to maintain the distinction between  $C_T$  and  $C_{DL}$ .

### 1. Presentation of Data

The proper presentation of data can be very helpful in indicating possible experimental errors and in suggesting the presence of various physical processes leading to the overall response. Because IS experiments often extend over a wide frequency range, it is usual to consider response as a function of the logarithm of frequency ( $f$  or  $\nu$ ) or angular frequency. One often sees plots of  $-Z''$  and/or  $Z'$  vs.  $\log(f)$ , or sometimes  $|Z|$  and/or  $\phi$  vs.  $\log(f)$  instead. Here  $\phi$  is the phase angle of the impedance;  $\phi \equiv \tan^{-1}(Z''/Z')$ . In the dielectric literature, plots of  $\tan(\phi)$  vs.  $\log(f)$  used to be common but are no longer.

One approach which is coming to be widely used is the plotting of  $\text{Im}(Z) = Z''$  (or  $-\text{Im}(Z) = -Z''$  in capacitive systems) vs.  $Z'$ , with frequency as a parametric variable. Such complex plane plots can be very instructive. Here, however, I wish to illustrate the usefulness of a further development in the presentation of IS data, the three-dimensional plot with perspective (55), an approach which shows the full data response in a single graph. The three dimensions of the plot are usually the real and imaginary parts of an immittance function and  $\log(f)$  or  $\log(\omega)$ . The alternative of using modulus and phase instead of real and imaginary parts is possible but usually turns out to be less useful. Finally, when the magnitudes of the immittance components vary by several orders of magnitude over the measured frequency range, as they often do in solid electrolyte studies, it proves useful to use logarithms of the real and imaginary parts in the 3-D plot.

Incidentally, many workers in the electrochemistry area use a nonstandard definition of impedance, one which amounts to writing  $Z = Z' - iZ''$  rather than  $Z = Z' + iZ''$ . Although this usage is convenient for systems which show capacitive rather than inductive response, it is an unwarranted redefinition of a long-established quantity. In order to avoid the hubris of Humpty-Dumpty in "Through the Looking Glass," a proper alternative is to write  $Z^* = Z' - iZ''$ , where  $Z^*$  is the complex conjugate impedance, and refer to the conjugate impedance in place of the ordinary impedance. When the proper definition of impedance is maintained, one may use any of the equivalent designations  $-\text{Im}(Z) = -Z'' = \text{Im}(Z^*)$  in plotting.

Figure 17 shows ordinary 3-D plots for the impedance of a simple equivalent circuit, typical of those often appearing in solid or liquid electrolyte IS studies (with  $C_g$  omitted). The two plots involve different viewing positions. The heavy line represents the full response and the other three curves its projections in the three planes. In

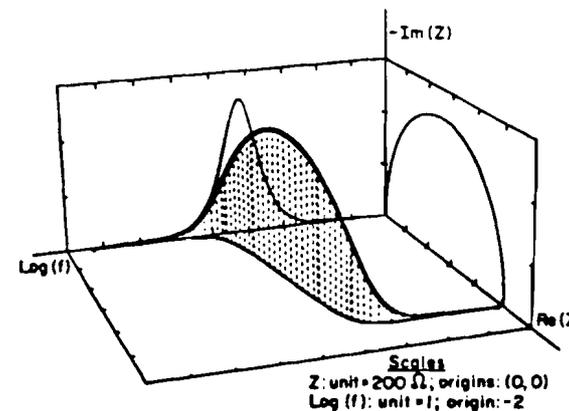
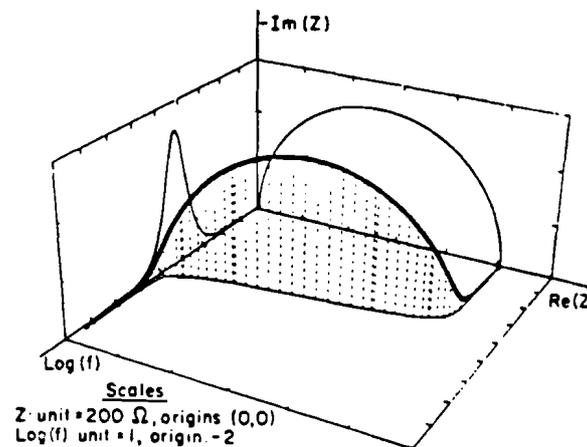
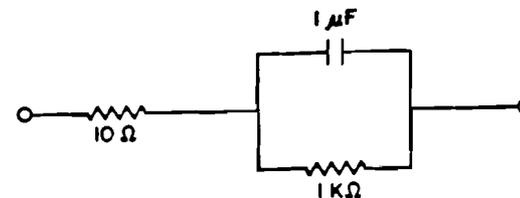


FIGURE 17

Simple equivalent circuit and two 3-D perspective plots of its response viewed from different directions (55).

addition to showing the full response, these plots thus include all three of the different 2-D plots commonly used in the past. Note that the two parallel elements in the equivalent circuit lead to a single time constant and thus to a semicircle in the complex plane, a common response shape. For even more realistic viewing, one could use a stereoscopic pair of 3-D plots.

Figures 18 and 19 illustrate the usefulness of 3-D plots in highlighting experimental errors in an IS study of the solid electrolyte Na  $\beta$ -alumina (56,57). The main response curve and the complex plane projection curve in Figure 18 show that the lowest frequency data point is inconsistent with the rest of the response. But note that the projections in the other two planes, the most common sorts of plots in the past, show no trace of this error! Their use alone, as in the original data analysis (58), thus gives no clue to the presence of the error. Now the complex modulus function,  $M = i\omega C_c Z$ , weights the higher frequency data points more heavily than the lower frequency ones. Since many higher frequency points in Fig. 18 are not well resolved with the scale used, a modulus 3-D plot seems desirable.

Figure 19 shows that such a plot allows one to identify the same low-frequency error discussed above and to discover two new problems in higher frequency regions. Here one sees a curving back at the highest frequencies which is not theoretically likely and thus suggests the presence of measurement errors in this region. In addition, the bad glitch at somewhat lower frequencies arose because of the shift during the measurements from one type of measurement apparatus to another, evidently without adequate cross calibration in an overlap region. Here only the low frequency error shows up in the conventional projection plot of  $M''$  vs.  $\log(f)$ .

These results underline the desirability of constructing 3-D plots, preferably of all four immittance functions, before any data analysis is carried out. With modern computer-controlled plotting, such plots are readily produced. Of course if bad points show up, measurements should be repeated. If that is impractical, outliers should either be eliminated or weighted weakly, and possibly mild smoothing should even be used (3).

## 2. Complex Nonlinear Least Squares Data Analysis

Even the most complete data presentations are only suggestive of the processes occurring in the system investigated; a complete characterization requires that some kind of a comparison be made between the data and a theoretical model and/or reasonable equivalent circuit, as depicted in Fig. 15. In the past various graphical and/or simple mathematical fitting procedures have been carried out, often involving subtractive calculations, which can be very inaccurate. Further, these approaches generally do not analyze all the data simultaneously, and they usually yield parameter estimates without any uncertainty measures. An approach which avoids these difficulties and has great resolving power as well is that of complex nonlinear

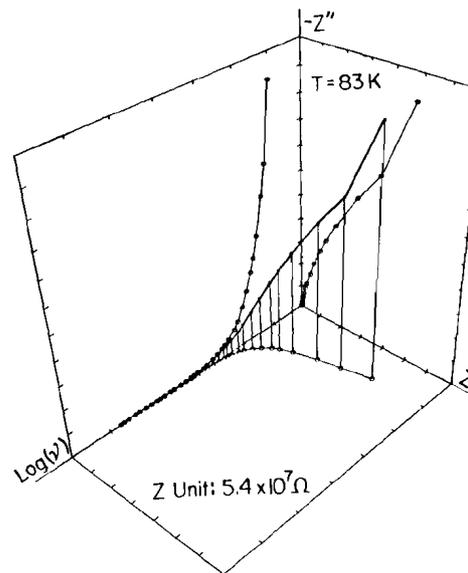


FIGURE 18

Three-dimensional perspective plot of 83 K Na  $\beta$ -Alumina impedance data (56-58).

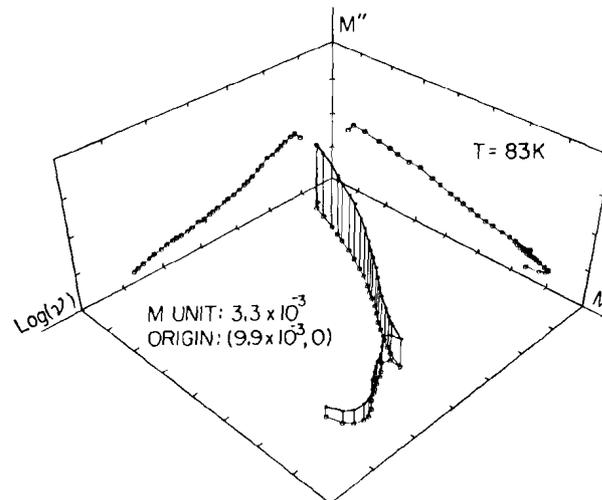


FIGURE 19

Three-dimensional perspective plot of 83 K Na  $\beta$ -Alumina complex modulus data (56-58).

least squares (CNLS) data fitting (59). Here all the real and imaginary data values (or the modulus and phase values) are fitted simultaneously by weighted, nonlinear least squares to a model or equivalent circuit, determining the best-fit estimates of all the free parameters, as well as first-order estimates of their standard deviations. The latter results are an essential part of the analysis since they indicate which parameters are well determined and which, if any, should be eliminated.

An illustration of the accuracy and resolution of CNLS fitting is presented in Fig. 20. Here the lumped-constant circuit shown was constructed using actual elements whose values, listed at the top, were separately measured at a few frequencies. The admittance of the full circuit was then measured with IS for many frequencies between 0.4 and  $10^4$  Hz. Three-D impedance and admittance plots are presented in the figure and show little resolution of the two main time constants of the system. CNLS led to a very good fit of the data, however, as well as the parameter estimates and standard deviations shown in parentheses. These values agree excellently with the individually measured ones and are, in fact, probably more accurate (55,59).

Finally, Fig. 21 shows a 3-D plot and the results of a CNLS fit of data obtained from IS measurements on the solid electrolyte  $\beta$ -PbF<sub>2</sub> with platinum electrodes. Although the circuit is rather similar to that of Fig. 20, the response is of very different character, primarily because of the needed presence in the circuit of the impedance  $Z_D$ , a constant phase element (CPE), a dce. Such elements will be discussed in the next section. The small values of the relative standard deviations of the parameters obtained from the fit show that it was a good one and that all the parameters present were needed. The heavy dots in the 3-D plot are the original data points while the fit predictions are shown by solid triangles. The projection lines from these points down to the bottom plane begin to show slight discrepancies (because of imperfect fitting) at the lowest frequencies, indicating that the circuit cannot represent the data perfectly in this region. Note that seven parameters have been well estimated here. Good estimates of even more parameters can be obtained from CNLS fitting when data extend over a sufficiently wide frequency range.

There are two further sources of possible ambiguity in CNLS fitting. First, a fit may involve only a local minimum rather than the absolute least squares minimum. This problem becomes worse the larger the number of parameters to be determined in a nonlinear least squares fit, but it can nearly always be circumvented by carrying out the fitting several times with very different initial values for the parameters. If the final parameter estimates are the same in all such fits, it is likely that the true least squares solution has been obtained.

Second, it is not always obvious what kind of weighting to use. In the absence of weights derived from replicating the experiment a number of times, unity weighting (UWT) or proportional weighting (PWT - the uncertainties of the components are taken

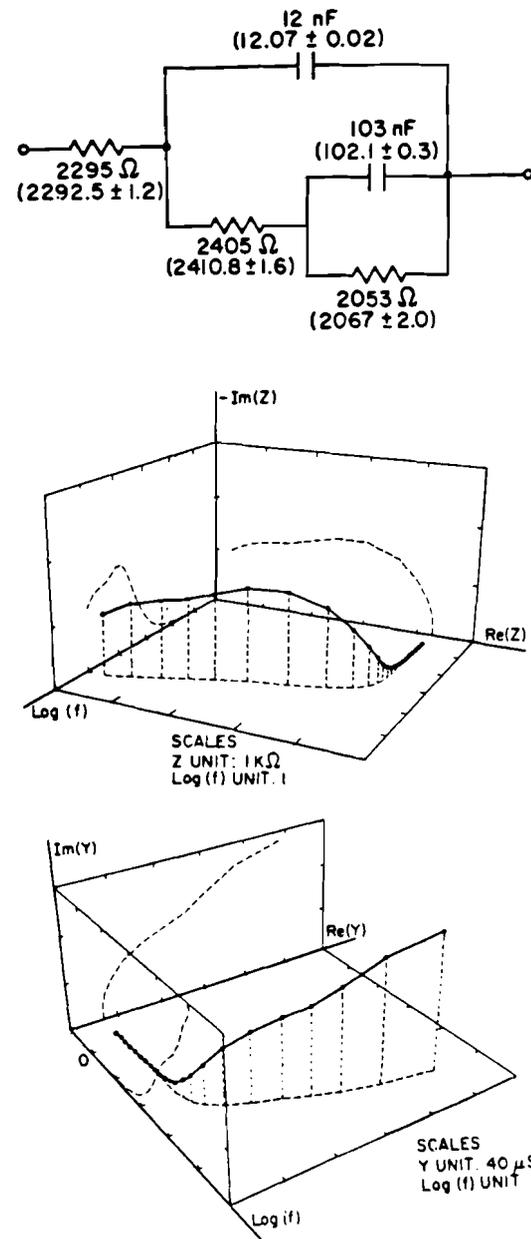


FIGURE 20

Three-dimensional perspective impedance and admittance plots of the response of the lumped constant ladder network shown. CNLS fit values shown in parentheses (55).

