# ELECTRODE KINETICS, EQUIVALENT CIRCUITS, AND SYSTEM CHARACTERIZATION: SMALL-SIGNAL CONDITIONS \*1.2

### DONALD R. FRANCESCHETTI and J. ROSS MACDONALD

Department of Physics and Astronomy, University of North Carolina, Chapel Hill, N.C. 27514 (U.S.A.)

(Received 17th January 1977)

## ABSTRACT

The small-signal steady-state response around the point of zero charge of an electrode/ material system is examined for an unsupported electrolyte (material) with two species of charge carrier of arbitrary mobilities and valence numbers and with arbitrary intrinsic/extrinsic conduction character, taking full account of bulk, electrode reaction, sequential adsorption, and diffusion processes. The exact solution of the transport equations of the problem for generalized Chang-Jaffé single-point boundary conditions is compared with the responses of a variety of plausible equivalent circuits, using a complex least squares fitting technique. A hierarchical circuit is found which closely reproduces the exact results when charge of one sign is completely blocked without adsorption, except for some of the cases in which diffusion and reaction effects interfere with each other. The circuit is composed of frequency-independent lumped capacitances and resistances separately identified with bulk, reaction, and adsorption/reaction processes and a single, finite-length, Warburg-like impedance for diffusion effects. Relations between the circuit elements and microscopic electrode/material parameters are found and apply irrespective of the time-frequency overlap between bulk, reaction, and adsorption processes. It is also found that the reaction and adsorption resistances and the adsorption capacitance are all strongly interrelated. The circuit may be used with simultaneous non-linear least squares fitting of the real and imaginary parts of experimental impedance data to obtain estimates of the values of circuit elements and thus of the values of the microscopic parameters characterizing the electrode/material system.

The relationship of small-signal response for overpotential-dependent electrode kinetics to that obtained for Chang-Jaffé boundary conditions is then considered. The reaction resistance and adsorption capacitance are found to be formally identical for Butler-Volmer (or Butler-Volmer-like) and Chang-Jaffé conditions. In the d.c. limit these quantities are unchanged, for the boundary conditions just mentioned, when a supporting electrolyte is added. A transformation of variables method is described which permits one to determine the smallsignal impedance of an electrode/material system with general overpotential-dependent firstorder electrode reaction kinetics from a compact-layer model for the small-signal overpotential and the small-signal response obtained for Chang-Jaffé boundary conditions. Exact impedance results are given for the case of a single species of mobile charge carrier. Analysis of this case indicates that the overpotential dependence of the boundary conditions has negligible effect on the small-signal response unless the cell is of microscopic thickness or the Debye length is comparable to the compact layer thickness and the electrode reaction is slow.

<sup>\*1</sup> Work supported by U.S. National Science Foundation (Grant No. DMR 75-10739).

<sup>\*&</sup>lt;sup>2</sup> In honour of the 60th birthday of Benjamin G. Levich.

### (I) INTRODUCTION

The nature of heterogeneous charge transfer processes is one of the central problems of electrochemical theory. Although notable contributions in this area have been made by Levich [1] and others [2], our understanding of all but the simplest charge transfer processes remains far from complete. On the experimental side, a crucial problem is how best to isolate the kinetics of electrode reactions from the sum of processes manifest in experimental measurements. In aqueous electrochemistry, the introduction of an indifferent or supporting electrolyte permits some separation of bulk and electrode processes. The unsupported case is, however, of intrinsic interest as well, and is the only accessible experimental situation when dealing with solid electrolytes, such as the  $\beta$ -aluminas and the silver halides, and with fused salts and oxides. Theoretical results for the electrical response of unsupported systems will be more and more needed as interest in the electrochemistry of the solid and molten states grows. The availability of such results will help to eliminate the practice often followed in the past of analyzing the response of unsupported systems with theoretical expressions derived for supported conditions.

Here, we shall be particularly concerned with the small-signal a.c. response to be expected when electrode reaction and adsorption effects [3-7] are present, and to a lesser extent, when diffusion effects are also significant. As Levich has pointed out [8], most electrode reactions involve an adsorption step. The results discussed here apply particularly to unsupported systems but will be compared in detail with the supported case. They have been derived for a small perturbing potential applied to an electrode/material system which is flat-band (zero electrode charge) in equilibrium.

Most derivations of the small-signal impedance of unsupported systems have employed the Chang-Jaffé boundary conditions [9], generalized when necessary for arbitrary valences of mobile charge [10]. Such boundary conditions involve the deviations in concentration of the mobile species at the plane of closest approach to the electrode from their equilibrium values. When ionic size is neglected, this plane is usually taken to be that of the effective electrode surface. On the other hand, much of the theory of electrode kinetics and most experimental analysis of supported situations involve the overpotential,  $\eta$ , which is taken to be either the potential difference between an electrode and the bulk of the material in a non-equilibrium situation minus any such potential difference under equilibrium conditions, or the fraction of this drop which falls across the compact part of the double layer. We shall be particularly concerned with the compatibility and distinguishability of these two approaches in the case of smallsignal response. In particular, it seems surprising that although the general expressions for the Warburg impedance differ appreciably for supported and unsupported conditions [11,12], those for the reaction resistance,  $R_{\rm R}$  (sometimes denoted  $R_{\theta}$ ), are essentially the same in the two cases [12,13]. Since singlepoint boundary conditions, such as the Chang-Jaffé ones, have some advantages for calculations in unsupported cases over those which involve two or more positions, as do those involving  $\eta$ , we shall also be concerned with relating the smallsignal response for  $\eta$ -dependent boundary conditions to that obtained in the Chang-Jaffé case.

The work which follows is divided into two main parts. The first (sections II through IV) will present and analyze results derived from the exact solution. assuming Chang-Jaffé boundary conditions, for the small-signal impedance of a cell with identical plane-parallel electrodes separated by a distance l. The cell material may exhibit intrinsic or extrinsic conduction with positive and negative charges of arbitrary mobilities,  $\mu_p$  and  $\mu_n$ , but usually with equal valence numbers:  $z_p = z_n \equiv z_e$ . In addition it will often be assumed for simplicity that neutral intrinsic centers are completely dissociated, as are any extrinsic centers present. Some results for  $z_n \neq z_p$  and incomplete intrinsic dissociation have been given elsewhere [10,12-17]. In this first part, the most appropriate approximate equivalent circuits will be established, and specific expressions will be presented relating circuit elements to more basic material/electrode parameters such as mobilities, reaction rate constants, etc. To the degree that such approximate equivalent circuits are adequate, they allow one to bypass the very complicated exact solution of the governing equations of the problem and to characterize material/electrode systems by fitting impedance-frequency data to an approximate equivalent circuit, thus obtaining estimates for circuit element values, and finally using these values and the known connecting equations to obtain the desired basic characterization parameters [12,15-18]. In the second, more basic part of this paper (sections V–IX), we shall be concerned with the relationship of the Chang-Jaffé boundary conditions to more general expressions for the rate of electrode reactions. We shall examine the extent to which equivalent circuit elements are independent of the precise form of boundary conditions, and of the presence or absence of a supporting electrolyte. We shall also indicate a procedure by which the exact solution obtained with Chang-Jaffé boundary conditions can be modified to yield the small-signal impedance appropriate to overpotential-dependent boundary conditions. The formal results obtained in this part should aid in identifying experimental situations most sensitive to the overpotential, and should, eventually, lead to the formulation of useful equivalent circuits for such circumstances.

## (II) GENERAL CIRCUITS AND SYMBOLS

All real systems are distributed in space. Therefore one cannot expect to find an equivalent circuit involving only lumped-constant, frequency-independent elements which exactly duplicates even the small-signal impedance of such a system. The circuit of Fig. 1a can, however, represent any small-signal impedance since  $C_i$  and  $R_i$  are frequency dependent [10,12]. The elements independent of frequency are the resistances  $R_D$  and  $R_E$ , and  $C_g = \epsilon/4\pi l$ , the geometric capacitance, where l is the distance between plane parallel electrodes and  $\epsilon$  the dielectric constant of the electrolyte material. All circuit elements will be given for unit electrode area.