$\beta$ -PbF<sub>2</sub> at 474 K

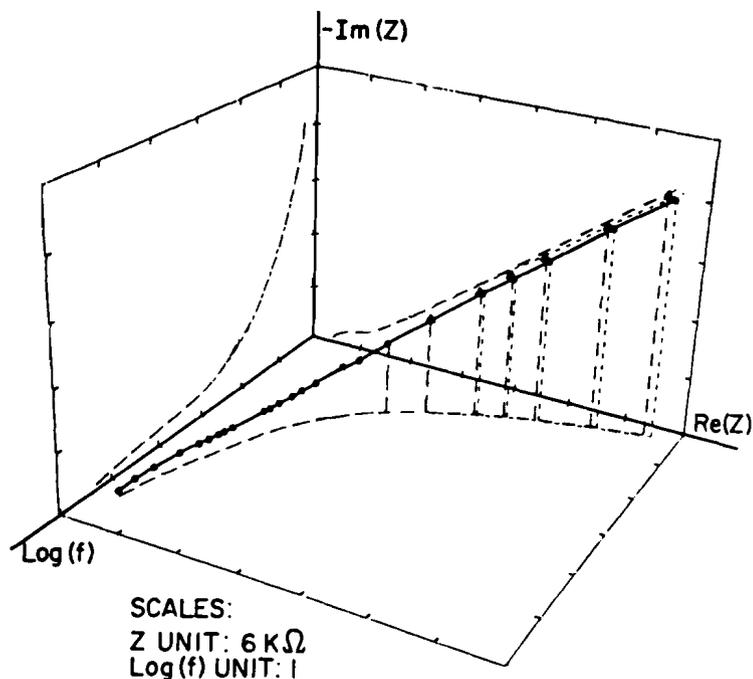
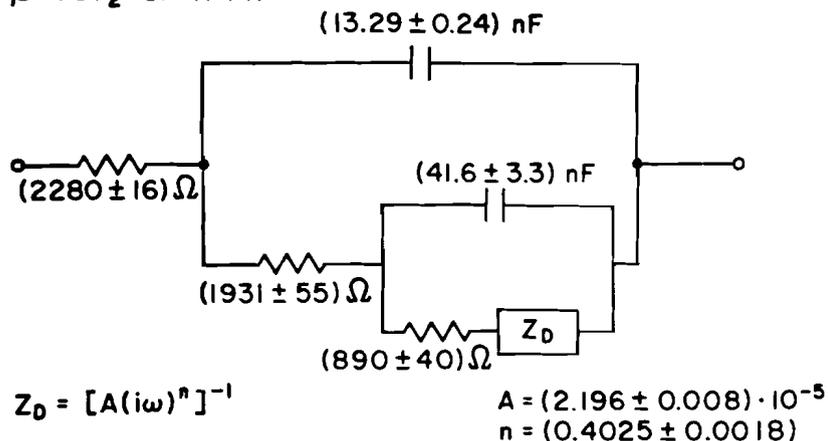


FIGURE 21

Three-dimensional perspective impedance plot of  $\beta$ -PbF<sub>2</sub> data and CNLS fit response for the circuit shown (55).

proportional to their magnitudes at each point) is customarily used. Luckily, the weighting employed has only a small effect on the parameter estimates when the errors present in the fit are reasonably small (59). It has been suggested that when the errors in the real and imaginary components are strongly correlated, modulus weighting (MWT) should be used (60). In this case the weights for both components are just  $|l|^{-2}$ , where  $l$  is the immittance function being considered. Now if one fits the data in their original form without transformation to another immittance form, as one should, and if the errors are random, as one would hope, they should be uncorrelated. But transformation from a given function to its complex inverse, as from impedance to admittance, will induce some correlation in the errors of the individual components at each frequency; then for comparison of fits with these two forms, MWT may indeed be most appropriate.

Computerized fitting has recently been criticized (61) because the deviations between the data and the fitting results (residuals) may show systematic behavior. Indeed they may, but this is a strength not a weakness of such methods as CNLS fitting! Such results provide very important information, namely that the model or equivalent circuit used in the fitting is not a perfect representation of the data. When the deviations are large enough, they are a stimulus to try to discover and eliminate systematic errors in the data themselves and/or to try more appropriate models or equivalent circuits. Although residuals are not usually calculated and examined in the older approximate (non-computerized or non-CNLS) analysis methods, as they are as a matter of course in the CNLS approach, they are always likely to be larger than with CNLS and thus to indicate systematic behavior more frequently, sometimes when it is only an artifact of the inadequate analysis procedures used.

#### B. Distributed Circuit Elements, Models, and Circuits

No matter how accurate and extensive one's data are, it is fair to say that the unexamined data set is not worth crowing about! Only when one has derived maximum enlightenment from it about the system involved has it served its purpose. To do so nearly always requires some comparison between the data and theoretical expectations, as discussed in the last section. A detailed model should always yield an expression for impedance vs. frequency, but it may or may not allow a useful equivalent circuit to be constructed. Whether or not such a circuit is available, the model impedance can be fit to the data using CNLS. On the other hand, when no model is available an often heuristic equivalent circuit must be used. Since real systems are distributed in space and their properties are frequently distributed as well (62), one usually needs to include one or more dees in the fitting circuit. These are elements which cannot be represented by a finite number of ordinary ideal circuit components but subsume the response of a distributed process, say diffusion, into a single expression. I shall discuss

some of them briefly in the next section, and then move on to consider some models and equivalent circuits which have been used to represent and analyze the s-s AC response of supported and unsupported solid and liquid electrolyte systems. Some pertinent reviews appear in Refs. 17,61, and 63-68.

### 1. Some Distributed Circuit Elements

The diffuse layer differential capacitance is itself a dce since it represents space charge response over a finite region of space. Although it shows some frequency dependence at very high frequencies (see the next section), such dependence may be neglected in the usual experimental frequency range. Many different expressions for its capacitance have been derived, depending on the exact physical conditions considered. Here I shall only give an approximate but usually adequate expression applying for the common situation of two identical, plane, parallel blocking electrodes separated by a distance  $\ell$  which contains many Debye lengths,  $L_D$ . Thus we shall actually be concerned, in the present case of the low-frequency-limiting differential capacitance, with two diffuse layer capacitances in series, one associated with each interface, and with  $C_g$  in parallel with the combination. As the general circuit of Fig. 16 shows, however, only in the low frequency limit can we take  $C_g$  in parallel with this combination. Since I shall be usually dealing with two identical electrodes in the following, when I am I shall define  $C_{d\ell}$  as the series combination of the two diffuse layer capacitances without the effect of  $C_g$  included, and take  $C_H$  as the series combination of the two inner layer capacitances. Then the (combined) double layer capacitance,  $C_{DL}$ , satisfies  $C_{DL}^{-1} = C_{d\ell}^{-1} + C_H^{-1}$ , and, for sufficiently low frequencies,  $C_T = C_{DL} + C_g$ .

Although the use of two identical electrodes, a common practice for solid materials, may seem a limitation, especially for liquid electrolyte situations where half-cells are often employed, this is not the case when no static potential difference appears across the cell. Because of symmetry, two-electrode s-s AC results may be considered to be equivalent to the results which would be obtained for two identical half-cells in series, with each half-cell involving the boundary conditions of the full cell at one end and that equivalent to an ohmic electrode, undisturbed bulk concentrations, at the other. Thus full-cell solutions include both cases.

Let us ignore for the moment the effect of any  $C_H$  by taking it infinite; then  $C_d$  and  $C_{DL}$  will be the same. Consider a situation where the continuum (igm) model is appropriate, and a static potential difference of  $\psi_a$  is applied across the electrodes; thus  $\psi_a/2$  occurs across each diffuse layer. Then one finds for the quasistatic differential capacitance (69,70)

$$C_T = C_g [(M) \operatorname{ctnh}(M)] \cosh(\psi_a/4V_T). \quad (4)$$

Here  $M$ , the number of Debye lengths in a half cell, is defined as  $\ell/2L_D$ . This expression for  $C_T$  is intensive, as it should be for an interface-related quantity, when  $M \gg 1$  and  $C_g$  plays a negligible role. When  $|\psi_a/V_T| \ll 1$ , one obtains the usual small-signal AC expression for  $C_T$  (not distinguished from  $C_{DL}$  by many authors) when  $M \gg 1$ , and one finds the extensive result  $C_T = C_g$  when  $M \ll 1$ .

I shall now turn to the consideration of frequency response which may be associated with a distribution of relaxation times or activation energies and which applies for a single, possibly wide, dispersion region. A very important dce, whose response, or response very close to it, appears over a limited frequency range in nearly every distributed situation and in most other dce's, is the constant phase element (CPE). Its admittance is of the form (2,3,53,62,71-74)

$$Y = A_0 (i\omega)^n, \quad (5)$$

where  $0 \leq n \leq 1$ . This element is not physically realizable at the extremes of frequency and so should be used in conjunction with other limiting elements or in truncated form. A degenerate form of the CPE, when  $n = 0.5$ , is infinite-length Warburg response associated with uniform diffusion in a right half space (75). It has been widely used in electrochemical IS studies but suffers from the same lack of physical realizability as the CPE. Its impedance is usually designated as  $Z_W$ , and it is an intensive quantity.

For a single dispersion region whose low frequency limited resistance is  $R_0$  and whose high frequency limiting value is  $R_\infty$  it is convenient to introduce the normalized impedance function (2)

$$I_Z = (Z - R_\infty)/(R_0 - R_\infty), \quad (6)$$

whose limiting real values are 1 and 0. Another dce associated with uniform diffusion but more physically plausible than the CPE or  $Z_W$  is the finite-length Warburg, impedance  $Z_D$ , where

$$I_{ZD} = \tanh(\sqrt{is})/\sqrt{is}, \quad (7)$$

and  $s \equiv \omega\tau_M$  is a normalized frequency. The time constant  $\tau_M$  involves mobilities or diffusion constants and the electrode separation,  $\ell$ . Since all real systems involve a finite separation of electrodes,  $Z_D$ , defined by Eqs. (6) and (7), should always be used in place of  $Z_W$ , although it formally reduces to  $Z_W$  when  $R_\infty = 0$  and  $s \gg 2$ . In this limit, the response is intensive, as appropriate for a region near an electrode. Note that in the zero frequency limit  $Z_D$  reduces to the impedance of a capacitor and resistor in parallel, even when  $R_\infty = 0$ . Here the response is extensive in character because diffusion effects then extend over the entire region between the electrodes.

The response form of Eq. (7), which is also the normalized input impedance of a finite-length shorted transmission line (76), first appeared in the present context in 1953 (77) for the unsupported situation and in 1958 (78) for the supported one. Comparisons of the two approaches (79) show that although the frequency response is of the same form, the coefficients and time constants involved are generally different, although the coefficients may be the same in one simplifying case. Franceschetti and Macdonald (76) have considered many more complicated diffusion effects in supported and unsupported small-signal response. Besides the above particular finite-length response, associated with a fast reaction at the electrode, another such limiting response appears when the diffusing entity is blocked (and possibly adsorbed) at the electrode (the analog of a finite-length transmission line with an infinite terminating resistance). Let its impedance be designated  $Z_{D0}$ . Then (76,80)

$$I_{ZD0} = \text{ctnh}(\sqrt{is})/\sqrt{is}, \quad (8)$$

which becomes purely capacitive in the low frequency limit but shows  $Z_W$  behavior again for  $|s| \gg 2$ . Responses of the above types can appear when the diffusing entity is either charged or neutral. Both types of response are seen fairly frequently in experimental results. It has even been suggested (80,81) that  $Z_{D0}$  response may arise in electrochromic thin films where the diffusing metallic ion is supported by electronic conduction.

Another important dce which has been widely employed in equivalent circuits for both dielectric and conductive systems leads to a complex plane curve which is a semicircle with its center depressed below the real axis, a common shape when a distribution is present (2,3,62,72,74,82). Its  $I_Z$  representation is

$$I_Z = [1 + (is)^n]^{-1} \quad (9)$$

where  $s$  is again a normalized frequency variable. This result, which has been termed the ZC dce, may either be considered as a response function in its own right or as the parallel combination of a resistance and a CPE. There are several other interesting combinations of a CPE and an ideal circuit element (3), but the ZC is the most common. Unfortunately, it is not physically realistic at both frequency extremes since it does not meet the criterion that its response reduce to that of a system with a single relaxation time at very low frequencies and to another single relaxation time in the limit of high frequencies (2,53,74). In many practical cases measurements may not extend to the regions where these deficiencies become apparent, however.

Many other dce's have been proposed over the years. Some of them are discussed in Refs. 2,3,62, and 83. Here, however, it will suffice to mention three of them of current interest: the Williams-Watts (WW), Exponential Distribution of Activation Energies (EDAE), and Gaussian Distribution of Activation Energies (GDAE) dce's. WW response has been found in many theoretical and experimental studies (many references are listed in the present Ref. 53), although most comparisons with experiment have been inadequate, in part because the integral definitions of the WW  $Z'$  and  $Z''$  functions are very difficult to evaluate accurately. Recently, however, an accurate approximation for WW response has been developed (84) and incorporated as an elective part of a powerful CNLS fitting program (available from the present author).

Although the GDAE and EDAE responses are also defined as integrals, they are readily evaluated numerically and are also included in the CNLS computer program. The general EDAE dce has been found to be able to fit very well the responses of nearly all the other dce's which have been proposed (2,83,84). For example, Fig. 22 shows the result of a CNLS fit of the EDAE model to accurate calculated WW response. When the system being investigated is thermally activated, as it often is, and shows evidence of distributed character (wider dispersions than arise from single-time-constant Debye response), the EDAE is probably the dce of choice, both because it is fully physically realizable and because it leads, unlike other models, to temperature dependence predictions in good agreement with experiment for the fractional frequency and time power-law exponents often found.

## 2. Circuits and Models

### a. General Discussion

The presence of a supporting, or indifferent, electrolyte in supported situations decouples the charged ionic species of interest from the rest of the charges in the system, thus making its electrical effects very much easier to calculate in an approximate but usually adequately accurate way. The situation is quite different for an unsupported solid or liquid where Poisson's equation strongly couples charges of both signs together. It is thus generally much more difficult to solve electrical response problems, particularly under large signal (nonlinear) conditions, in unsupported than in supported situations. Here I will primarily consider s-s solutions for unsupported conditions, finishing with some numerical results for the highly nonlinear situation where a static bias p.d.,  $\psi_a$ , is present as well as a small sinusoidal p.d.

When an equivalent circuit involves only ideal elements, it is found that some circuits with the same number of elements but with different interconnections may yield exactly the same impedance for all frequencies (53,64,67). Three such circuits are shown in Fig. 23. The first is a series type, the second essentially parallel, and the third a hierarchical connection. The circuit elements are named differently in

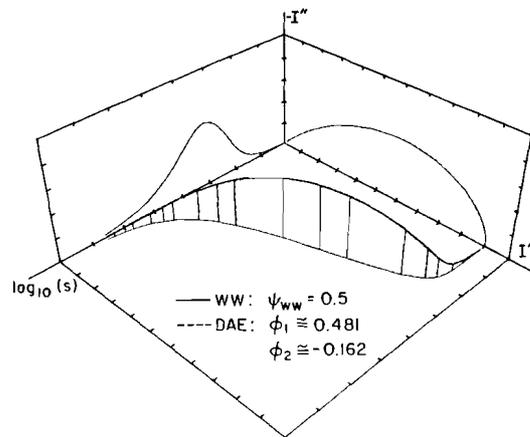


FIGURE 22

Three-dimensional perspective impedance plot showing a comparison of accurate WW response (solid lines) with response obtained (53) by fitting the EDAE model to the "data" by CNLS (dashed lines).

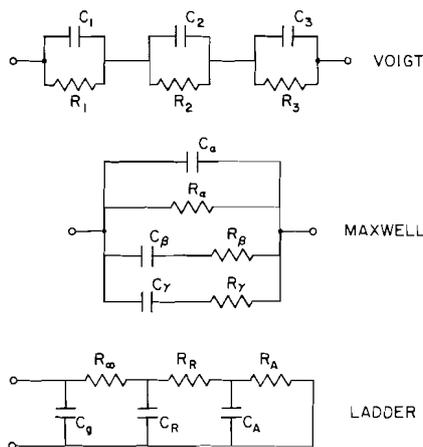


FIGURE 23

Three circuits which can have exactly the same impedance-frequency relation (67). ©1981 IEEE.

each circuit because they must have different values in order that the impedances of all three circuits be the same. This ambiguity may sometimes make it difficult to find the most appropriate circuit for a given situation, but it can usually be eliminated by considering the dependences of the circuit elements on one or more other experimental variables besides frequency, as mentioned in Section IIIA. Further, it turns out that when the circuit being investigated requires the presence of one or more dce's which involve CPE-like behavior the ambiguity discussed here disappears (82). For all the circuits presented in this section, the resistances and capacitances shown are taken to be frequency independent unless otherwise noted.

In the following circuits I shall follow prior usage in defining  $R_{sol}$  as the solution resistance for liquid materials, but I shall use  $R_{\infty}$  as a more general definition of the high frequency limiting bulk resistance of either a liquid or a solid material. In many electrolyte equivalent circuits the quantity  $C_{DL}$  (or  $C_{dl}$ ) appears defined as just the double-layer capacitance without distinction being made between the three concepts here denoted by  $C_{dl}$ ,  $C_{DL}$ , and  $C_T$ . When an expression is given for it, it is usually that of the Eq. (4)  $C_T$  in the  $s \rightarrow \infty$  situation:  $\epsilon_B/4\pi L_D$  for a single electrode or  $\epsilon_B/8\pi L_D$  for two identical electrodes. Here  $\epsilon_B$  is the dielectric constant of the bulk material. Since  $C_{DL}$  turns out to be closely associated with charge transfer reactions at an electrode involving a reaction resistance  $R_{ct}$ , or  $R_R$ , I shall often denote  $C_{DL}$  as  $C_R$ .

Figure 24 a-e shows some representative equivalent circuits which have been proposed over the years as appropriate representations of the response of supported (liquid) electrolytes. The circuit of Fig. 24-f is for a membrane with only charge of a single sign present in the membrane, somewhat similar to a supported situation. Other circuits are discussed in Refs. 61,63,92, and 93. Note that only the last of the Fig. 24 circuits includes  $C_g$  and a few do not include  $R_{sol}$ . Although some of these circuits have been used for data analysis, it is unfortunate that rarely have several different circuits been used to analyze the same data in order to try to discover which one is the more appropriate, and hardly any supported-situation data have been analyzed with CNLS. Such fitting and comparisons are still much needed, especially since the presence of dce's in circuits of this kind eliminates most of the possibility of ambiguity discussed above. The important circuit of Fig. 24-a is known as the Randles circuit. Randles (86) calculated expressions for  $R_{ct}$  and  $Z_W$  appropriate for the simple charge transfer reaction



FIGURE 24

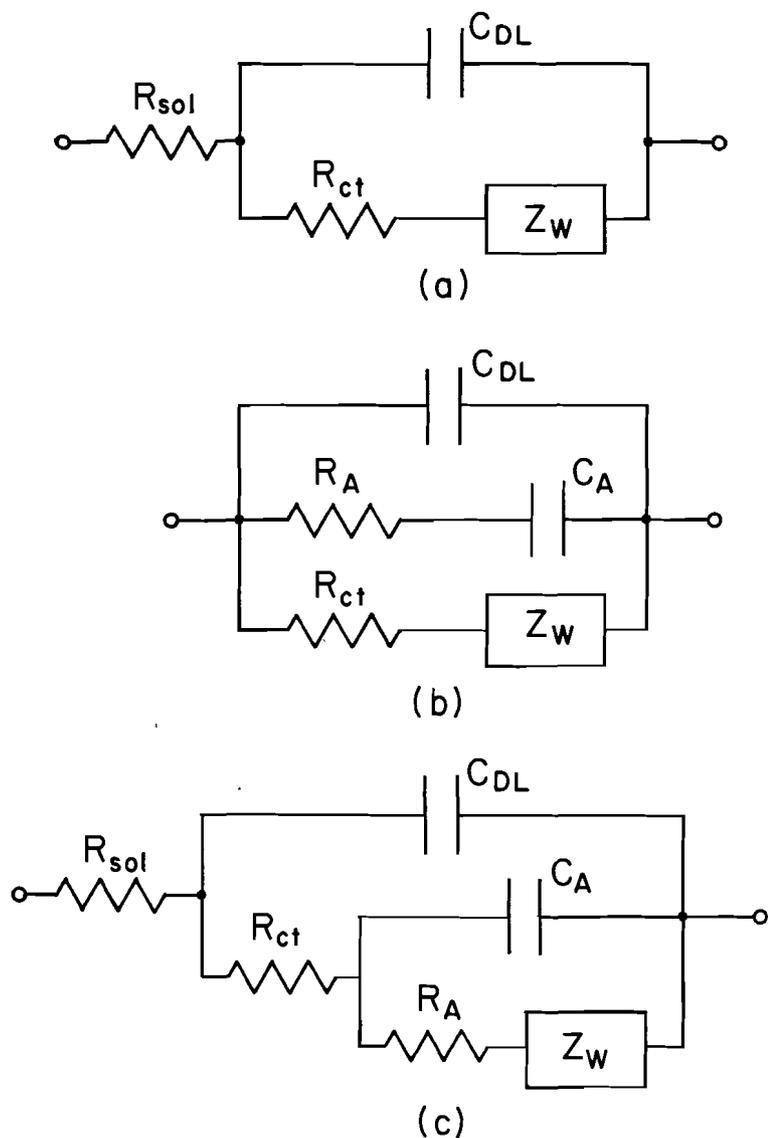


FIGURE 24 CONTINUED

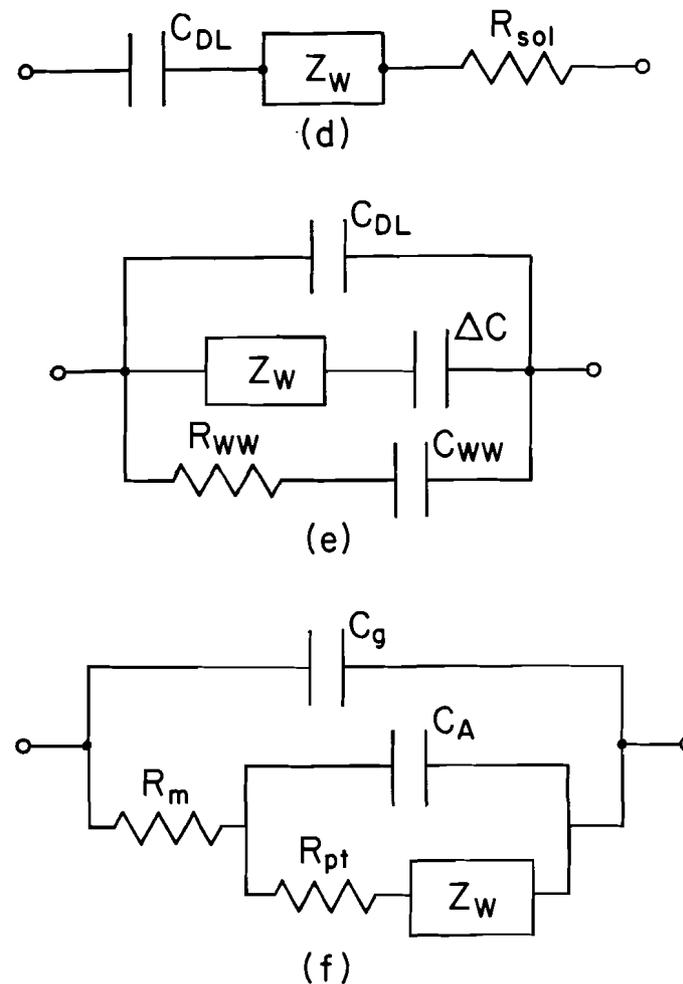


FIGURE 24

Some circuits proposed for the impedance of a supported electrode-material situation; (a) "Randles" (86), (b) Laitinen and Randles (87), (c) Llopis et al. (88), (d) Barker (89), (e) Timmer et al. (90), (f) de Levie and Vukadin (91); a membrane situation; see text. Here  $R_A$  and  $C_A$  are adsorption resistance and capacitance;  $\Delta C$  is the capacitance difference between low and high frequency;  $R_{ww}$  and  $C_{ww}$  are Warburg-like elements for diffusion-controlled adsorption;  $R_m$  is a membrane (bulk) resistance; and  $R_{pt}$  is a phase transfer resistance.

where  $n$  is here the total number of electrons transferred in the reaction, and Ox and Red are oxidized and reduced species.

An important difference between supported and unsupported conditions is associated with the mobilities of the charges. Most supported situations are present in liquid electrolytes, where both positive and negative species are mobile, usually without a tremendous difference in mobilities. Unsupported situations occur, however, in fused salts and in solids with ionic or electronic conduction. Although charges of both signs may be mobile in solids and have comparable mobilities, it is common to encounter situations where the difference in mobility is so large that the slower charges may be taken completely immobile over the time scale of the experiment.

#### b. Unsupported Conditions: Models and Theoretical Results

The earliest correct treatment of the s-s frequency response for an unsupported situation appeared in 1953 (77). It involved uni-univalent charges of arbitrary mobilities, complete blocking conditions at the two identical electrodes, and no applied static p.d. This theory and most of those discussed below apply to semiconductors as well as to solid or liquid electrolytes, but I shall emphasize the latter materials here.

No full theory of s-s frequency response for unsupported conditions with partial discharge at the electrodes appeared for some time after the above work. Such discharge occurs when a charge transfer reaction, such as that of Eq. (10), is present. Although I obtained, over a period of some years, many new theoretical results (64,79,85,95-103) incorporating the simple discharge boundary conditions of Chang and Jaffé (94), these results were made more complicated and harder to use by their analysis in terms of the equivalent circuit of Fig. 16-a, and later by the use of the first circuit shown in Fig. 23. The Fig. 16-a circuit isolates the zero-frequency limiting resistance of the system,  $R_D$ , and  $R_\infty$  is given by the parallel combination of  $R_D$  and  $R_F$ . By contrast, the Fig. 16-b circuit separates out the high frequency elements,  $R_\infty$  and  $C_g$ , of the total response and turns out to lead to much simpler analysis and fitting (85,104).

The Chang-Jaffé (C-J) boundary conditions, which do not take an inner layer into account but do involve a pure concentration overpotential, were later generalized by Lányi (105) and the present author (64,100,101,104) by taking the discharge parameters for positive and negative charges complex and frequency dependent in such a way that the possible presence of sequential specific adsorption, as well as an electrode reaction, could be simply included. Some resulting complex plane curve shapes are shown in Fig. 25. Note that each semicircle involves a single time constant, such as  $\tau_R \equiv R_R C_R$  for the reaction arc. The negative loops in 25-a imply the presence of inductive or negative differential resistance and capacitance response. It

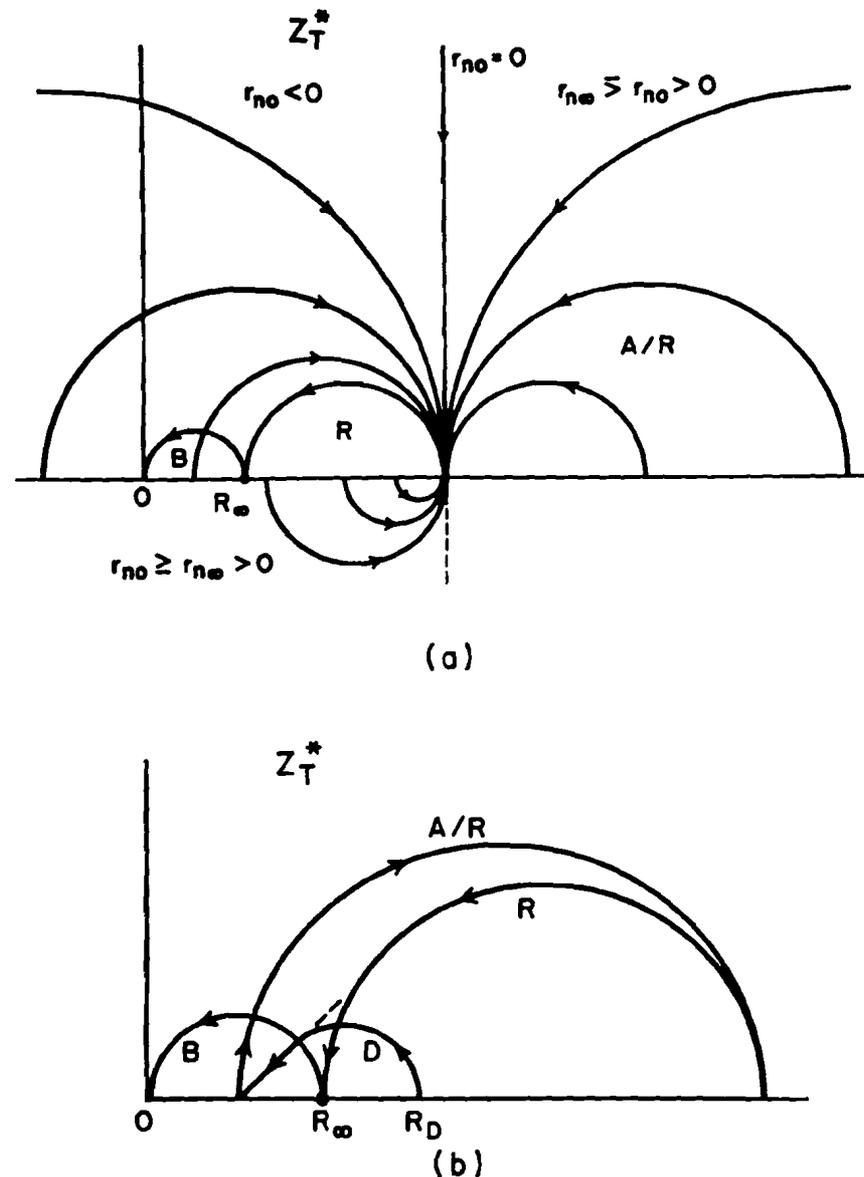


FIGURE 25

Complex plane response curves for adsorption-reaction (A/R) situations (64,104). Arrows denote direction of increasing frequency. Here R identifies a reaction arc, B a bulk arc, and D a diffusion arc. The  $r_n$ 's are rate constant parameters. The curves in (a) apply for  $\pi_m \gg 1$ , and those in (b) for  $\pi_m = 1$  and  $-\infty < r_{no} < -2$ .

has been shown (104) that the representation of the adsorption response in terms of negative resistance and capacitance is preferable to the introduction of a non-physical inductance. The rather exotic sorts of behavior shown here have actually been observed when adsorption is present.