Clearly  $R_D$  is the d.c., or zero frequency limiting resistance of the system. Further, the solution for the small-signal impedance [10] involves an  $R_i(\omega)$  which goes to zero as  $\omega \to \infty$ . Thus the parallel combination of  $R_D$  and  $R_E$  must be the high-frequency limiting resistance,  $R_{\infty}$ , the bulk or solution resistance of the system. Let  $G_D \equiv R_D^{-1}$ ,  $G_E \equiv R_E^{-1}$ , and  $G_{\infty} \equiv R_{\infty}^{-1}$ . The branch of the circuit of Fig. 1a containing  $R_E$  must be purely capacitive in the limit of low frequen-



Fig. 1. Two general types of equivalent circuits whose impedances may be made to agree at all frequencies with that following from small-signal theory.

cies. On the other hand, one can represent general small-signal system response in a significantly different way by means of the circuit of Fig. 1b. Here the branch containing  $R_{\infty}$  must be purely resistive in the limit of low frequencies, and we must have  $R_{\rm D} \equiv R_{\infty} + Z_{\rm s0}$ , where the subscript zero denotes the low-frequency limit. Secondly, of course when  $\omega \to \infty$ ,  $Z_{\rm s} \to Z_{\rm s\infty} = 0$ . Further, on comparing the two circuits one notes that  $Z_{\rm s}(\omega) = Z_{\rm i}(\omega)$  in the  $R_{\rm D} = \infty$ , completely blocking situation.

A very complicated expression for  $Z_i(\omega)$  has been given [10] which follows from the exact solution of the small-signal equations governing conduction processes with Chang-Jaffé boundary conditions in the full dissociation situation. Some aspects of the more general solution applicable when dissociation may be incomplete [15–18] and when specific adsorption effects are present [16,19,20] have also been discussed. Similar exact expressions for  $Z_s$  in these situations have also been found; here we shall be mainly concerned with approximating  $Z_s$  as well as possible by an equivalent circuit whose circuit elements can be related to basic material/electrode parameters.

Let us consider  $G_{\infty}$  in more detail. Let  $p_e$  and  $n_e$  be the unperturbed bulk values of the positive and negative charge concentrations. Then  $G_{\infty} \equiv G_n + G_p$ , where  $G_n \equiv (e/l)(z_n\mu_n n_e)$ ,  $G_p \equiv (e/l)(z_p\mu_p p_e)$ , and e is the proton charge. It will be useful in the following discussion to define  $\pi_z \equiv z_n/z_p$ ,  $\pi_m \equiv \mu_n/\mu_p$ ,  $\tilde{n} \equiv n_e/n_i$ ,  $\tilde{p} \equiv p_e/p_i$ ,  $\pi_e \equiv \pi_m(\tilde{n}/\tilde{p})$ , and  $\pi_f = \pi_z(\tilde{n}/\tilde{p})$ . Here,  $n_i$  and  $p_i$  are intrinsic bulk concentrations in the absence of extrinsic centers;  $z_n n_i = z_p p_i$  from bulk electroneutrality; and for both small and full dissociation of intrinsic centers and full

dissociation of extrinsic ones,  $\tilde{n} \cong \phi + \chi$  and  $\tilde{p} \cong \phi - \chi$ , where  $\phi \equiv (1 + \chi^2)^{1/2}$ . The quantity  $\chi$  is  $(N_D^+ - N_A^-)/(z_n n_i + z_p p_i)$  and is a measure of the relative amount of extrinsic conduction.  $N_D^+$  and  $N_A^-$  are the concentrations of ionized donor and acceptor extrinsic centers, and the material is thus intrinsic (or compensated) when  $\chi = 0$ .

In order to subsume many results in one, it will often be convenient to deal with normalized variables [10]. We normalize resistances with  $R_{\infty}$  and capacitances with  $C_{\rm g}$  and denote such normalization by the subscript "N". Then for example,  $R_{\rm RN} \equiv R_{\rm R}/R_{\infty}$ . The corresponding time constant is  $R_{\infty}C_{\rm g} \equiv \tau_{\rm D}$ , the dielectric relaxation time. It will be employed to normalize other time constants and to define the normalized frequency  $\Omega \equiv \omega \tau_{\rm D}$ . Most processes of present interest occur in the range  $\Omega \gtrsim 1$ . We may now write  $G_{\rm pN} \equiv G_{\rm p}/G_{\infty} = [1 + (G_{\rm n}/G_{\rm p})]^{-1} = (1 + \pi_{\rm e})^{-1} \equiv \epsilon_{\rm p}$ . Similarly  $G_{\rm nN} \equiv (1 + \pi_{\rm e}^{-1})^{-1} \equiv \epsilon_{\rm n}$  and  $\epsilon_{\rm n} + \epsilon_{\rm p} \equiv 1$ . It will also be useful to define  $\delta_{\rm p} \equiv (1 + \pi_{\rm f})^{-1}$  and  $\delta_{\rm n} \equiv (1 + \pi_{\rm f}^{-1})^{-1}$ .

Thus far we have dealt with  $C_g$  and  $R_\infty$ , common to all conduction problems. While  $R_D$  and  $R_E$  are general frequency-independent elements, one must introduce boundary conditions characterizing the material/electrode interface in order to evaluate them. The Chang-Jaffé boundary conditions involve [9,10] the dimensionless boundary parameters  $r_n$  and  $r_p$  which are real and frequencyindependent when electrode reactions occur without the formation of an adsorbed intermediate species. If  $r_n = 0$ , the mobile negative charges are completely blocked (no reaction), while if  $r_n = \infty$  the reaction occurs instantaneously.

It has been found [19,21] that the formation of adsorbed intermediates, say from the negative carrier, can be incorporated in the governing equations and their solution by making the relevant r-parameter complex and frequency dependent, e.g.,  $r_n \rightarrow r_n^*$ . In the simplest case (see later discussion), only a single adsorption internal relaxation time,  $\tau_{na}$  or  $\tau_{pa}$ , occurs for each adsorbed species, and the complex boundary parameter  $r_n^*$  takes on the real values  $r_{n0}$  at  $\omega = 0$ and  $r_{n\infty}$  for  $\omega \rightarrow \infty$ . In the absence of adsorption,  $r_{n0} = r_{n\infty} \equiv r_n$ , real and frequency independent. The effective heterogeneous reaction rates associated with  $r_{n0}$  and  $r_{n\infty}$  are  $k_{n0} \equiv (D_n/l)r_{n0}$  and  $k_{n\infty} \equiv (D_n/l)r_{n\infty}$ . Here  $D_n$  is the diffusion coefficient of the negative mobile charge carriers, and we assume the adequacy of the Einstein relation  $D_n = (kT/ez_n)\mu_n$ , where k is Boltzmann's constant and T is the absolute temperature. Similar relations apply for the positive carriers. Note that when  $r_{n\infty} = r_{p\infty}$ , for example,  $k_{n\infty}$  is not necessarily equal to  $k_{p\infty}$ ; instead  $k_{n\infty} = (D_n/D_p)k_{p\infty}$ , or  $k_{n\infty} = \pi_z^{-1}\pi_m k_{p\infty}$ .

We may now write general expressions for  $R_{\rm DN}$  and  $R_{\rm EN}$ . Let  $g_{n0} \equiv 1 + (r_{n0}/2)$ ,  $g_{p0} \equiv 1 + (r_{p0}/2)$ , and  $g_{s0} \equiv \epsilon_n g_{p0} + \epsilon_p g_{n0}$ . Then one finds [10,13]

$$R_{\rm DN} = g_{\rm n0}g_{\rm p0}/(g_{\rm n0}g_{\rm p0} - g_{\rm s0})$$
  
=  $[\epsilon_{\rm n}\{1 + (2/r_{\rm n0})\}^{-1} + \epsilon_{\rm p}\{1 + (2/r_{\rm p0})\}^{-1}]^{-1}$  (1)

and

$$R_{\rm EN} = g_{\rm n0}g_{\rm p0}/g_{\rm s0} = [(\epsilon_{\rm n}/g_{\rm n0}) + (\epsilon_{\rm p}/g_{\rm p0})]^{-1}$$
(2)

The important quantity  $Z_{sNO} \equiv R_{DN} - 1$  may be written

$$Z_{\rm sNO} \equiv R_{\rm DN} - 1 \equiv (R_{\rm EN} - 1)^{-1} = g_{\rm s0} / (g_{\rm n0} g_{\rm p0} - g_{\rm s0})$$
$$= [1 + (\epsilon_{\rm n} r_{\rm p0}/2) + (\epsilon_{\rm p} r_{\rm n0}/2)] / [(\epsilon_{\rm n} r_{\rm n0}/2) + (\epsilon_{\rm p} r_{\rm p0}/2) + (r_{\rm n0} r_{\rm p0}/4)]$$
(3)



Fig. 2. The equivalent circuit of Fig. 1a in normalized and dissected form. Normalized resistances, not conductances are shown.

It is now illuminating to present the circuit of Fig. 1a in normalized form, involving  $Z_{\rm TN} \equiv Z_{\rm T}/R_{\infty}$ , the normalized total impedance. Figure 2 shows the circuit in terms of normalized capacitances and resistances. Here, where the results apply to two identical electrodes, we have divided the  $2/\epsilon_n r_{n0}$  term of eqn. (1) into two equal parts, with each part representing a sort of low-frequency-limiting normalized reaction-adsorption resistance for a single material/electrode interface. As we shall see later, however,  $R_{\infty}/\epsilon_n r_{n0}$  is not the ordinary single-electrode reaction resistance which follows from the analysis. Note that since  $R_{\infty}/\epsilon_n \equiv$  $G_{n}^{-1} \equiv R_{n}, R_{\infty}/\epsilon_{p} \equiv G_{p}^{-1} \equiv R_{p}, \text{ and } G_{p} + G_{n} = G_{\infty}, R_{D} \text{ reduces to just } R_{\infty}, \text{ as it}$ should, when  $r_{n0} = r_{p0} = \infty$ . For this condition,  $R_E = \infty$ , and the un-normalized circuit then reduces to  $C_g$  and  $R_{\infty}$  in parallel. Alternatively, when  $r_{n0} = r_{p0} = 0$ ,  $R_{\rm D} = \infty$ , and  $R_{\rm E} = R_{\infty}$  in this completely blocking situation. The circuit of Fig. 2 is one way of showing directly the degree to which positive and negative mobile charges may be associated with separate resistive elements and current paths. Thus for example, in un-normalized terms the path involving the resistance  $R_{\infty}$ - $[\epsilon_n^{-1} + (2/\epsilon_n r_{n0})]$  may be written  $R_n[1 + (2/r_{n0})]$ , involving only quantities associated with the negative carriers.

## (III) SOME SPECIFIC CIRCUITS

We shall here limit our consideration of specific adsorption to those situations characterized by a single internal relaxation time for each species (see section Vb), and define normalized adsorption relaxation times  $\xi_{pa} \equiv \tau_{pa}/\tau_D$  and  $\xi_{na} \equiv \tau_{na}/\tau_D$ . Full specification of a given normalized system (in the absence of recombination) then requires, in general, values of the parameters:  $(r_{p\infty}, r_{p0}; r_{n\infty}, r_{n0};$ 

$$\xi_{pa}, \xi_{na}; \pi_{m}, \pi_{z}; \chi, M). \text{ Here } M \equiv l/2L_{D} \text{ and the Debye length } L_{D} \text{ is}$$

$$L_{D} \equiv [\epsilon k T/4 \pi e^{2} (z_{n}^{2} n_{e} + z_{p}^{2} p_{e}]^{1/2}$$
(4)

An exact solution for this rather general case has been obtained and will be published subsequently. Now, for simplicity, in sections III and IV we shall take  $r_p^* = 0$  so that  $r_{p\infty}$ ,  $r_{p0}$ , and  $\xi_{pa}$  are zero. Then, positive carriers are blocked without adsorption and reaction and adsorption processes involve only the negative carriers. In addition, we shall assume that  $z_n = z_p \equiv z_e$  so that  $\pi_z = 1$  and  $n_i =$  $p_i \equiv c_i$ . For a material/electrode system of this kind, we now need specify only  $(r_{n\infty}, r_{n0}, \xi_{na}, \pi_m, \chi, M)$  values. This notation will be employed subsequently to characterize the systems discussed.

For  $r_p^* = 0$ , we immediately find from eqns. (1) and (3),

$$R_{\rm DN} = \epsilon_{\rm n}^{-1} [1 + (2/r_{\rm n0})] \tag{5}$$

and

$$Z_{\rm sNO} \equiv R_{\rm DN} - 1 = (2/\epsilon_{\rm n} r_{\rm n0}) + (\epsilon_{\rm p}/\epsilon_{\rm n}) = (2/\epsilon_{\rm n} r_{\rm n0}) + \pi_{\rm e}^{-1}$$
$$= (2/\epsilon_{\rm n} r_{\rm n\infty}) + [2(\epsilon_{\rm n} r_{\rm nm})/(\epsilon_{\rm n} r_{\rm n\infty})(\epsilon_{\rm n} r_{\rm n0})] + \pi_{\rm e}^{-1}$$
(6)

where  $r_{nm} \equiv r_{n\infty} - r_{n0}$ . The reason for dissecting  $Z_{sN0}$  into three separate terms will shortly become apparent. No separation of  $Z_{sN0}$  into a simple sum of two or three (normalized) resistances seems possible when  $r_{p0}$  is non-zero. On the other hand, when  $r_{p0} = 0$  but  $r_{p\infty}$  and  $\xi_{pa}$  are arbitrary, a separation of the form of eqns. (5) and (6) remains possible.

When diffusional effects are negligible, a condition which obtains when  $\pi_{\rm e} > 10^2$  or so [16,20], and the real and imaginary parts of  $Z_{\rm T}^*(\omega) \equiv {\rm Re}(Z_{\rm T})$  – i Im $(Z_T)$  for the  $(r_{n\infty}, r_{n0}, \xi_{na}, \pi_m, \chi, M)$  case are plotted as parametric functions of frequency in the complex plane, one obtains curves of the form shown in Fig. 3a. Since adsorption is a form of electrode reaction and is associated with charge transfer, even though direct current flow may be completely blocked, it has been designated "A/R" in Fig. 3, while reaction alone is designated "R". Similarly "B" denotes bulk response associated with  $R_{\infty}$  and  $C_{g}$  in parallel. The arrows indicate the direction of increasing frequency. When  $r_{n\infty} = r_{n0} \equiv r_n$ , no A/R effects occur. When  $r_{n\infty} \neq r_{n0}$ , such effects lead to semicircles in the various positions shown. Expressions relating  $r_{n\infty}$ ,  $r_{n0}$ , and  $\xi_{na}$  to more fundamental properties of the system have been presented elsewhere [16,20] and will be discussed in later sections. Usually  $r_{n0}$  may be expected to be positive; it cannot fall in the range  $-2 < r_{n0} < 0$ , however, since any such value would cause the overall  $R_D$  to be negative, an unstable situation. When  $r_{n0} > r_{n\infty} > 0$ , it is clear that the response must involve inductive or negative resistance and capacitance elements even though  $R_{\rm D} > 0$ . Impedance plane curves of this form have often been found experimentally [6,22].

We shall soon demonstrate that the  $\pi_e^{-1}$  contribution to  $R_{\rm DN}$  is associated with diffusion effects. The bulk semicircle in the complex  $Z_{\rm TN}^*$  plane contributes a normalized resistance of unity to  $R_{\rm DN}$ . Therefore, any quantity in  $R_{\rm DN}$  much smaller than unity may safely be neglected. Thus, the curves of Fig. 3a, which show no diffusion effects, are appropriate for  $\pi_e > 10^2$ , or, equivalently,  $\pi_m > 100$ - $(\phi - \chi)/(\phi + \chi)$ . On the other hand, those in Fig. 3b involve a non-negligible







Fig. 3. Complex plane plots of  $Z_T^*$  for the  $r_p^* = 0$ , loosely coupled  $(r_{n\infty}, r_{n0}, \xi_{na}, \pi_m, \chi, M)$  situation with (a)  $\pi_e > 10^2$ ,  $\epsilon_n r_{n\infty} \simeq 1$  and various values of  $r_{n0}$ ; (b)  $\pi_e \simeq 1$ ,  $\epsilon_n r_{n\infty} \simeq 0.8$  and  $\epsilon_n r_{n0} \simeq -3$ .



Fig. 4. Possible equivalent circuits which include reaction (a-f) and adsorption-reaction (b-f) effects. Appropriate when bulk and reaction effects are well separated in time and frequency.

diffusion contribution, marked "D" in the Figure, for which  $\pi_e \simeq 1$ . Curves of just this complicated type have actually been observed under some conditions [22]. In general, the diffusion arc need not occur at lowest frequencies; it can, in fact appear between the bulk and reaction semicircles, between reaction and adsorption ones, or at the low frequency side of the adsorption semicircle [16].