The most complete theory using the generalized C-J boundary conditions appeared in 1978 (85). It leads to a complicated expression for the  $Z_s$  of Fig. 16; involves arbitrary mobilities, valence numbers, and discharge parameters; and treats both intrinsic and extrinsic conduction possibilities, with inclusion of dynamic dissociation and recombination effects. It thus includes the five important processes: charge separation near an interface, adsorption-desorption, charge transfer at an electrode, mass transport (diffusion effects), and intrinsic-extrinsic generation-recombination. Its results are too complicated to yield a useful equivalent circuit in the most general case, but such circuits may be found for some less general situations. Of course when an equivalent circuit is derived from the exact solution, expressions for the circuit elements in terms of microscopic parameters of the model follow immediately. In the present overview I shall not define in this way all the elements appearing in the equivalent circuits discussed since the detailed relations are available elsewhere.

It is possible to obtain a simple equivalent circuit for the completely blocking, intrinsic, equal valence numbers, equal mobilities case, with or without recombination. One finds (85) the exact result that  $Z_s = Z_{s0}$  is made up of a capacitance  $C_g t_1$  in series with a resistance  $R_\infty t_1^{-1}$ , where  $t_1 \equiv [(M\sqrt{\psi})\text{ctnh}(M\sqrt{\psi}) - 1]$  and  $\psi \equiv 1 + i\omega\tau_D$ . These elements are thus frequency dependent in the  $\omega \approx \tau_D^{-1}$  region where bulk effects dominate. In the usual lower frequency region where  $\omega \ll \tau_D^{-1}$  and interface effects dominate, however, they are essentially frequency independent;  $t_1 \approx r - 1$ ; and  $r \equiv (M)\text{ctnh}(M)$ , a quantity usually much greater than unity. Then the series resistance can be neglected compared to  $R_\infty$  and the capacitance becomes just the usual  $C_{dl} = C_g(r - 1)$ . In the limit of low frequencies,  $C_T = C_g + C_{dl} = rC_g$ , in full agreement with the result of Eq. (4) when  $\psi_a = 0$ .

Exact results are considerably more complicated when the mobilities are unequal; then diffusion effects usually appear even in the completely blocking case (77,85,106). The limiting low frequency finite-length-diffusion capacitance following from  $Z_D$ , sometimes called a pseudocapacitance, is proportional to  $\ell$  and may be very much larger than  $C_{dl}$  (79,85,96-98). When  $\psi_a$  is non-zero, exact analytic solution of the coupled set of nonlinear differential equations which determine transient response or s-s frequency response is impossible, but Franceschetti and Macdonald (70,107,108) have solved the equations numerically for many different cases of interest. The static potential difference,  $\psi_a$ , may include an applied component and/or intrinsic Frenkel layer contributions.

The frequency response of material in finite-length half cells with one completely blocking electrode or in full cells with two such electrodes, has been calculated (70) for several values of the mobility ratio,  $\pi_m \equiv \mu_n/\mu_p$ , and many values of  $\psi_a^* \equiv \psi_a/V_T$ . Some representative complex plane impedance and admittance results for a half cell with  $\pi_m = 5$  are presented in Fig. 26. The equivalent circuit of Fig. 27-a was found, by CNLS fitting, to represent the data well with  $\psi_a$  zero, positive, or negative. Compare the supported-case circuit of Fig. 24-d. For  $\psi_a = 0$  and  $\pi_m = 1$ , it turns out that  $Z_D = 0$ ,  $R_1 = R_\infty$ , and  $C_2 = C_{dl}$ , as given above. We have used the designations  $R_1$  and  $C_2$  here in place of  $R_\infty$  and  $C_{dl}$ , as given above. We have used the designations  $R_1$  and  $C_2$  here in place of  $R_\infty$  and  $C_{dl}$  to emphasize the dependences on  $\psi_a$  found for these quantities and for the parameters of  $Z_D$ . These dependences are in agreement with expectations for charge accumulation and depletion layers; that for  $R_1$  is very small, and that for  $C_2$  agrees very closely with appropriate quasi-static  $\psi_a$ -dependent analytic expressions (70), such as that of Eq. 4, for the cases considered.

For the  $\psi_a = 0$  full-cell situation where positive charges are taken completely blocked at the electrodes and negative ones may react at the electrode with an arbitrary rate constant,  $k_n$ , Macdonald and Hull (109) have used CNLS fitting of an appropriate circuit to the exact theoretical response (85) in order to investigate how the circuit elements depend on  $\pi_m$  and on recombination effects. The best fitting circuit found is shown in Fig. 27-b. Notice that it would be identified as a Randles circuit (with a finite-length rather than infinite length diffusion impedance) if supported behavior were being considered. Attention was concentrated on the  $\omega\tau_D \ll 1$  frequency region, and for  $\pi_m = 1$  exactly the above result for  $C_{dl}$  was found from the fitting. But  $C_{dl}$  increased rapidly for  $\pi_m > 1$  and quickly dropped for  $\pi_m < 1$  to about 0.7 times its  $\pi_m = 1$  value, or, more precisely, to  $C_g(r_1 - 1)$  for  $\pi_m \ll 1$ . Here  $r_1 \equiv (M_1)\text{ctnh}(M_1)$  and  $M_1 \equiv \ell/L_{D1}$ . The latter result may be readily understood. When  $\pi_m < 0.1$ , the effective Debye length is no longer that appropriate when charges of both sign are mobile,  $L_D$ , but is well approximated by the one-mobile value,  $L_{D1} = \sqrt{2}L_D$ .

The resistance  $R_R$  also showed interesting and important behavior. Although it is usually taken to be the reaction resistance, proportional to  $k_n^{-1}$ , it was found to be non-zero and dependent on  $M^{-1}$  even when  $k_n$  was taken infinite. Such pseudo reaction rate response, associated with the drag of charges of one sign on those of the other sign and not with a finite reaction rate at all, can lead to entirely incorrect estimates of reaction rate values when it is unrecognized; and even when its presence is accounted for, it sets an upper limit on the maximum reaction rate value which can be reliably estimated when using CNLS to fit data as accurately as possible to the present circuit.

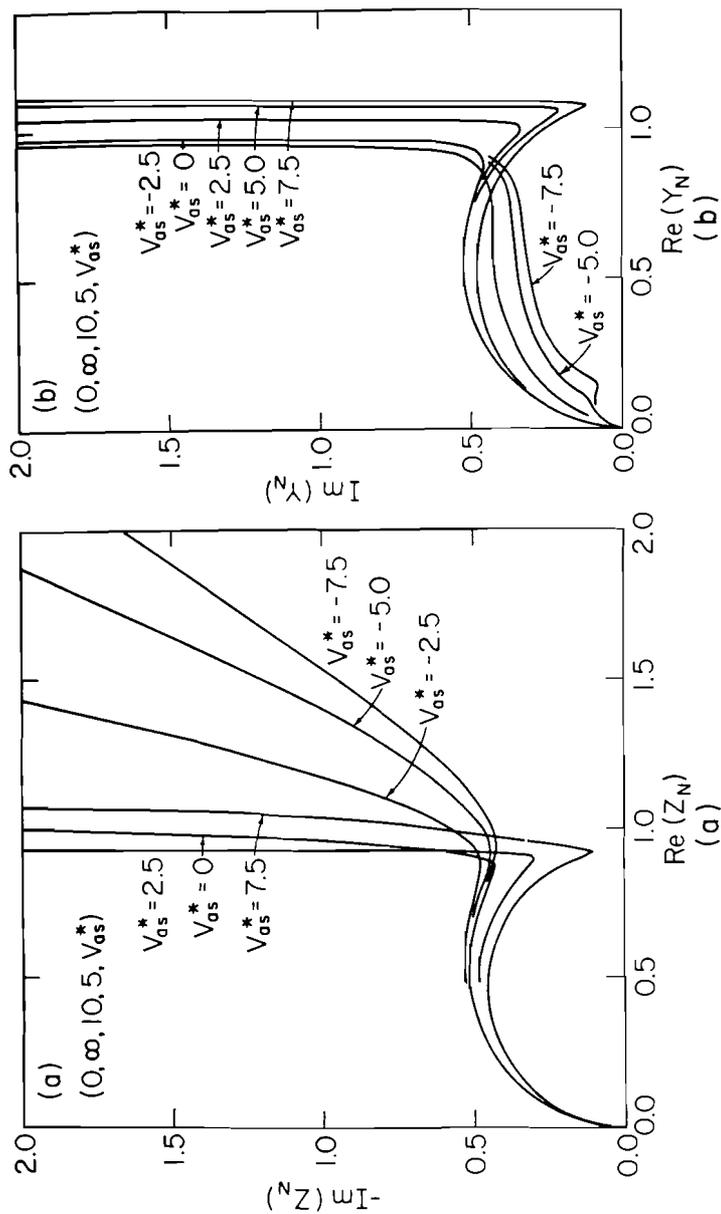


FIGURE 26  
 Impedance (a) and admittance (b) plane plots for a half cell with a blocking electrode,  $M = 10$ , and  $\tau_m = 5$ , for several values of the normalized applied static potential difference (70).

For the rest of the discussion I shall be concerned only with the one-mobile situation (a single species of mobile charge present) appropriate for many solids. Charge of one sign is taken immobile, and is uniformly distributed in the absence of recombination, while that of the other sign is assumed to be mobile and may react or be blocked at the electrodes. Archer and Armstrong (66) have discussed the equivalent circuit of Fig. 27-c for a blocked, one-mobile situation with specific adsorption. Since it has no DC path, it allows no Faradaic current and thus no charge transfer reaction occurs. Although the exact  $s$ - $s$  solution (85) yields a relatively simple expression for  $Z_S$  for the general one-mobile case, it still does not lead to a relatively simple equivalent circuit when recombination is possible and dissociation is incomplete. In the full dissociation limit, however, it does yield a simple circuit, that of Fig. 28 when all the  $Z_D$ 's are taken zero and  $C_R = C_{DL} = C_{dl}$ . The resulting hierarchical structure is then equivalent to the ladder network of Fig. 23 and is also equivalent in form to the supported-case circuit of Fig. 24-c when one  $Z_D$  in Fig. 28 is taken non-zero and is approximated by  $Z_W$  and  $C_g$  is ignored.

Actually, the exact solution shows that the  $C_R$  in Fig. 28 should be replaced by the impedance  $Z_{s0}$ , identified above for the completely blocking situation, but with  $M$  and  $r$  replaced by  $M_1$  and  $r_1$  since  $L_{D1}$  rather than  $L_D$  is the appropriate bulk Debye length in the present one-mobile case. Thus, the Fig. 28 circuit, with the restrictions above, is only accurate in the  $\omega\tau_D \ll 1$  frequency region. In this region it can, however, lead to all the kinds of complex-plane curve shapes shown in Fig. 25-a. Note that when  $R_A = \infty$  only adsorption is present but the structure is different from that of the Fig. 27-c circuit. When  $R_A$  and  $Z_{D3}$  are both zero, one has the situation of heterogeneous reaction without adsorption. As shown above, the basic one-mobile situation involves no diffusion elements, but if a neutral reaction product diffuses in both the electrode and in the solid, at least two non-zero  $Z_D$ 's may need to be included in the Fig. 28 circuit (67,76,110,111), but their effects will usually show up only at very low frequencies.

One might ask how the quasi-static circuit of Fig. 9 for diffuse and inner layer capacitances could be extended to be consistent with the reaction-adsorption parts of Fig. 28. A tentative suggestion is as follows. When a reaction is present,  $C_B$  will be paralleled by a low resistance and their combined effects could probably be ignored in the measurable frequency range. Then if one identified  $C_Y$  as  $C_H$  and  $C_{DO}$  as  $C_{dl}$ , their series combination is just  $C_R$ . One needs only to add  $R_R$  in series with  $C_A$ , and  $R_A$  in parallel with it, to obtain the pertinent part of the Fig. 28 circuit.