It has been found that, exclusive of diffusion effects, exact impedance results may be very well represented in the  $r_p^* = 0$  case by Voigt-type circuits of frequency-independent elements, such as those in Fig. 4a and b. Figure 4a is appropriate when adsorption is absent ( $r_{n\infty} = r_{n0}$ ), while 4b applies when it is present. Further, when bulk and reaction effects and reaction and adsorption effects are well separated in time or frequency (loosely coupled case), it turns out that  $R_1$ and  $C_1$  may be identified with  $R_{\infty}$  and  $C_g$ ,  $R_2$  and  $C_2$  with the reaction circuit elements  $R_R$  and  $C_R$ , and  $R_3$  and  $C_3$  with the A/R elements  $R_A$  and  $C_A$ , respectively. Expressions relating these quantities to more basic material/electrode parameters have already been obtained [13,16] for the Voigt-type circuit of Fig. 4b. When coupling is not weak, these relations are no longer accurate for this circuit, however, and are then not useful in determining basic material/electrode parameters from experimental data.

Therefore, we decided to investigate the usefulness, in the above sense, of the five circuits shown in Fig. 4b-f, all of which may be made to exhibit the same  $Z_{T}(\omega)$  for all  $\omega$  if the elements are properly interrelated. Most earlier authors who have suggested circuits of this form have ignored  $C_1 \cong C_g$  and taken  $R_1$  as the bulk or solution resistance. Possible dangers in this approach have been discussed elsewhere [18] in the small M (e.g.  $M < 10^2$ ) case, one where bulk-reaction separation is poor. The circuit of Fig. 4c was apparently first proposed by Cole in the present context [23] and was later suggested by others [6]. Several authors [6,7] have proposed essentially the Fig. 4d circuit. In order to compare the utility of these circuits we simultaneously fitted the real and imaginary parts of  $Z_{\rm TN}(\Omega)$  "data" by a special non-linear least squares method [18], obtaining a standard deviation  $s_f$  for the overall fit and estimates of circuit element parameter values and their standard deviations. Loose and close coupled reaction-adsorption situations of both the  $r_{n\infty} > r_{n0} > 0$  and  $r_{n0} > r_{n\infty} > 0$  types were considered; system input parameter values used here and later are summarized in Table 1. The  $\pi_m = 10^{20}$  values are computer approximations to  $\infty$ .

System identification	r <sub>n∞</sub>	<i>r</i> <sub>n0</sub>	ξ <sub>na</sub>	$\pi_{\mathrm{m}}$	x	М
A	1	0.5	10 <sup>10</sup>	10 <sup>20</sup>	0	$\sqrt{2 \times 10^6}$
В	1	0.5	10 <sup>9</sup>	$10^{20}$	0	$\sqrt{2} \times 10^8$
C D	$2 \\ 2$	4 4	$10^{11}$ $10^{11}$	$10^{20}$ $10^{20}$	0 0	$5 imes 10^4 \ 5 imes 10^9$
Ε	0	0	_	1	0	3
F	2	2	-	10 <sup>20</sup>	0	10 <sup>5</sup>
G	2	2	-	10 <sup>20</sup>	0	1

Values of  $(r_{n\infty}, r_{n0}, \xi_{na}, \pi_m, \chi, M)$  used in fitting experiments

TABLE 1

#### TABLE 2

Relations between normalized circuit parameters and material/electrode characterization properties

They are only applicable for circuit (b) when reaction and adsorption effects are well separated in time and frequency

Cir- cuit (Fig. 4)	R <sub>2N</sub>	C <sub>2N</sub>	R <sub>3N</sub>	$C_{3\mathrm{N}}$ or $L_{3\mathrm{N}}$	$R_{3N} \cdot C_{3N}$ or $L_{3N}/R_{3N}$
(b), (d)	$2/\epsilon_{n}r_{n\infty}$	$r_{\rm e} + \epsilon_{\rm n} r_{\rm n\infty}$	$2 \epsilon_{\rm n} r_{\rm nm} / (\epsilon_{\rm n} r_{\rm n\infty}) (\epsilon_{\rm n} r_{\rm n0})$	$\xi_{\rm na}(\epsilon_{\rm n}r_{\rm n\infty})^2/(2\epsilon_{\rm n}r_{\rm nm})$	$\xi_{na}(r_{n\infty}/r_{n0})$
(c)	$2/\epsilon_{n}r_{n\infty}$	$r_{\rm e} + \epsilon_{\rm n} r_{\rm n\infty}$	$-2/\epsilon_{n}r_{nm}$	$-2 \xi_{na}/\epsilon_n r_{nm}$	ξ <sub>na</sub>
(f)	$2/\epsilon_{\rm n}r_{\rm n0}$	$r_{e} + \epsilon_{n} r_{n\infty}$	$2/\epsilon_{n}r_{nm}$	$\xi_{na}(\epsilon_n r_{nm})/2$	ξ <sub>na</sub>
(e)	$2/\epsilon_{\rm n}r_{\rm n0}$	$r_{\rm e} + \epsilon_{\rm n} r_{\rm n\infty}$	$-2\epsilon_{n}r_{nm}/(\epsilon_{n}r_{n\infty})(\epsilon_{n}r_{n0})$	$-2\xi_{\rm na}(\epsilon_{\rm n}r_{\rm nm})/(\epsilon_{\rm n}r_{\rm n0})^2$	$\xi_{\rm na}(r_{\rm n\infty}/r_{\rm n0})$

These and other fitting experiments made it possible to determine how the various circuit elements depend on the input parameters or functions of such parameters. These results, shown in normalized form in Table 2 for the five circuits, are particularly appropriate for  $M > 10^2$ , where  $R_{1N} \cong R_{\infty N} \equiv 1$  and  $C_{1N} \cong C_{gN} \equiv 1$ . The quantity  $r_e \equiv (M_e) \operatorname{ctnh}(M_e)$ , where  $M_e \equiv l/2 L_{De}$ , appearing in the expression for  $C_{2N}$  in Table 2 depends on the effective mobilities of positive and negative charges and may be well approximated by  $r \equiv (M) \operatorname{ctnh}(M)$  when  $\pi_m \to \infty$  and appreciable intrinsic recombination is present or, in the absence of recombination, when  $\pi_e \ll r_e$ . On the other hand, with little or no recombination, appreciable M, and  $\pi_e > 10 r_e$ ,  $M_e$  is well approximated by  $M\delta_n^{1/2}$  in the present  $(r_p^* = 0, r_n^*)$  situation. Since for  $\pi_z = 1$ ,  $n_e = \tilde{n}c_i$ ,  $p_e = \tilde{p}c_i$ , and  $\delta_n \equiv \tilde{n}/(\tilde{n} + \tilde{p}) = 0.5 + (\chi/2 \phi)$ , one finds that

$$M\delta_{\rm n}^{1/2} \equiv M_{\rm n} \equiv l/2L_{\rm Dn} \equiv (l/2) [\epsilon kT/4 \ \pi (ez_{\rm e})^2 n_{\rm e}]^{-1/2} \tag{7}$$

which involves the effective Debye length  $L_{\rm De} = L_{\rm Dn}$  appropriate for negative charges alone mobile. Thus when  $M_{\rm e} \cong M \delta_{\rm n}^{1/2}$ ,  $C_{\rm 2N}$  is primarily associated with the more mobile negative charge carriers in a  $(r_{\rm p}^* = 0, r_{\rm n}^*)$  situation. Incidentally, when  $\chi = 0$  and  $\pi_{\rm e} = \pi_{\rm m} \sim M$ , it has been found that the reaction arc is a slightly depressed semicircle, one with its center below the real axis [13]. The use of the frequency-independent parameters  $R_{\rm R}$  and  $C_{\rm R}$  is then a poorer approximation, one which may be improved by means of a distribution-of-relaxation-times approach [16].

The fitting experiments showed, as expected, that for a given system all five circuit fits yielded the same  $s_f$ , one representative of a very good fit. Further, for loosely coupled conditions (cases A and C), all circuit fits (including that of 4b) yielded parameter-value estimates in good agreement with those given by the expressions in Table 2. This was not the case, however, for the Voigt-type circuit (b) fits under close coupling conditions. Table 3 summarizes results for  $R_{2N}$  for the four systems, comparing circuit (b) and (d) predictions. Similar results were found for the other parameter comparisons. The number of significant figures shown for the  $R_{2N}$  values are consistent with the estimated values

**TABLE 3** 

Some fitting results for circuits (4b) and (4d) for various input situations

TABLE 3								
Some fitting	results for circ	uits (4b) and (4	d) for various in	aput situations		-		
System	A		в		С		D	
Quantity	(q)	(q)	(p)	(q)	(q)	(q)	(p)	(q)
20	5.97 ×	10-7	7.07 ×	10 <sup>-9</sup>	1.37 X	10 <sup>-5</sup>	1.99 ×	10-10
$R_{2N}$	1.999600	2.00000	1.6077677	2.0000000	1.00000	1.00000	1.084337358	1.000000000

of parameter standard deviations derived from the fit. Fits were carried out in double precision arithmetic on an IBM 370-155 computer. Note that  $s_f$  tends to increase with decreasing M.

Circuit (b), which has been employed extensively in the past [13,15-18,20], is less useful for characterization than the other circuits. Since all four others yield results in agreement with the expressions of Table 2, independent of the closeness of reaction-adsorption coupling, one is faced with the choice of which one of them to use as a standard. Note that when  $r_{n\infty} > r_{n0} > 0$ , so that  $r_{nm} > 0$ , circuits (c) and (e) involve negative values of  $L_3$  and  $R_3$ , while when  $r_{n0} > r_{n\infty} > 0$ , it is circuits (b), (d), and (f) which involve negative values of  $C_3$  and  $R_3$ . One perhaps plausible choice which entirely avoids negative values would be to use circuit (d) for  $r_{\rm nm} \ge 0$  and circuit (c) for  $r_{\rm nm} < 0$ . They both reduce to circuit (a) when  $r_{\rm nm} = 0$ . Note that circuit (c), for example, is impractical when  $r_{\rm n0} = 0$ since the  $R_2$  and  $R_3$  of this circuit are then equal and opposite, and the system must be purely capacitative in the limit of low frequencies, leading to fitting difficulties. If circuit (c) is restricted to  $r_{nm} < 0$  situations, this particular difficulty does not arise but a conceptual one does. As there is no provision for a magnetic field in the present one dimensional model [10], the introduction of an inductance in an equivalent circuit is not as readily rationalized as that of a resistance or capacitance. This alternative is rendered even less attractive by the fact that the inductance required is often enormous, suggesting extensive storage of energy in a magnetic field. Our normalization is such that the un-normalized  $L_3$  corresponding to  $L_{3N}$  of Table 2 is  $L_3 \equiv \tau_D R_\infty L_{3N} = 2 \tau_D R_\infty \xi_{na}/(-\epsilon_n r_{nm}) = 2 R_\infty \tau_{na}/(-\epsilon_n r_{nm})$ . For systems C and D, where  $r_{nm} = -2$ ,  $L_{3N}$  from Table 2 is  $10^{11}$ . Even for  $\tau_D = 10^{-8}$  s and  $R_\infty = 1 \Omega$ ,  $L_3$  is then  $10^3$  H. For  $L_{3N} = 10^5$  and the same values of  $\tau_{\rm D}$  and  $R_{\infty}$ ,  $L_3$  is a mH, and values obtained from experimental data will generally be larger. When  $r_{nm} < 0$ , it seems preferable to consider that adsorption leads to negative resistance and negative capacitance contributions to the total impedance, rather than to a large positive inductance. Therefore, in subsequent work, we shall employ circuit (d), or a generalization of it, for all values of  $r_{nm}$ .

## (IV) AN IMPROVED EQUIVALENT CIRCUIT

We have seen that the circuit of Fig. 4d provides, in general, an exceptionally good fit in the unsupported cases considered. We have not, however, examined systems in which diffusion effects are significant, or in which bulk and reaction effects are not well separated. For these situations a more general circuit is needed. The one proposed in Fig. 5 is an elaboration of that of Fig. 1b, using part of 4d. Note that it carries over unchanged the R and A/R parts of the Fig. 4d circuit and adds an impedance  $Z_D$  to account for diffusion effects. With  $Z_D = 0$ , the circuit is of a continued fraction or hierarchical (ladder network) form rather than the mixed form of the Fig. 4d circuit. Further, in view of the preceding discussion, we can now specifically identify the  $R_i$ ,  $C_i$ (i = 1, 2, 3) elements in terms of bulk, reaction, and adsorption/reaction processes in time and frequency). Finally, because of its hierarchical form, the present circuit ensures, in accordance with both observation and the exact theoretical results, that bulk effects occur at



Fig. 5. Most appropriate equivalent circuit accounting for bulk, reaction, adsorption, and diffusion.effects.

higher frequencies than reaction effects, and reaction effects at higher frequencies than adsorption effects. In this section we investigate the applicability of this circuit and discuss its elements.

De Levie and Vukadin [24] have proposed a circuit somewhat similar to that of Fig. 5 for a thin-membrane conduction problem. The similarity may be misleading, however, since their model differs in a number of respects from ours. Theirs involves a single species of ionic charge present within the membrane, and an excess of indifferent electrolyte outside the membrane. They also assume, in effect, that reaction and adsorption processes are independent, requiring the existence of separate pre-reaction and pre-adsorption sites. In the present work, on the other hand, only a single type of pre-reaction site is required since an adsorption-reaction sequence is assumed. One may have reaction without adsorption effects but adsorption, if it occurs, forms part of the overall sequence of electrode reaction. As the results of Table 2 show, the reaction and adsorption resistances and the adsorption capacitance are then closely coupled through their dependences on  $r_{n\infty}$  and  $r_{n0}$ .

Since the present model, with two species of mobile charge carrier within the electrolyte, must accommodate diffusion effects even in the absence of reaction and adsorption (ohmic or completely blocking  $(r_{n\infty} = r_{n0} = 0)$  conditions),  $Z_D$  must, for the present case, be placed as shown in Fig. 5 and not in series with  $R_R$  or  $R_A$ . Previous work [13,15,16,25] has suggested that it is often a good approximation to express  $Z_D$  as a finite-length Warburg impedance of the form

$$Z_{\rm DN} \simeq \pi_{\rm e}^{-1} [\tanh(i\Omega bM^2)^{1/2} / (i\Omega bM^2)^{1/2}]$$
(8)

where  $b \equiv \delta_n \delta_p / \epsilon_n \epsilon_p$  and thus depends, as does  $\pi_e$ , on both  $\pi_m$  and  $\chi$ . It will be noted on comparison with eqn. (5) or (6) that the relation  $R_{\rm DN} \equiv 1 + R_{\rm RN} + R_{\rm AN} + Z_{\rm DN0}$  is exactly satisfied when the expressions for  $R_{\rm RN}$  and  $R_{\rm AN}$  given in Table 2 for circuit 4d are employed along with that which follows from (8) for  $Z_{\rm DN0}$ . It is found that the present form of  $Z_{\rm DN}$  is particularly applicable when  $\pi_e$  is of the order of  $10^{-2}$  or larger and when M is appreciable, say  $M \gg 10^2$ . Its deficiencies outside of these regions, and, hopefully an improved expression for  $Z_{\rm DN}$  itself, will be discussed elsewhere.

The quantities  $R_{\infty}$  and  $C_{g}^{-1}$  are extensive, while the foregoing expressions for  $R_{\rm RN}$ ,  $C_{\rm RN}$ ,  $R_{\rm AN}$ , and  $C_{\rm AN}$  indicate that their non-normalized forms are intensive as they should be since they are associated only with electrode-interphase regions. On the other hand,  $Z_{\rm D}$  is intensive when the tanh term is essentially unity (ordinary infinite-length Warburg response) and extensive for sufficiently small  $\Omega$ . It is worthwhile to examine the un-normalized forms of the intensive quantities, given for a single electrode/material interface, in some detail. We shall denote such one-electrode quantities with a subscript 1. We obtain

$$R_{\rm R1} = 0.5 R_{\rm RN} R_{\infty} = (r_{\rm n\infty} G_{\rm n})^{-1} = (kT/ez_{\rm e})/(ez_{\rm e} n_{\rm e} k_{\rm n\infty})$$
$$= (RT/Fz_{\rm e})/(Fz_{\rm e} n_{\rm e} k_{\rm n\infty})$$
(9)

and

$$R_{\rm A1} = 0.5 R_{\rm AN} R_{\infty} = R_{\rm n} (r_{\rm n0}^{-1} - r_{\rm n\infty}^{-1}) = [kT/(ez_{\rm e})^2 n_{\rm e}] [k_{\rm n0}^{-1} - k_{\rm n\infty}^{-1}]$$
(10)

where R is the gas constant, F the Faraday constant, and  $n_e$  must be expressed in mol cm<sup>-3</sup> in the last equation of (9). Equation (10) and the structure of Fig. 5 show that reaction and adsorption processes are interrelated: the adsorption path involves the reaction path even when  $r_{n0} = 0$ , for which  $R_A = \infty$  and one has a completely blocking pure adsorption case. This is why we have denoted the adsorption process by A/R instead of A. The quantity  $(R_{R1} + R_{A1}) =$  $R_{\infty}/\epsilon_n r_{n0}$  is the total low frequency limiting resistance arising from adsorption and reaction processes at a single electrode/material interface, in agreement with the normalized quantities  $(\epsilon_n r_{n0})^{-1}$  shown in Fig. 2.