We have given little attention to the effect of  $C_H$  so far since its presence is ignored when C-J boundary conditions are employed. Luckily, a transformation of variables method has been developed (104) which allows known exact  $s$ - $s$  solutions using even generalized C-J reaction-adsorption parameters to be transformed to solutions

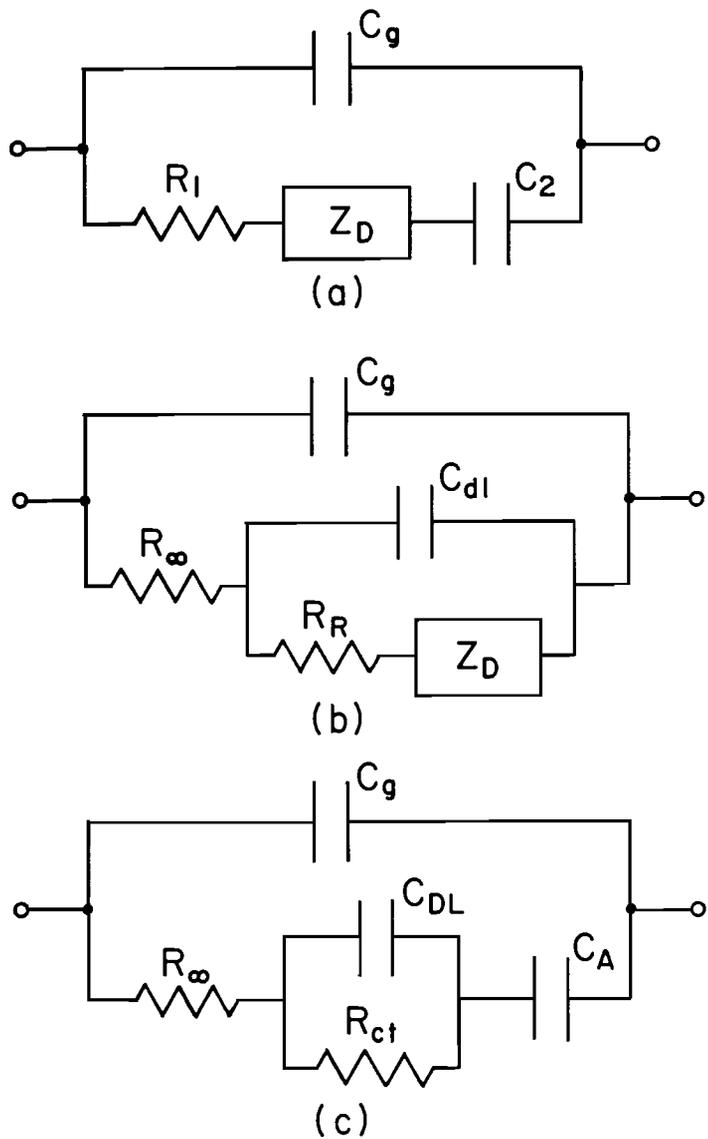


FIGURE 27

(a) Equivalent circuit appropriate for one or two blocking electrodes, no specific adsorption, arbitrary  $\pi_m$ , and either without or with an applied static bias p.d. (b) Equivalent circuit appropriate in the small-signal, arbitrary mobilities situation (109). (c) Equivalent circuit presented by Archer and Armstrong (66) for one-mobile blocking conditions.

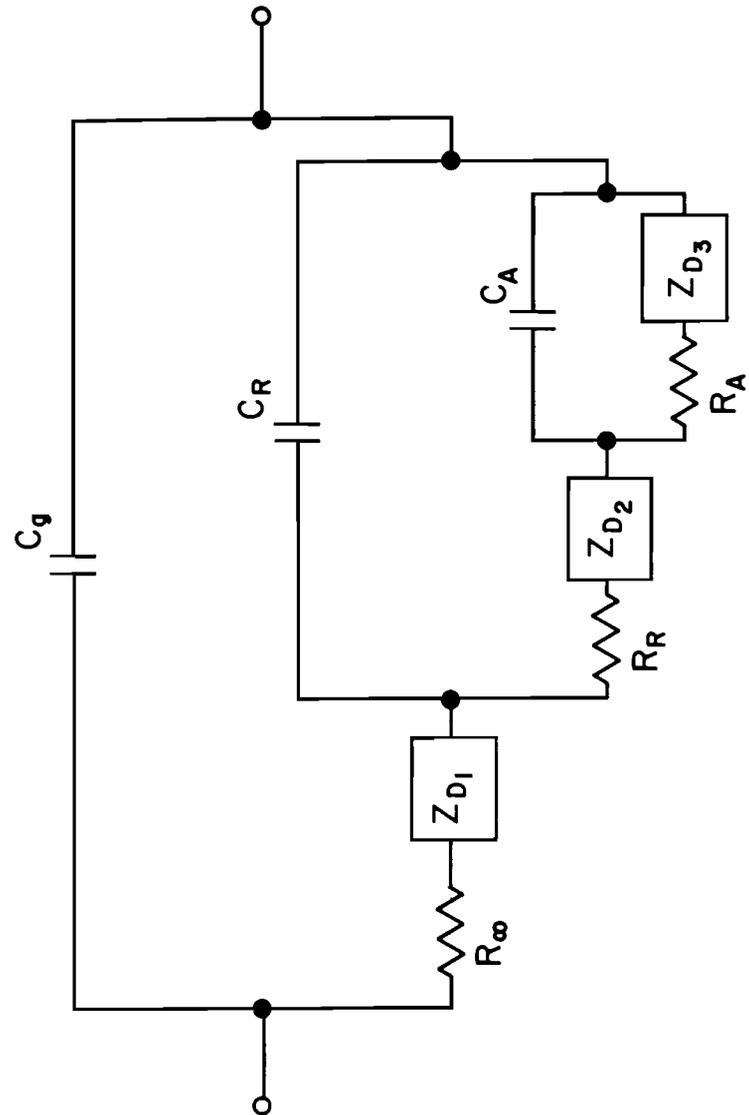


FIGURE 28  
General equivalent circuit. For the one-mobile situation without diffusion of reaction products, all  $Z_D$ 's are zero (67,85). © 1981 IEEE.

taking proper account of  $C_H$  and involving even more general overpotential-dependent, first-order electrode reaction kinetics than conventional Butler-Volmer (B-V) kinetics. When this method is applied for the present one-mobile case without adsorption, it leads (112,113) to the exact equivalent circuit of Fig. 29-a. This circuit shows that it is possible to separate out all  $C_H$  effects into a separate series circuit which reduces to just  $C_H$  when the mobile carrier is completely blocked. Here  $C_{ga}$  is the geometric capacitance of the system excluding the two inner layer regions and  $R_{\infty a}$  is the bulk resistance also excluding these regions. The exact solution for the total impedance  $Z_T$  is relatively complicated and although it could be used directly for CNLS fitting, it is useful to derive simpler approximate results (112,113).

Such results are embodied in the equivalent circuits of Fig. 29-b and 29-c. That of 29-b is quite accurate even up to  $\omega\tau_D = 1$ , while that of 29-c is a good approximation up to  $\omega\tau_D = 0.1$  or so. It is surprising that the complicated circuit of 29-b can be well approximated by a circuit of the same form as its left half, the ordinary  $C_H = 0$  solution, but this is indeed the case. The exact s-s solution shows that to a good approximation  $C_1 = C_g$ , and  $R_1 = R_{\infty}$ . Further, when the kinetics used are simplified to B-V form, it turns out (104,113) that  $R_2$  is exactly  $R_R$ , entirely unchanged by the presence of  $C_H$ . The identity of the present unsupported-case  $R_R$  with the conventional  $R_{ct}$  reaction resistance used in supported situations and derived for B-V kinetics was pointed out long ago (98). In addition, it has been shown (104) that the unsupported and supported expressions for the adsorption capacitance  $C_A$  are also identical.

But  $C_2$  is not generally equal to  $C_{DL}$  even for B-V kinetics. The results do show, however, under what specific conditions the conventional approximation is appropriate. For the general kinetics a complicated expression for  $C_2$  is obtained (113) which involves most of the parameters of the Fig. 29-b circuit. The result is much simplified for B-V kinetics but still involves  $R_R$ . It turns out, nevertheless, that for ordinary conditions in cells with large  $M$ , it is a good approximation to set  $C_2 = C_{DL}$ , where  $C_{DL}^{-1} = C_{dl}^{-1} + C_H^{-1}$  as usual. Then the Fig. 29-c circuit is just that long used for both supported and unsupported conditions. For thin membranes with small  $M$  most of these results definitely do not apply, however, and the exact results should be used for fitting (113).

Finally, Franceschetti and I have obtained numerical solutions for the present situation with static bias applied for both full cells and half cells (108). Typical complex plane results are shown in Fig. 30 for C-J and for B-V kinetics. Although the curves look very similar for the two cases, notice the quite different biasing currents listed. The Fig. 29-c circuit was found to be quite adequate to represent the results, but except for  $C_1$  the parameter values only agreed with those discussed above under zero-bias conditions. Although  $R_1$  was found to have only small bias dependence,  $R_2$

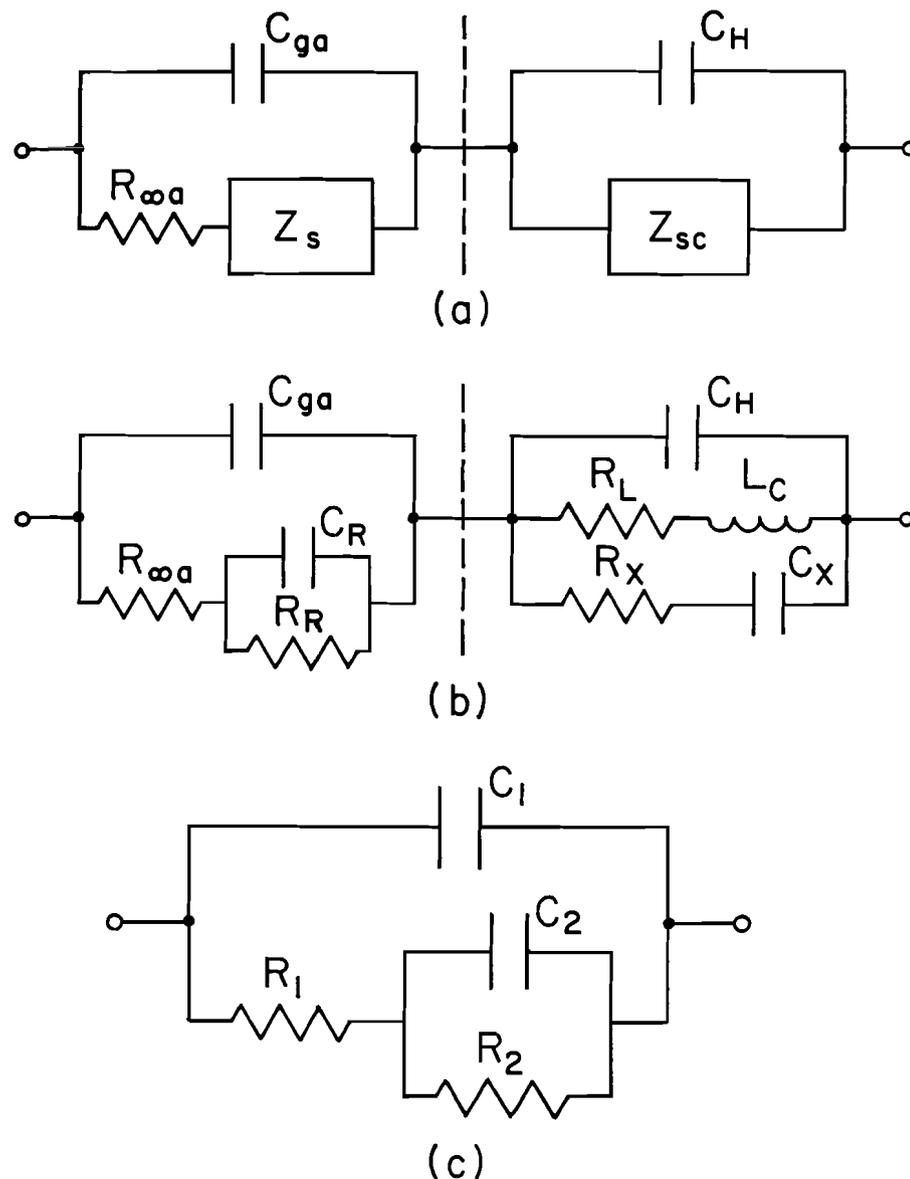


FIGURE 29

Equivalent circuits which take the inner layer into account. Applicable for the one-mobile situation with general reaction kinetics (113). (a) Exact small-signal circuit; (b) first approximate circuit; (c) second approximate circuit, appropriate with or without a Faradaic current flowing.

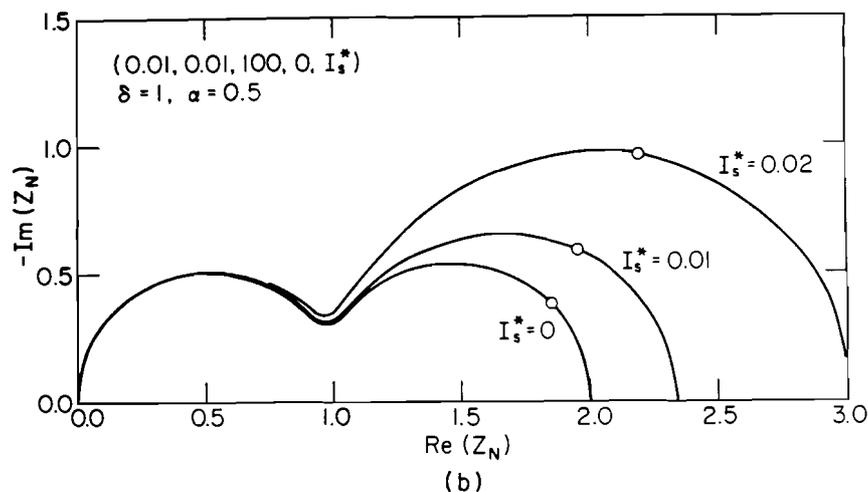
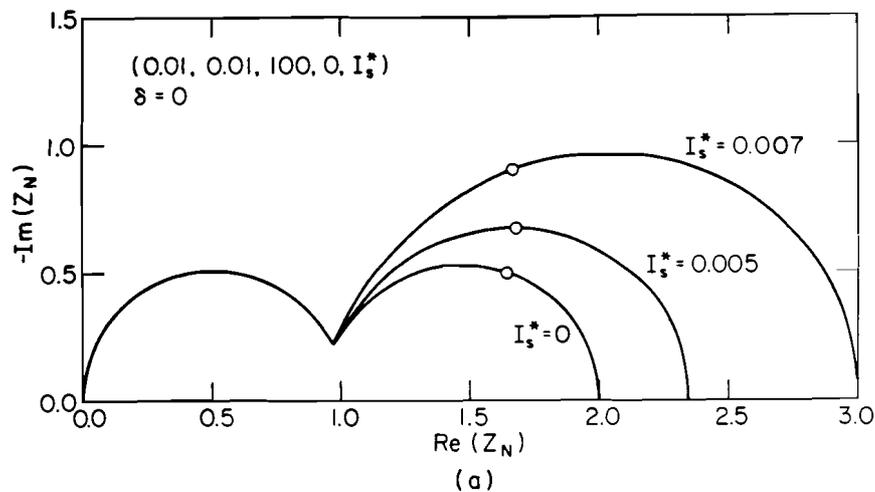


FIGURE 30

Impedance plane plots for  $M = 100$  symmetrical cells with several biasing currents (108). (a) Chang-Jaffé electrode kinetics; (b) Butler-Volmer electrode kinetics. These two figures were originally presented at the Spring 1979 Meeting of the Electrochemical Society, Inc. held in Boston, Mass.

and  $C_2$  varied appreciably and systematically with bias but showed considerably less variation for B-V than for C-J kinetics.