As we shall verify shortly, the appropriate expression for  $C_{\rm RN}$  for the circuit of Fig. 5 turns out to be slightly different from that given in Table 2 for  $C_{\rm 2N}$ . The applicable expression for the present  $\pi_z = 1$  situation with two identical plane parallel electrodes is

$$C_{\rm RN} = r_{\rm e} - 1 \tag{11}$$

The intensive part of this expression is just  $(C_{\rm RN} + 1) = r_{\rm e}$ , in exact agreement (for  $M_{\rm e} = M$ ) with early calculations of the differential capacitance in a simple two-electrode situation [26]. For a single electrode and  $M_{\rm e} > 3$ , the un-normalized form of this intensive quantity becomes

$$2(C_{\rm RN} + 1)C_{\rm g} = 2 C_{\rm g}r_{\rm e} \cong \epsilon/4 \pi L_{\rm De}$$
<sup>(12)</sup>

where  $L_{\rm De}$ , the effective Debye length, involves the concentrations of those charges which are mobile in the frequency region where the reactance of  $C_{\rm RN}$ is significant. The quantity in (12) is thus just the appropriate diffuse double layer capacitance associated with a single electrode for the relevant situation. Finally, we may express the un-normalized adsorption capacitance associated with a single electrode/material interface as

.. ....

$$C_{A1} \equiv 2 C_{AN} C_{g} = (\xi_{na} C_{g}) (\epsilon_{n} r_{n^{\infty}}^{2} / r_{nm})$$
  
$$= (r_{n^{\infty}} / r_{nm}) (\tau_{na} r_{n^{\infty}} G_{n}) = (k_{n^{\infty}} / k_{nm}) (\tau_{na} / R_{R1})$$
  
$$= (k_{n^{\infty}}^{2} / k_{nm}) (ez_{e} / kT) (ez_{e} n_{e}) \tau_{na}$$
(13)

 $\mathbf{284}$ 

System in	out choices ide	ntified in Table	1							
System	ы		н		G		В		D	
Quantity	4d	5	4d	5	4d	5	4d	5	4d	ß
Sf	$2.8 \times 10^{-1}$	$3.5 \times 10^{-2}$	$9.6 \times 10^{-6}$	$3.2 \times 10^{-6}$	$5.8 \times 10^{-2}$	$3.5 \times 10^{-4}$	$7.1 \times 10^{-9}$	$2.4 \times 10^{-9}$	$2.0 imes10^{-10}$	$6.7 \times 10^{-11}$
C <sub>RN</sub> (fit)	3.0187 ± 0.02	2.01482 ± 0.002	70712.6785 ± 1	70709.6782 ± 0.3	3.473 ± 0.2	0.16116 ± 0.0008	$100,000, 000, 001.1 \pm 0.6$	99,999, 998.7 ± 0.2	3,535,533, 908.1 ± 0.8	3,535,533, 905.0 ± 0.3
C <sub>RN</sub> (for- mulas)	3.01491	2.01491	70712.6781	70709.6781	3.1613 <del>6</del>	0.16136	100,000, 001	99,999, 999	3,535,533, 908	3,535,533, 905

Comparison of fitting results for  $s_f$  and  $C_{\rm RN}$  obtained with the circuits of Fig. 4d and Fig. 5 **TABLE 4** 

285

where  $k_{nm} \equiv k_{n\infty} - k_{n0}$ . Note that  $C_{A1} = \infty$  and the  $C_A$ ,  $R_A$  branch of the circuit of Fig. 5 is shorted out whenever  $k_{n\infty} = \infty$  or  $k_{n\infty} = k_{n0}$ . There are thus no adsorption effects when the reaction rate is infinite or when it is real and frequency independent.

Numerous fittings, covering a wide range of M and other input parameters, have been carried out in order to compare the Fig. 4d and Fig. 5 circuits in normalized form. First,  $R_{1N}$  and  $C_{1N}$  in 4d and  $R_{\infty N}$  and  $C_{gN}$  were allowed to be free parameters. Next, we fixed  $C_{1N}$  and  $C_{gN}$  at their theoretically expected values of unity and let  $R_{1N}$  and  $R_{\infty N}$  remain free. Finally, the results were compared with those obtained when all these quantities were fixed at unity. Although the fits with more free parameters led to smaller values of  $s_{\rm f}$ , they also led to estimates of  $C_{2N} \cong C_{\rm RN}$  (Fig. 4d) and  $C_{\rm RN}$  (Fig. 5) less accurate than those obtained with the normalized bulk parameters fixed at unity. Therefore, subsequent fitting was carried out with the fixed values  $R_{\infty N} = 1$  and  $C_{gN} = 1$ , in direct agreement with Fig. 5.

It was found that  $s_f$  values obtained with the 4d circuit were always appreciably larger than those found using the Fig. 5 circuit, no matter what the value of M and degree of bulk-reaction overlap. Thus parameter estimates obtained from the Fig. 5 circuit were always more accurate than those obtained from 4d fits. A comparison of fits for these two circuits is presented for  $C_{\rm RN}$  in Table 4 for five of the system inputs specified in Table 1. Other parameter comparisons were similar. The  $\pm$  terms are estimated parameter standard deviation values obtained as part of the complex least squares fits. It will be noted, on comparison of values of  $C_{\rm RN}$  from fitting and those calculated from  $C_{\rm RN} = r_e + \epsilon_n r_{n\infty}$  (Fig. 4d circuit) and  $C_{\rm RN} = r_e - 1$  (Fig. 5 circuit), that for several of these fits the estimated parameter standard deviation values were orders of magnitude larger than they should have been [18]. All fitting results support the conclusion that the Fig. 5 circuit is superior to that of Fig. 4d and should be used in preference to it.

### (V) BASIC EQUATIONS AND GENERALIZED BOUNDARY CONDITIONS

#### (a) In the absence of specific adsorption

Although the preceding discussion has been concerned with a symmetrical cell constructed with two identical non-ohmic electrodes, it will be simpler in discussing the effects of different boundary conditions to treat a cell with a single non-ohmic electrode. We thus consider a simple, one-dimensional cell (an idealized half-cell) with electrodes at x = 0 and  $x = l_h + d$ , where the left electrode is taken to be ohmic for all carriers, while the right electrode is somewhat polarizable. The electrolyte is treated as continuous from x = 0 to  $x = l_h$ , which includes the diffuse part of the double layer at the polarizable electrode, while the behavior of the compact part of the double layer, of width d, will be incorporated in the boundary conditions. Within the former region, the fundamental quantities: concentrations p and n, faradaic currents  $I_p$  and  $I_n$ , total current I, and (macro) potential V are assumed to obey the familiar equations [10]:

$$\frac{\partial p}{\partial t} = \frac{-1}{z_{\rm p}e} \frac{\partial I_{\rm p}}{\partial x} \tag{14}$$

$$\frac{\partial n}{\partial t} = \frac{1}{z_{\rm n}e} \frac{\partial I_{\rm n}}{\partial x} \tag{15}$$

$$I_{\rm p} = z_{\rm p} e \left( -\mu_{\rm p} p \, \frac{\partial V}{\partial x} - \frac{\mu_{\rm p} kT}{z_{\rm p} e} \, \frac{\partial p}{\partial x} \right) \tag{16}$$

$$I_{\rm n} = z_{\rm n} e \left( -\mu_{\rm n} n \, \frac{\partial V}{\partial x} + \frac{\mu_{\rm n} k T \, \partial n}{z_{\rm n} e \, \partial x} \right) \tag{17}$$

$$\frac{\partial^2 V}{\partial t \partial x} = -\frac{4\pi}{\epsilon} \left( I - I_{\rm p} - I_{\rm n} \right) \tag{18}$$

and

$$\frac{\partial^2 V}{\partial x^2} = -\frac{4 \pi e}{\epsilon} \left( z_{\rm p} p - z_{\rm n} n + z_{\rm n} N_{\rm D}^+ - z_{\rm p} N_{\rm A}^- \right) \tag{19}$$

where  $\epsilon$  is the dielectric constant and  $(z_n N_D^+ - z_p N_A^-)$  is the time independent, uniform background charge due to the presence of extrinsic centers, assumed to be fully ionized.

The boundary conditions appropriate to the ohmic electrode are  $p(0) = p_e$ and  $n(0) = n_e$ , and the ohmic electrode is fixed at the zero of potential, V(0) =0. Let  $V(l_h) = \zeta$ , the zeta potential [27], and  $V(l_h + d) = V_{ah}$ , the total applied potential. As in the preceding discussion, the cell is taken to be flat-band at open circuit, so that  $\zeta = 0$  when no current is flowing and no external bias has been applied. We define the overpotential as  $\eta \equiv V_{ah} - \zeta$ , the potential drop across the compact part of the double layer, and will use the term overpotential exclusively in this sense throughout the remainder of this work.  $\eta$  is defined as a difference of macropotentials; it is reasonable to expect that the difference in micropotentials which enters into microscopic models of the charge transfer and adsorption processes [28,29] can, to satisfactory approximation, be related to the difference in macropotentials, at least under small-signal conditions.

Before we present boundary conditions for p and n at the polarizable electrode, the consequences of which will be treated in detail in the following sections, we consider a more general class of electrode reactions, those of the form

 $\mathbf{r} \rightleftharpoons \mathbf{0} + n e^{-} \tag{20}$ 

which occur in a single step. Here r and o indicate reduced and oxidized species, of charges  $q_r$  and  $q_o \equiv q_r + ne$ , respectively, and  $e^-$  denotes an electron transferred to or from the electrode. The reaction rate v is usually taken to be of the form

$$v = k_1 c_r f_1(\eta) - k_2 c_o f_2(\eta) \tag{21}$$

where  $f_1$  and  $f_2$  are specified functions of the overpotential  $\eta$ , with  $f_1(0) = f_2(0) = 1$ ;  $k_1$  and  $k_2$  are rate constants for the forward (oxidation) and reverse (reduction) reactions; and  $c_r$  and  $c_o$  are the concentrations of species r and o at their planes of closest approach to the electrode/electrolyte interface. If both r and o are mobile charged species in the electrolyte, the faradaic currents  $I_r$  and  $I_o$  of the species r and o in the vicinity of the electrode are given by  $I_r = q_r v$ ,  $I_o = -q_o v$ , while the faradaic current,  $i_f$ , of electrons into the electrode is  $i_f = -nev$ .

287

At equilibrium v = 0 and necessarily  $k_1 c_{re} = k_2 c_{oe}$ , where  $c_{re}$  and  $c_{oe}$  are the equilibrium concentrations. The quantity  $i_0 \equiv -nek_1 c_{re} = -nek_2 c_{oe}$  is the exchange current, the current to the electrode due to the forward reaction alone at equilibrium, equal to the current from the electrode due to the reverse reaction alone.

The present small-signal exact solution has been derived [10] for a single mobile species of positive charge and a single mobile species of negative charge. Thus it does not apply, in its present form, when p or n is oxidized or reduced at the electrode to form yet another charged species mobile in the electrolyte. It does apply to two important special cases of eqn. (20), that in which the product of the electrode reaction (the oxidized or reduced form of the carrier) passes into the electrode at constant concentration (as in the case of a parent-metal electrode), and that in which the product of the electrode reaction is held in solution at constant concentration (as in gas evolution at constant partial pressure). In the former case, the net charge transferred to the electrode (ion plus electrons) is equal to the charge on the carrier before reaction, and the faradaic current in the compact double layer may be viewed as consisting of the original carriers. In the latter case, the product species must be neutral (since the concentration of a single charged species cannot be externally controlled), and the faradaic current of electrons in the compact double layer is equal to the faradaic current of the reactant species at its plane of closest approach to the electrode.

For those situations just enumerated to which the present small-signal exact treatment applies, we assume the most general overpotential-dependent boundary conditions that we need deal with to be of the form

$$I_{pR} = z_{p} e[k_{p} p_{R} f_{1p}(\eta) - k_{p} p_{e} f_{2p}(\eta)]$$
(22)

and

$$I_{nR} = -z_n e[k_n n_R f_{1n}(\eta) - k_n n_e f_{2n}(\eta)]$$
(23)

where the subscript "R" designates a quantity evaluated at  $x = l_h$ , assumed to be the common plane of closest approach to the electrode for both carriers. Here the constant concentrations of the product species have been expressed in terms of the equilibrium concentrations of the mobile charges. The above boundary conditions encompass the simple Butler-Volmer relations [30],

$$I_{pR} = z_p e[k_p p_R \exp\{-\alpha_p z_p e \eta/kT\} - k_p p_e \exp\{(1 - \alpha_p) z_p e \eta/kT\}]$$
(24)

$$I_{nR} = -z_n e[k_n n_R \exp\{\alpha_n z_n e\eta/kT\} - k_n n_e \exp\{-(1-\alpha_n) z_n e\eta/kT\}]$$
(25)

where  $\alpha_p$  and  $\alpha_n$  are transfer coefficients, which formally reduce to the Chang-Jaffé boundary conditions [9,10],

$$I_{\rm pR} = z_{\rm p} e k_{\rm p} (p_{\rm R} - p_{\rm e}) \tag{26}$$

and

$$I_{\rm nR} = -z_{\rm n}ek_{\rm n}(n_{\rm R} - n_{\rm e}) \tag{27}$$

when  $\eta$  is taken to be zero.

For small-signal a.c. response one defines  $p \equiv p_e + p_1 \exp(i\omega t)$ ,  $n \equiv n_e + n_1 \exp(i\omega t)$ ,  $V \equiv V_1 \exp(i\omega t)$ ,  $I_p \equiv I_{p1} \exp(i\omega t)$ ,  $I_n \equiv I_{n1} \exp(i\omega t)$ ,  $I \equiv I_1 \exp(i\omega t)$ 

and obtains from the continuum equations (14)--(19),

$$i\omega p_1 = \frac{-1}{z_p e} \frac{dI_{p1}}{dx}$$
(28)

$$i\omega n_1 = \frac{1}{z_n e} \frac{dI_{n1}}{dx}$$
(29)

$$I_{\rm p1} = z_{\rm p} e \left( -\mu_{\rm p} p_{\rm e} \frac{\mathrm{d} V_{\rm 1}}{\mathrm{d} x} - \frac{\mu_{\rm p} kT}{z_{\rm p} e} \frac{\mathrm{d} p_{\rm 1}}{\mathrm{d} x} \right)$$
(30)

$$I_{n1} = z_n e \left( -\mu_n n_e \frac{\mathrm{d}V_1}{\mathrm{d}x} + \frac{\mu_n kT}{z_n e} \frac{\mathrm{d}n_1}{\mathrm{d}x} \right)$$
(31)

$$i\omega \frac{dV_1}{dx} = \frac{-4\pi}{\epsilon} (I_1 - I_{p1} - I_{n1})$$
(32)

and

$$\frac{\mathrm{d}^2 V_1}{\mathrm{d}x^2} = \frac{-4 \,\pi e}{\epsilon} \left( z_\mathrm{p} p_1 - z_\mathrm{n} n_1 \right) \tag{33}$$

It should be noted that the  $\omega \to 0$  limits of (28)–(33) are exactly the smallsignal steady-state d.c. forms of (14)–(19). On defining  $V_{ah} \equiv V_{ahl} \exp(i\omega t)$ ,  $\zeta \equiv \zeta_1 \exp(i\omega t)$ , and  $\eta \equiv \eta_1 \exp(i\omega t)$ , Taylor expanding the f's in (22) and (23) about  $\eta = 0$ , and dropping non-linear terms, one obtains small-signal boundary conditions which may be written in the form

$$I_{p1R} = z_{p} e[k_{p} p_{1R} + (z_{p} e \eta_{1} / kT) \gamma_{p} p_{e}]$$
(34)

and

$$I_{n1R} = -z_n e[k_n n_{1R} + (z_n e \eta_1 / kT) \gamma_n n_e]$$
(35)

where

$$\gamma_{\rm p} \equiv \frac{kTk_{\rm p}}{z_{\rm p}ep_{\rm e}} \left[ \left( \frac{\mathrm{d}f_{1\rm p}}{\mathrm{d}\eta} \right)_{\rm 0} - \left( \frac{\mathrm{d}f_{2\rm p}}{\mathrm{d}\eta} \right)_{\rm 0} \right]$$
(36)

$$\gamma_{n} \equiv \frac{kTk_{n}}{z_{n}en_{e}} \left[ \left( \frac{df_{1n}}{d\eta} \right)_{0} - \left( \frac{df_{2n}}{d\eta} \right)_{0} \right]$$
(37)

and a subscript zero affixed to a derivative indicates that it is to be evaluated at equilibrium. Thus defined,  $\gamma_p$  and  $\gamma_n$  have the same dimensions as the rate constants  $k_p$  and  $k_n$ . For the special Butler-Volmer case, eqns. (24) and (25),  $\gamma_p = -k_p$  and  $\gamma_n = k_n$ , while for Chang-Jaffé conditions, eqns. (26) and (27),  $\gamma_p = \gamma_n = 0$ .