For both supported and unsupported situations, IS  $s$ - $s$  measurements often do not agree with ideal theoretical results. For example, the  $R_R$ - $C_R$  reaction arc appearing in the complex impedance plane is not always found to be a perfect semi-circle with its center on the real axis but often is depressed, with its center below the real axis. Although the exact  $s$ - $s$  theory yields some such depression when  $\pi_m$  is appreciably different from unity (98), the possible amount of depression is insufficient to explain most results. Further, "diffusion" arcs often have high-frequency power-law exponents different from the theoretical  $n = 0.5$  value. Although it appears that the general hierarchical circuit of Fig. 28 (with one or more  $Z_D$ 's set to zero) is an appropriate starting point for fitting either supported or unsupported data, it clearly must be modified for use with data showing non-ideal behavior. One approach which often helps is to replace one or more of the ideal circuit elements or  $Z_D$ 's by more general dce's such as ZC's, WW's, or EDAE's.

Although considerable  $s$ - $s$  frequency response data, both supported and unsupported, have been analyzed, the analysis employed has often fallen short of the state of the art. A representative list of unsupported solid materials whose data have been analyzed might include Na  $\beta$ -alumina (single crystal) (56,57);  $(KBr)_{0.5}(KCN)_{0.5}$  (single crystal) (83); polyphenylene-oxide (polymer film) (106);  $\beta$ - $PbF_2$  (single crystal) (111); lithium nitride (single crystal) (114); and zirconia-yttria (polycrystalline) (115). The data have not always been plotted in ways that show up dubious points; CNLS fitting has not always been used; and most important, too few different models or equivalent circuits have been fitted for a given set of data to allow a best choice to be established with some confidence. Much yet remains to be done, both in developing new theoretical models [e.g., see the recent work on response of three-phase electrodes (116)], and in analyzing data sets in ways worthy of them.

#### Acknowledgments

First, I wish to thank the Army Research Office for their continuing support of my work. Second, it is a pleasure to acknowledge the important contributions of the many associates who have worked with me in the present area over the years, most especially C.A. Barlow, Jr. and D.R. Franceschetti. They met the hard parts head on.

## ACRONYM DEFINITIONS

cm	continuum model
cpm	continuum primitive model
dce	distributed circuit element
dm	discrete model
dpm	discrete primitive model
gedm	Grahame cutoff disk model
igm	ideal-gas model
lgm	lattice-gas model
llgm	layered lattice-gas model
mlgm	modified lattice-gas model
modm	modified cutoff disk model
nm	non-primitive model
p.d.	potential difference
s-s	small-signal
3-D	three dimensional
B-V	Butler-Volmer
C-J	Chang-Jaffé
CHC	Cooper-Harrison catastrophe
CNLS	complex nonlinear least squares
CPE	constant phase element
EDAE	exponential distribution of activation energies
EDL	electrical double layer
ESP	electrode surface plane
GC	Gouy-Chapman
GCS	Gouy-Chapman-Stern
GDAE	Gaussian distribution of activation energies
IHP	inner Helmholtz plane
IS	impedance spectroscopy
MWT	modulus weighted least squares
OHP	outer Helmholtz plane
PWT	proportional weighted least squares
UWT	unweighted least squares
WW	Williams-Watts

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## DISCUSSION

[The following lecture and discussion took place after Dr. Macdonald's address.]

**Dr. Roger Parsons, (Discussion Leader) University of Southampton:** Thank you very much, Ross, for a broad survey. It is a pleasure to be able to continue with the discussion of this problem of electrical double layers and impedance of electrodes and particularly to remember that Ross, as he said, has been a modeler of double layer capacity curves for a very long time and that his 1954 paper was really the first of the detailed models of the measurement of capacity which in particular was based on the experiments made by David Grahame, the first accurate experimental results for this quantity. Although the general features had been known in the work of Frumkin, Grahame provided detailed experimental results which could be modeled in this way.

I would like to start perhaps by talking about impedance although that came second in Ross' talk partly because obviously one has to be able to measure the impedance first in order to get good experimental results for the capacity of the electrical double layer, and I think there have been, in fact, far too few measurements in the simple double layer field over a very wide frequency range.

In fact, frequency dependence measurements for what Ross as a physicist called blocked electrodes, what we as electrochemists call ideal polarized electrodes have been mostly made in rather complex systems of adsorption of organic materials. One thinks of the work of Melik-Gaikazyan in Moscow and of Lorenz in Leipzig who made detailed models of these systems. Rather little has been done in the simpler systems with no specific adsorption, no organic adsorption, and offhand the only measurement I can remember which covers a really wide frequency range is that of Armstrong who showed that the capacity of the double layer in the case of an ideal polarized or blocked electrode, blocked mercury electrode in a non-specifically adsorbed electrolyte showed no frequency dependence up to the region of 1 megahertz.

I think what frequency measurements have been made in these liquid types of systems have been over a much more restricted range, and this is largely because of the experimental inadequacy, that is people have had potentiostats with limited frequency range and that sort of thing. So that I think the electrochemical side of the community has fallen behind the solid state side of the community in these measurements of frequency dependence, and I think it is very important that we do apply the rigorous methods of analysis which Ross has demonstrated in the second part of his talk, to good experimental measurements.

As I say, a lot more has been done on the solid electrolyte side, and of course of the semiconductor side, and there have been numerous arguments about frequency dependence of semiconducting interfaces which perhaps wouldn't have taken place if

people had considered more accurate or more detailed analyses of equivalent circuits, rather than simply plotting the raw experimental data as a function of frequency.

Now, I would like to turn to the earlier part of Ross' lecture, because naturally that is the part which interests me specifically, and to talk about models of the double layer, and particularly the comparison of these with experiment.

I think it is remarkable that such a simple system has turned out to be so complex in its understanding. I think we can still usefully divide this interfacial region into three parts, the diffuse layer part where we have no specific interaction of the components of the solution with the electrode, the inner layer part and the metal, or semiconductor, but I shall talk mostly about metals. Strictly speaking, we ought to solve the problem as a whole and not divide it up into three parts, but this division into three parts does seem to be a useful one, and I shall stick to it for this part of the discussion and talk about those three parts separately, and I would like to start by talking about the diffuse part of the double layer.

Let me first of all talk about the diffuse layer and point out that although I think the model which Ross talked about, the idea of a lattice gas model, is certainly going to be extremely useful, the conventional Gouy-Chapman theory is still remarkably good.

Let me remind you of some calculations which were done in 1964 by Hurwitz and Sanfeld in which they allowed for not only the finite size of the ions in the diffuse part of the double layer but, also, the effect of dielectric saturation in that region and point out in some detail that the capacity of the Gouy-Chapman layer, that is, not the total capacity but just that of the diffuse region, was modified only to a rather small extent at rather extreme charge values when you used an improved model, and the general result of their work, which I think is still quite valid, is that if you are interested in a relation between amount of substance, adsorbed charge or total charge and potential in that region, then there are fairly substantial deviations from the Gouy-Chapman theory as you increase the electrical conditions and make the charge greater or the potential greater, but if you are interested in the relation between charge and charge, for example, the amount of cation adsorption and the amount of anion adsorption, then the modification simply shifts you a bit up on the line, but you are still on that line. A good expression of the relation between amounts of substance in the double layer and charge on the electrode is still given by Gouy-Chapman theory for 1-1 electrolytes.

Now, that has been maintained by the simulations of Torrie and Valleau which Ross mentioned, and this is one example of their data; what they call the modified Gouy-Chapman theory, MGC, is simply a Gouy-Chapman theory with an inner layer. It uses the full equations of the diffuse layer model, and their simulation points are the points on this diagram, and you see that the amount adsorbed as a function of distance is remarkably good in the Gouy-Chapman model. That is for a reduced charge entity of .3 which if you take .3 nanometer spherical ions is about 50 microcoulombs per square centimeter. So, it is quite a large charge on the electrode.

Similar sort of results were obtained by them for one mol  $\ell^{-1}$  solution, and even in one mol  $\ell^{-1}$  solution, when you look at the potential distance relation, it is still not too bad. There are deviations at that charge in the potential profile, although they are not so serious in the concentration profiles.

On the other hand, if you go to unsymmetrical or higher charged electrodes, if you look at 2-1 electrolytes, then the discrepancies are really enormous. The Gouy-Chapman theory breaks down in a very substantial way for these unsymmetrical or highly charged electrolytes. As I say, this is a 2-1 electrolyte, and it would be interesting to know whether a lattice gas model can cope with that sort of situation of an unsymmetrical electrolyte.

One of the problems with diffuse layer theory is that it is very difficult to test it experimentally. You can test it against a computer simulation and show up some of the deficiencies in that way, but it is difficult to do an experimental test. We attempted one a few years ago with some success, I think, again, for rather dilute solutions and including unsymmetrical electrolytes which appear to show that in the region of about 0.1 mol  $\ell^{-1}$  solution the model was reasonably adequate. So, my feeling is that a lattice gas model may take us further than the Gouy-Chapman theory, and for that reason is important, but for many simple situations where we have less highly charged electrolytes, less extreme conditions, the Gouy-Chapman theory will do reasonably well.

Now, it is important that we do know this because there are many ways in which we use the theory of the diffuse layer, not only in electrode electrolyte interfaces but in other situations, for example, in colloid chemistry we use it to determine true surface areas of colloidal suspensions. We, also, need it in order to define the situation at metal electrodes when we come to think about specific adsorption because although people have talked about specific adsorption in different terms, what they always actually do when they calculate the amount of material which is specifically adsorbed is to compare the experimental adsorption with that calculated from Gouy-Chapman theory, and for that reason one needs to have accurate models of the diffuse layer.

So, let me turn to the second region, the inner region in which, also, Ross has made substantial contributions, first of all in the question of the inner layer in the absence of ionic penetration; that is a simple situation where you have a metal surface faced by a diffuse layer, and what we generally believe is a monolayer of solvent molecules in between.

In his first paper on this subject in 1954, Ross emphasized the model which I think has become fairly widely accepted. There are critics, and we shall certainly hear from them, but most people accept the idea that the general shape of this curve is due to dielectric saturation of this monolayer, that is rotation of dipoles resulting in a saturation effect combined with a certain amount of electrostriction, and I think it is

perhaps interesting to give a direct piece of experimental evidence for that electrostriction part.

If you look at the reflection spectrum of an electrode in the visible and you analyze this in terms of the change in the reflectance due to change in double layer structure, it is possible, as Alan Bewick showed first, that you can analyze the part due to the inner layer in terms of the compression effect in the inner layer.

As you increase the charge, and this shows the results for polycrystal and single crystal gold surfaces, as you go to negative charges, there is a change in the density of that inner layer by an amount of about up to 10 percent, depending on the face of the crystal, and I think this is quite reasonable and fairly direct experimental evidence for that electrostriction effect.

The fact that I have shown you results for solid metal electrodes brings me on to the point that I think a lot of double layer modeling has concentrated on those results of David Grahame's. Those results were, of course, of critical importance for the development of double layer models, but in more recent years, we have had results from other metals which are, I think, now equally reliable, and let me show you one example of experimental results for a silver electrode. This is a single crystal silver electrode for a particular orientation exposing the (110) surface. That is a surface with a rail-like structure, and for an anion which appears to be not specifically adsorbed, that is we have a situation here where we have this rather simple model of a metal surface up against a space charge in the electrolyte, that is a diffuse double layer. You will notice first of all that the curve in this case is remarkably symmetrical and the capacities are on the whole rather larger than they are for the mercury electrode.

Now, if you assume that this can be represented as a series equivalent circuit of the inner layer capacity in series with the diffuse layer, and you use Gouy-Chapman theory to subtract off the diffuse layer part, the remaining inner layer capacitance is essentially concentration independent. There is a slight dependence in this region here at the more positive charges, but it is very slight, and the inner layer capacitance shows this rather high value with its maximum at zero charge and a rather symmetrical sort of behavior.

This is fairly general as far as we know for this type of electrode. That is another face of silver, and that is a particular face of gold on the same scale which shows rather similar behavior, and what I want to do by superimposing these is to contrast that with the mercury electrode at zero degrees celsius which is the condition where you have the maximum of the value of this hump which features in so many of the theories, and to contrast that behavior of mercury with the behavior of these solid metals, so that I think that this sort of experimental result has broadened the range of types of behavior which the models have to account for, and many of the recent models have attempted to do this.

I should, also, mention in terms of more recent experiments that more direct studies of solvent behavior in the inner layer are now possible both by infrared reflection spectroscopy and by Raman spectroscopy. These seem to suggest that there is some degree of polymerization of the water in the inner layer, and that makes one think that perhaps models which represent the solvent as a simple hard sphere assembly with a dipole, either point or finite is bound to be oversimplified. Not everybody agrees about that, but there are certainly more sophisticated sorts of behavior of interfaces of this type which must depend on something like hydrogen bonding or more sophisticated aggregation types of behavior of the solvent molecule. Going back to the Grahame experiment, that is where we start from. Staying with mercury, there is a notable isotope effect. As we compare water with  $D_2O$ , it is about 5 percent in the capacity, and this is difficult to account for obviously by a model which is just a hard sphere with a dipole.

If we look at adsorption of organic species where we could change the structure in a rather simple way, these old results of one of my MSc students shows the behavior of sodium maleate, that is the maleate anion where you have the two carboxyl groups on the same side of the molecule with that of fumarate where you have them on the opposite side. These two anions are adsorbed to a very similar extent, but yet they change the directly observable features of the capacity curve by a remarkable way, and this seems likely to be due to the interaction of the different geometries of the anion with solvent.

One gets even more surprising results in the case of sugar-related molecules where there is a very minor change in the structure of the molecule, simply a geometrical change or a chiral change at one carbon atom, and again, a directly reflected change in the observed capacity curve.

So, I think I would agree very much with Ross in his remark that we have a mountain still to climb, that this sort of behavior is going to require much more sophisticated models to account for the complexity of water structure. We all know that water is a very complicated liquid.

Let me then go on to the second region or another section of the second region where we have specific adsorption, and again, make the point that we tend to concentrate in our modeling too much on mercury and make this point by looking again, at a silver electrode with the adsorption of halide ion and point out that if we look at different faces of the silver ion, the silver electrode where we simply have a different geometrical structure of the metal surface that you can see even qualitatively that the observed capacity curve changes very substantially as you change from one face to another.

That is one aspect of the problem, and if we look in more detail at one particular face, this is again the (110) face, and we are adsorbing chloride ion in the presence of a

non-adsorbed anion, the hexafluorophosphate ion, these curves show you the curve in the absence of adsorption in the case of the  $\text{PF}_6^-$  by itself. As we add chloride ion, the capacity increases over the whole range which chloride ion is adsorbed. It is desorbed, of course, at more negative potentials as a result of the electric field, and then it adsorbs as you go through to more positive potentials.

Now, one feature which I think is important here when you think about the model of the cut-off disk and the transition perhaps from a disordered structure here to a hexagonal ordered structure at higher concentrations and then perhaps a limiting structure due to the repulsive forces between the anions adsorbed in a monolayer on the surface, is first of all one quantitative contrast of these results with those of mercury is that we can go to much higher coverages in the case of solid metals. We can get up to a structure here which is almost a saturation. It is a  $c(5 \times 2)$  structure which fits into the rails of that (110) surface, and if the experimental results in the analysis are sufficiently accurate, and it does become less accurate at the more highly adsorbed region, at the more positive charges, but they seem to indicate that we are getting a really saturated monolayer of halide ion, that is something like 110 microcoulombs or something like  $10^{15}$  ions per square centimeter at the more positive end of the curve.

It is difficult to imagine how this can happen when you have a full charge on the ions in the monolayer because of the strong repulsive forces so that one other possibility that one must consider, I think, is the fact that the ions transfer some of their charge as they become chemisorbed on the electrode, and you can see that perhaps this does happen, if you analyze these results in more detail by looking at the potential shift which occurs as a result of the anion being adsorbed on the electrode surface.

Now, the conventional way of plotting these is to consider a constant charge on the electrode, let us take a line like this, where we have a constant charge on the silver electrode. We change the concentration so that we change the amount adsorbed, and we get a series of points as the solution concentration increases, going along this line.

However, you can interpolate on here the situation where you have a charge on the metal electrode exactly the same as the charge on the adsorbed monolayer. In other words, you have an electrically neutral system which corresponds to the anion adsorbed onto the metal surface, and that is indicated by the red point on that diagram.

The slope of that line is not too dissimilar from the sort of results you get in ultra high vacuum when you dose a silver surface with in this case a bromide ion. These are the most detailed results in the literature. You notice first of all that the shift of potential, the change in the work function as a function of the bromide on the surface is remarkably linear right up to the monolayer behavior, and this is, also, remarkably linear, although over a rather smaller range. The slope of those curves is given here which in the case of silver (111) bromide in the gas phase is 26 millivolts per microcoulomb per square centimeter adsorbed.

The red entries here correspond to ultra high vacuum system. The blue entries correspond to the liquid system with silver electrodes, the green to mercury electrodes in aqueous solution, and the one black entry to mercury in a non-aqueous solution.

Now, if you interpret the slope of those plots in terms of an ion adsorbing with its image in the metal surface, that is a dipole with unit charge on the ion and on the metal, the internuclear distance between those charges is a few tens of picometers, that is a few tenths of an angstrom; in other words, that dipole is a very short dipole if it retains its full charge, so that this sort of result suggests that in modeling the adsorption of anions on the surface, not only of mercury but of solid metals in the vacuum and in solution that one has to consider that this ion does not retain its full charge, and this needs to be taken account of in the modeling.

Let me finally turn to the metal surface. I do not have much to say about the metal surface. A long time ago, O. K. Rice in 1926, suggested that there would be a diffuse layer in the metal surface, as well as in the aqueous solution adjoining it, and this idea has been taken up more recently after being discarded for many years. It was first realized that this diffuse layer in the metal is of rather small dimension, the Thomas-Fermi screening distance being rather short because of the high concentration of carriers in the metal. Nevertheless, as the potential changes, the charge and therefore the local density of electrons in the surface changes, and the electronic profile in the metal surface will change with potential; this could, and indeed may well contribute substantially to the experimental capacitance, and particularly Badiali et al in Paris and Henderson and Schmickler in Bonn and San Jose and Dogonadze and Kornyshev in Moscow have modeled this situation and suggested that there is, in fact, a substantial contribution from metal. Ross mentioned the recent work of Henderson in terms of the mean spherical approximation and an exact statistical theory of this situation of hard sphere ions with hard sphere dipoles. He has extended this with Schmickler and combined it with a model for the electron distribution in metal, and very recently they have extended the electrolyte model in a rather empirical way away from the potential of zero charge, and they have, in fact, produced, with rather few adjustable parameters though admittedly with some, a model of the capacity curve over substantial ranges of charge which compares fairly reasonably with experimental capacity, so that I think what one needs now is a way of examining the contribution of the metal and perhaps electroreflectance will provide that. It tells us quite a lot about electron structure in the metal surface, but at the moment it doesn't help us, as far as I know in terms of the experimental capacity, so that I think there are many aspects of the electrode solution interface in particular which have been developed both experimentally and theoretically to a remarkable extent in the last few years, but there is still a lot to do, and I am sure that the discussion will bring out not only perhaps some answers, but some questions.

So, may I ask for questions, and may I ask people who contribute to the discussion to stand up, use the microphone and identify themselves when they want to make a contribution.

John Bockris, would you like to lead off?

**Dr. John O'M. Bockris, Texas A&M University:** It has been said that there is a mountain of difficulties in front of us here. Before I get to mention some four of them, I would like to put in a historical point because I have been in this game about as long as Ross Macdonald, and I would like to say a word of appreciation about Ross' work in respect to water dipoles and the double layer. I think that most persons who deal in this field talk about Watts Tobin and perhaps BDM, but it is often that the pioneering work which Ross Macdonald put in on water in the double layer gets left out. We should acknowledge the reconsiderable contributions made in the early 1960's.

Now, to the four points that I would like to make to contribute to the discussion. The first concerns the  $C_{\text{dipole}}$ , which is supposed to explain capacitance humps, perhaps most of the humps in the mercury case. Perhaps it does. However, I want to point out that a considerable numerical difficulty turns up in these interpretations if one takes into account the interaction between these dipoles, as we did in B.D.M.

You see, one measures  $C_{\text{double layer}}$ , and then the relation is:

$$\frac{1}{C_{\text{double layer}}} = \frac{1}{C_{\text{ions}}} + \frac{1}{C_{\text{dipole}}}$$

If one neglects lateral interaction,  $C_{\text{dipole}}$  is fairly small, so that its variation with potential has important effects on  $C_{\text{double layer}}$ . However, directly  $C_{\text{dipole}}$  is effected by lateral interaction, it becomes large, and the effect on  $C_{\text{double layer}}$  is greatly decreased.

So, any interpretation of a hump which is dipole dependent then has got to take into and ask how much that C dipole effect gets expunged by the effects of dipole-dipole interaction. That is my first point.

My second point is to refer to the part of the C-q relation which is often neglected. Ross did give it a passing mention, it is the part on the left, or the positive end where it goes up. It has been discussed along the years but seldom quantitatively, and I would like to point out that if you take into account some reasonable equations for the growing dispersion interactions between the ions, the lateral dispersion interactions which are independent of charge, you can make a reasonable account of the positive region. Of course, it may, also, be that we are losing some charge and forming some chemical bonds across the double layer as it gets more positive.

Then two last points concern some of the remarks that Roger Parsons has been making, and I would like to say that the validity of the diffuse layer corrections worries

me a good deal more than it worries him. I think the situation is difficult to test. You can test one theory against another, but where are the clear independent testing experiments? For example, how about  $C_{\text{diffuse}}$  calculated from diffuse layer theory and measured by radio tracer measurements?

Now the use we make of diffuse layer theory is in the concentrated part, always up at 0.1 molar and 1 molar when we are calculating our specific adsorptions, and that is just then that the theory becomes weakest; and I must say that looking back on my own work, for example, and that of others, I suspect the results we have had on  $q_{\text{specific adsorption}}$  at more concentrated situations are doubtful because they have always had to use the Gouy theory; and I welcome Ross' contribution here and believe that it may lead to some better approximation.

Lastly and briefly then, in respect to the Thomas-Fermi length, this is a fairly new dimension, although it came with O. K. Rice in 1929, and surely it should be given more attention than we are doing. It should be in the center of the game especially in respect to solid electrodes, and surely one can look at the great differences in capacitance that we see in these solid electrodes, often as far as the inner layer goes as a function of the effect of that Fermi length on the capacitance.

Thank you.

**Dr. Parsons:** Ross?

**Dr. Macdonald:** Thank you for your kind words, John, and I would like to pick up just a little bit on the matter of the field penetration model that both you and Roger mentioned. I fully agree that it is a fascinating and an interesting area. I would like to bring out a point that I did not think was made entirely clear by the discussions. I have something about it in my paper but did not have time to discuss it in this talk. The original Rice calculation led to a contribution to the thickness of the inner layer of a few tenths of angstroms, maybe up to .4 or so, and the idea was field penetration into the metal, as Roger said, the Thomas-Fermi distance, but my understanding of the modern treatments of Schmickler and others is that they have done a little more quantum mechanics, and the treatment, instead of increasing the thickness of the inner layer, decreases the thickness because of electron wave function overlap out into the inner layer itself, so that the first treatment gave a positive contribution to the thickness. The modern one seems to yield a negative one, and in fact, it involves a certain amount of dependence on whether the charge on the metal is positive and negative, just as one would expect for electron wave function overlap.

**Dr. Parsons:** Yes, I think that is true, and I think, also, the point is that it is not just the static contribution. It is the fact that the effective edge of the electron profile changes with potential which is important.

They have, also, developed the models with sufficient sophistication by using a jellium model with pseudopotentials to represent the ionic cores in the lattice. They are able to make a prediction about the effect of geometry of the surface.

**Dr. J. M. Saveant, (Speaker) Universite de Paris:** You showed, just a small question about the capacity curve you showed in the presence of mannitol and sorbitol, and you had very sizeable differences between the two, and as you mentioned, the two compounds differ very little. Have you any kind of explanation?

**Dr. Parsons:** Not really, only that there must be some relation with water structure, but I must say that those results surprised me very much. They have only been done once, that is true, but they have been done on other types of compounds. There are other examples where very small geometric differences do provoke large changes in capacity.

**Dr. Macdonald:** Let me make one more minor comment about the diffuse layer. I generally agree with the comments of both John and Roger. I think that the diffuse layer is interesting in its structure and its calculation, primarily again because it is there, and it is something that we would like to really understand in detail, but from the same point of view or even from another point of view, one might say that if there is something that does not make any particular experimental difference, then why should you care what it is doing?

I care, and some other people care, but it is true that as John points out, it may not make all that much difference in many cases whether you use the Gouy-Chapman model or whether you use a more complicated model. Particularly though, as you go toward saturation, a more complicated model is desirable, but it is just in that region where the effects of the diffuse layer are obscured. There, one over its capacitance is small and other effects dominate.

So, while the Gouy-Chapman may be, in fact, quite adequate for many calculations, even if it is, I think it is of interest to try to get a better model, and if nothing else, to compare it with Monte Carlo simulation results, and maybe in the future it will be possible to compare it over a wider range with actual experimental results, though it is hard to see how.

**Dr. Parsons:** Perhaps I could interject at that point that it is possible to do a limited experimental test by looking at the adsorption of cations of different charge. When you have two cations which are non-specifically adsorbed, and the experiment we did was with potassium and magnesium, the amount adsorbed is sensitive to the potential profile, and as I pointed out, it is the potential profile which is sensitive to the model.

Now, in that test that we did carry out with Sergio Trasatti, the comparison of adsorption of magnesium and potassium seemed to fit in reasonably well with Gouy-Chapman theory. Certainly the concentrations were not as high as one mol  $\ell^{-1}$ . They were about the region of 0.1 mol  $\ell^{-1}$ , but that seems to me the way to go, if you want to test Gouy-Chapman theory in the more detailed way.

Martin?

**Dr. Martin Fleischmann, (Speaker) University of Southampton:** What concerns me, and John Bockris has alluded to this, is what independent methods have we really got? In the development of the theory, what has usually been done is to use the Gouy-Chapman theory or some modification in order to obtain information about the inner Helmholtz layer, and as John mentioned, we really do need independent checks. If you use diffraction techniques, you find that the behaviour is much more complicated than is normally assumed for the interpretation of electrochemical measurements as I will show this afternoon. The solvent and the ions show long range ordering and spectroscopy shows that there is interaction between the ions and the solvent and between the ions and organic species. There is some hope that such measurements could be made quantitative. So, it might, in fact, be more sensible to go the other way around, namely, to measure the total capacity of the double layer and then go backwards and try to get some estimate of the diffuse double layer capacity, if that is what one is interested in.

We ought, perhaps, to try during these two and one-half days to find some time to discuss how we could test the part of the solution further removed from the inner double layer, what methods we might have available, and what techniques could be developed. For example, infrared reflection/adsorption spectroscopy, which depends on the modulation of the light beam between the perpendicular and parallel polarization states should be able to test the amounts of material and the distribution of material right into the body of the solution, if it were done in a sufficiently detailed way, and that might be a profitable approach.

**Dr. Peter Schmidt, Oakland University:** Two comments have been made that I would like to comment further upon, one by Martin and one by Professor Macdonald.

The Monte Carlo approach is an interesting one which is underexplored right now. I think what I am finding, and I do Monte Carlo calculations to stimulate kinetics, is that the theory which has evolved over the years, largely from formal statistical mechanics and largely from attempts to apply it using continuum ideas, has to be modified drastically when one tries the Monte Carlo methods.

Martin's comments, at this time, with respect to an experimentalist point of view, in fact, support this. The theory and the experiment demand a change of view, I think, in how we are going to model a number of things. The insistence on the diffuse double layer or the insistence on the dielectric continuum with respect to electron transfer theory as examples, force us into a way of thinking which, when you try to go to a Monte Carlo type of approach, is impossible to implement. As a matter of fact, what one finds is that the Monte Carlo approach requires that you think in terms of very discrete, which is probably a silly way to say it, but certainly discrete molecular and atomic models with specific forms of interactions between them and then build that up, eventually reaching the semidiscrete and continuum limits. In the process of so doing, I think one will find that there are new experiments which will be suggested.

The enthusiasm for the Monte Carlo method which is growing, and I think will grow in the next five years to perhaps an overwhelming degree, should be tempered with the fact that I think we gain in the end a tremendous amount of physical insight when we attempt to generalize, as we have always done with theory and its development in the past, to find simpler expressions which encompass a wide variety of phenomena and include accurate accounts for points in large sets of data.

In contrast, the Monte Carlo method really gives you a number. You can make all sorts of assumptions, but it is sometimes difficult to trace the physics and the chemistry, especially when the Cray computer is at work generating these numbers for us at lightning speed in the middle of the night, whenever you can get time on it.

Thank you.

**Dr. Parsons:** Thank you. I think, also, it is worth pointing out that the Monte Carlo results which I showed and which Ross was talking about done by Torrie and Valleau are not for a system of discrete solvent particles. They are for a system of spherical ions moving in the dielectric continuum, so that this is only really a test of the Gouy-Chapman theory in its own predictions. It is not a test of the experimental situation, not even very close to it.

**Dr. Mark Wrighton, (Discussion Leader) Massachusetts Institute of Technology:** Roger, I would like to ask you a question first. You showed data concerning the adsorption of chloride on silver as a function of potential and concentration of chloride. In that data, you showed a region where, or one voltage in fact, where there was no change in the capacitance as a function of chloride concentration. What can you conclude special about that point?

**Dr. Parsons:** I have no answer to that, I am afraid. You are talking about a sort of isosbestic point. I don't know. As far as I know, it is not a special point. It is a coincidence, but it does occur in all capacity curves, and it occurs, also, as a function of temperature in Grahame's curves, but in that case it is an entropy maximum, but in this case I don't know any particular feature that we can get out of those curves. It is one of the things we still have to explain.

**Dr. Wrighton:** I have a question that concerns impedance spectroscopy. I would suspect that most of the people are, in fact, chemists, not physicists, at least those in this room, and we are accused of being narrowminded. Perhaps singleminded is better, but we focus on molecular structure and reactions, and I wonder considering that with impedance spectroscopy you can come up with a number of equivalent circuits to become consistent with the data, whether impedance spectroscopy is going to be generally useful to people who want to understand structured reactivity?

**Dr. Macdonald:** May I answer that?

**Dr. Parsons:** Please?

**Dr. Macdonald:** I tried to allay that fear somewhat but obviously did not entirely succeed. First of all, one will never find two or more equivalent circuits that can fit the data equally well unless they are made up only of R's and C's. In most cases, however, the data cannot be fit by just R's and C's because distributed elements are required as well. When distributed elements are needed, only one circuit generally is found to be able to fit the data.

Secondly, even if it were the case that two different equivalent circuits could fit the data equally well, we can generally distinguish between them on physical bases by varying other things like temperature. The big ambiguity though, as I said, is that some of the older heuristic distributed circuit elements, Cole-Cole, Havriliak-Negami, and many other such elements, were just kind of put together to give the sort of shape that one found experimentally, and from them you can find a distribution of relaxation times, but it may be virtually meaningless. A good fit does not necessarily imply that the corresponding one distribution is the true one of the system because it turns out that there is a great deal of holistic behavior here. One can take quite different distributions of relaxation times and calculate the frequency response from them and find that except perhaps to .1 percent differences in the wings, they will give almost exactly the same response, behavior which means, of course, that it is almost impossible to go from always inaccurate experimental frequency response back to a meaningful distribution of relaxation times. It isn't quite so bad for distribution of activation energies, but again, the point is that one really needs a detailed many-body long-range interaction theory of the motion of charges in a solid or liquid that yields impedance as a function of frequency, and usually one does not have that, although Franceschetti and I have produced a reasonably simple one that has been adequate for some cases. Anyway, one usually does not have available a sufficiently accurate microscopic theory, and even when one does it, it is exceedingly complicated. If one does not have such a theory available, one does have to use some kind of an equivalent circuit, and as I tried to bring out, it will usually require at least one and maybe more than one distributed circuit element. That is where ambiguity may enter, in that two or three different distributed elements might yield equally good fits. As I said, an exponential distribution of activation energies distributed element can fit all of the other ones, both symmetric and unsymmetric in frequency very well, but they do not all have the same temperature dependence predictions, particularly of the power-law exponents, and so by changing temperature and oxygen tension and other things one at least has a hope to distinguish between possible elements and find a most plausible circuit. But without having looked at all possible ones, one obviously cannot say that a given circuit is the absolute best one because you probably have not found it. Nevertheless, you can at least get the best that you have tried, and can distinguish it from all others on the basis of simplicity and variation of parameters with temperature and other things of that kind.

While I am at the microphone, I would like to say another quick word about Monte Carlo, picking up the discussion we just had. I agree pretty much with what was said there. The Torrie and Valleau treatments use a homogeneous background dielectric constant of 78.5, or something like that, for a water situation, and yet you have ions all through the solution. Certainly in the neighborhood of an ion you would expect that the surrounding water molecules would be rotated and would not be as free to move and therefore to yield the full bulk dielectric constant. Thus, a much better Monte Carlo treatment, which would be much more difficult but eventually will certainly be possible in my opinion, is if one considers both discrete ions and molecules, and does Monte Carlo on them, assuming for the molecules that they have finite or infinitesimal permanent dipoles and allows both the ions and the molecules to have induced polarizability as well. All of this together will lead to a position-dependent effective dielectric constant, insofar as such a concept is then pertinent at all. On the average it may lead to a reasonable value, but this is a very difficult prescription, particularly because when we eliminate the background dielectric constant of 78, we greatly increase the coulomb interactions between ions, and it is very, very difficult to make Monte Carlo work under those conditions, which is, of course, why a value of 78 has been used so far.

**Dr. Parsons:** Martin?

**Dr. Fleischmann:** I have a comment on Mark Wrighton's comment and a question for Ross Macdonald. Of course, it is true that one is worried about the applicability of impedance spectroscopy, but if one approaches it from the chemical point of view, this has in a sense, a bad side, but at the same time a good side, namely that you can observe other impedance elements. For example, you can get inductances or negative resistances. For example, looking at our Chairman of this meeting you will recall the passivation curves of a metal which has regions of negative resistance or what used to be called the dynatron characteristic in passivation. So, very strange phenomena can appear, and just because of their strangeness, you say "This must have some sort of unique interpretation." I think that when you go to rather complicated systems, in a way the system does help you to carry out an analysis.

I have a question for Ross, which concerns the non-linear regression routines which we have also been interested in over the years, but there is a problem, really about the observability of vectors. Generally speaking the information derived depends on the orthogonality of the vectors in Hilbert space. If they are colinear you will never get anything at all. How do you assess the situation? There are other possible no-value judgement type data processing techniques, such as maximum entropy methods. How would your judgement be now of using non-linear regression techniques versus, say maximum entropy data processing?

**Dr. Macdonald:** That is a hard question. Before I address that, let me just show one slide to pick up something Martin just said. The bottom AR curve that I showed is in fact, a region of adsorption that has both negative differential capacitance and negative resistance.

The part up at the top shows positive differential adsorption capacitance but negative resistance. So, all of these are included, and in fact, arise from the Franceschetti-Macdonald model that I spoke of, one that is represented pretty well by a hierarchical equivalent circuit of the kind that I showed where one lets the differential capacitance and resistances become negative when they need to. In fact by using a complex relaxation time in the model, one generalizes a reacting model to a reactive-adsorption situation, and it is that that can lead to these rather complicated curves with positive and negative capacitances and all the rest.

I should say about inductance that while it is true that inertial effects of charge carriers can clearly lead to inductive effects, these will generally appear at 100 megahertz or higher, beyond the usual range of interest. When one makes impedance spectroscopy measurements and finds what appear to be inductive effects, if they are not due to just the wiring of the cell, and that is a very small inductance, one often finds an inductance that might have to be as large as one henry or something of that nature. I prefer to consider that as a negative capacitance. It then is a negative capacitance of reasonable value, and the inductive value, if it were a true inductance, would represent a tremendous amount of storage of energy in a magnetic field. In fact, all one has here is just the kind of a phase shift which one can represent either by inductance or by negative capacitance and resistance, but personally I prefer the negative capacitance approach as being a clearer situation, but it, again, is just a way of showing different kinds of phase shifts coming in.

Do you want to say something to that, before I go to your other question?

**Dr. Fleischmann:** You said catalysis would give you something which will be inductive?

**Dr. Macdonald:** I believe that I can represent almost any circuit that contains an inductance by negative resistances and capacitances.

**Dr. Fleischmann:** Whether that is bulk or —

**Dr. Macdonald:** Maybe not. For electrocrystallization, though, or something like that where you might have inductive phase shift, it is not plausible to believe that there is a lot of storage of energy in a magnetic field under those conditions either. So, who knows? But I think we should look at it carefully.

Now, as to your question about analyzing data with complex nonlinear least squares, let me bring up first an important point that bears on what you said but that I did not discuss. When one carries out nonlinear least squares fitting of some data, one usually does not do just fitting with unit weight or no weighting at all. The reason for

this is that often in these measurements one has a variation of the real or imaginary or both parts of the data over a wide frequency range where it can vary by a factor of 100 or 1000 or more. So, we have some very small pieces of data and some very large ones. If we use unity weighting, then only the large ones would determine the parameters, and that would not be very sensible. In the region where they are small, you still want to determine the parameters that are appropriate in that region. So, one has to use non-unity weighting, and one of the possibilities is to use weighting that is determined by taking the individual data values and saying that the uncertainty of a value is proportional to its magnitude. This is what I call proportional weighting. Then one takes one over the square of that as being the actual weight for the point and does that individually for the real and imaginary parts. Other people take the modulus of the data and use that in determining the weighting. I have just been doing some numerical experiments that suggest that the modulus approach is not very appropriate, but certainly you do need to use some kind of weighting different from unity for most typical data. If the data vary only by a factor of three, which is usually not the case, then you do not need to. The other point is that if the data is exceedingly accurate, and I mean, very, very, very accurate, then it doesn't matter what kind of weighting you use, you will get the right answer, but usually you do not have such accurate data.

Now, as to using other methods than complex nonlinear least squares, I should mention that some people believe that it is worthwhile to use, for example, Kronig-Kramers relations. They measure the real part and then do an integration over all frequencies to get the imaginary part from that and vice versa and then see how they agree. If you have no model, no equivalent circuit with which to compare the data, that is, indeed, a good thing to do. I was talking to Digby Macdonald recently, and he said sometimes when he carries out such an analysis, and he is one of the leaders of this approach, that he gets disagreement, that when he does the Kronig-Kramers on the real part, it does not lead to what he measured on the imaginary part. Such a result means that the system is not minimum phase, which is quite surprising, but it is within the realm of possibilities in some cases and may particularly arise from time variation of the properties of the system.

As to the matter of the vectors being colinear, let me approach that indirectly by saying that the more parameters that you are trying to determine from the data, the higher order minimization problem you have in vector space. You might have 10 parameters to determine, and you are then trying to find an absolute minimum in 10 dimensions, and particularly when you are dealing with nonlinear situations, as you virtually always are in terms of how the parameters enter the model, it turns out that you have to solve the least squares fit by iterative methods, and it does not always converge to the absolute minimum but instead to a local minimum in that complicated 10-dimensional space, and so, in that sense the approach is not absolutely objective, but there are ways to try to get around this somewhat. One of them is to start from many

different positions or guesses of your parameters, and if all such runs come out with a final set of parameters that is the same, the result is likely to be the least squares solution. I have developed a complex nonlinear least squares program, which incidentally is available for anybody who wants it, that has two stages. It first does a least squares fitting by very powerful methods that do not have to invert a system matrix, and it always converges, but it does not always necessarily converge to the right answer. I then take the results of the first stage and feed them into a more sensitive Marquadt algorithm that does not always converge but does usually converge if it is close to the right answer. So if the results of the first stage, when fed into the second one, do not converge, then that is good evidence that one should go back and try a different set of parameter guesses and see what happens.

When the vectors are colinear, first of all, the procedure may not converge, but if it converges, one might find two parameter estimates that are either very nearly the same and/or may not be very well determined, or at least one parameter estimate that is not well determined. If its relative standard error is of the order of 30 percent or more, the data just cannot determine that parameter adequately. If that is the case, one wipes it out of the circuit and tries again without it, and one generally finds that the other parameter uncertainties are improved by doing that.

So, one has many different choices and things to try here. It doesn't always work, but it does usually work. Also, when one obtains a reasonable fit to the circuit, one does not have to do Kronig-Kramers analysis because the circuits that are used are all minimum phase and guarantee that the real and imaginary parts of their response satisfy the Kronig-Kramers relations. This is a useful result since there are problems with Kronig-Kramers analysis. Ideally it requires data all the way from zero to infinite frequencies, which means that since one does not have such data, it is necessary to extrapolate in those regions, and that can possibly lead to some errors.

As far as minimum entropy and maximum entropy and things like that are concerned, I have looked a bit at the problem of deconvolution, which is where this approach has particularly been used in seismic and other geophysics problems. In fact, it was more or less invented by John Burg for geophysical application, the entropy approach, and —

**Dr. Parsons:** Ross, I think we should come to —

**Dr. Macdonald:** I will finish in 1 second. All I can say is that my own investigations have suggested that it is not very useful in this particular area, but maybe somebody else who is smarter than I can do better with it.

**Dr. Parsons:** Thank you very much. Sorry to cut you off, but we are running out of time, and I am sure there are other questions, but it is appropriate that Ross has the last word, and let us thank him very much, indeed, for his speech.

**Dr. Macdonald:** As the last word, or two, I want to thank Roger for his cogent comments and most interesting work.