It should finally be noted that the small-signal response of a symmetrical cell of length l + 2 d with two identical electrodes is equal to that of two half-cells of length l/2 + d with their ohmic electrodes connected, provided that there is no generation or recombination of charge carriers, and the cell is flat-band at equilibrium. To see that this is so we consider the symmetrical cell to be centered at x = 0 and take  $V_1(-l/2 - d) = -V_{al}/2$  and  $V_1(l/2 + d) = V_{al}/2$ , where  $V_a =$  $V_{al} \exp(i\omega t)$  is the potential drop across the entire cell. The small-signal boundary conditions at the right-hand electrode, eqns. (34) and (35), and the corresponding conditions at the left electrode may then be written

$$I_{p1}(l/2) = z_{p}e\{k_{p}p_{1}(l/2) + \gamma_{p}z_{p}ep_{e}[(V_{a1}/2) - V_{1}(l/2)]/kT\}$$
(38)

$$I_{n1}(l/2) = -z_n e\{k_n n_1(l/2) + \gamma_n z_n e n_e[(V_{a1}/2) - V_1(l/2)]/kT\}$$
(39)

$$I_{p1}(-l/2) = -z_{p}e\{k_{p}p_{1}(-l/2) + \gamma_{p}z_{p}ep_{e}[(-V_{a1}/2) - V_{1}(-l/2)]/kT\}$$
(40)

$$I_{n1}(-l/2) = z_n e\{k_n n_1(-l/2) + \gamma_n z_n e n_e[(-V_{a1}/2) - V_1(-l/2)]/kT\}$$
(41)

where the overpotentials at both electrodes have been expressed as potential differences. Now, if  $\{p_1(x), n_1(x), V_1(x), I_{p1}(x), I_{n1}(x), I_1\}$  denotes the solution of the small-signal equations (28)–(33) satisfying the boundary conditions (38)– (41), one may readily verify that  $\{-p_1(-x), -n_1(-x), -V_1(-x), I_{p1}(-x), I_{n1}, (-x), I_1\}$  satisfy the same equations and boundary conditions. Thus  $p_1, n_1$ , and  $V_1$  are odd functions of x, so that  $p_1(0) = n_1(0) = V_1(0) = 0$ , equivalent to the boundary conditions assumed at x = 0 (the ohmic electrode) for the half-cell. The impedance of the symmetrical cell is  $-V_{a1}/I_1$ , twice that of the half-cell.

## (b) In the presence of specific adsorption

We shall also consider the case in which one of the carriers (taken to be n for definiteness) is adsorbed at the electrode with possible charge transfer

$$\mathbf{n} \to \Gamma + z_1 e^{-1} \tag{42}$$

and where the adsorbed species  $\Gamma$  may further react to form species c,

$$\Gamma \to c + z_2 e^- \tag{43}$$

The corresponding kinetic equations are taken to be

$$I_{nR} = -z_n e v_1(n_R, \Gamma, c, \eta) \tag{44}$$

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = v_1(\mathbf{n}_{\mathrm{R}}, \Gamma, \mathbf{c}, \eta) - v_2(\mathbf{n}_{\mathrm{R}}, \Gamma, \mathbf{c}, \eta)$$
(45)

and

$$\frac{\mathrm{d}c}{\mathrm{d}t} = v_2(n_\mathrm{R},\,\Gamma,\,c,\,\eta) \tag{46}$$

where  $v_2$  is set equal to zero if no c is formed (simple specific adsorption), and (46) is deleted if c is held constant.

The small-signal impedance associated with the reaction sequence of eqns. (42) and (43) has been studied by Armstrong and Henderson [7] and by Macdonald [19], while the special case of simple specific adsorption has been studied by Lányi [21] and by Macdonald and Jacobs [20]. The system considered by Armstrong and Henderson differs in a number of respects from that treated by the latter authors. Armstrong and Henderson consider the case in which c is a mobile species in the electrolyte, for which c in (44)–(46) must be designated  $c_R$  and dc/dt in (46) should be replaced by  $-I_{cR}/(z_n - z_1 - z_2)$ . A high concentration of supporting electrolyte is implicitly assumed, so that  $v_1$  and  $v_2$  may be expanded in terms of  $\Gamma$  and  $\eta$  alone (provided that the diffusion of n and c to the electrode is sufficiently rapid), and the faradaic current is set equal to

$$i_{\rm f} = -z_1 e v_1 - z_2 e v_2 \tag{47}$$

(in the present notation). The quantity  $i_f$  is clearly the faradaic current of electrons into the electrode. Under the assumption of a fully supported system it may be argued that  $i_f$  is then also the total faradaic current of n's, c's, and supporting ions in the electrolyte near the electrode, since these ions will move to offset the build-up of charge on the electrode and in the adsorption plane. Armstrong and Henderson, and later, Armstrong et al. [31] further treat situations in which diffusion is slow, in which  $\Gamma$  is mobile in the electrolyte, and in which c flows into the electrode, but in each case fully supported conditions are assumed.

The exact small-signal impedance derived by Macdonald [10] for the unsupported case may readily be generalized to include the reaction sequence  $n \rightarrow \Gamma \rightarrow c$ , provided that c does not pass into the electrolyte, except perhaps as a neutral species held at constant concentration. As was the case in our discussion of the one-step redox reaction, eqn. (20), this requirement arises because the exact solution was obtained for a single mobile positive species and a single mobile negative species. As we mentioned in section II, the generalization involves the introduction of a complex, frequency-dependent rate constant, first suggested by Lányi [21], further developed by Macdonald [19] and Macdonald and Jacobs [20], and even further generalized in the present work.

In the small-signal a.c. case, with  $\Gamma = \Gamma_e + \Gamma_1 \exp(i\omega t)$  and  $c = c_e + c_1 \exp(i\omega t)$ , eqns. (44)–(46) become, after Taylor series expansion and some rearrangement,

$$I_{n1R} = -z_{n}e\left[\left(\frac{\partial v_{1}}{\partial n_{R}}\right)_{0}n_{1R} + \left(\frac{\partial v_{1}}{\partial \Gamma}\right)_{0}\Gamma_{1} + \left(\frac{\partial v_{1}}{\partial c}\right)_{0}c_{1} + \left(\frac{\partial v_{1}}{\partial \eta}\right)_{0}\eta_{1}\right]$$
(48)

$$(1 + i\omega\tau_{\Gamma})\Gamma_{1} = -\alpha_{\Gamma n}\tau_{\Gamma}n_{1R} - \alpha_{\Gamma c}\tau_{\Gamma}c_{1} - \alpha_{\Gamma \eta}\tau_{\Gamma}\eta_{1}$$
(49)

$$(1 + i\omega\tau_{c})c_{1} = -\alpha_{cn}\tau_{c}n_{1R} - \alpha_{c\Gamma}\tau_{c}\Gamma_{1} - \alpha_{c\eta}\tau_{c}\eta_{1}$$
(50)

where  $\alpha_{\Gamma n} \equiv (\partial (v_2 - v_1)/\partial n_R)_0$ ,  $\alpha_{\Gamma c} \equiv (\partial (v_2 - v_1)/\partial c)_0$ ,  $\alpha_{\Gamma \eta} \equiv (\partial (v_2 - v_1)/\partial \eta)_0$ ,  $\alpha_{cn} \equiv -(\partial v_2/\partial n_R)_0$ ,  $\alpha_{c\Gamma} \equiv -(\partial v_2/\partial \Gamma)_0$ ,  $\alpha_{c\eta} \equiv -(\partial v_2/\partial \eta)_0$ ,

$$\tau_{\Gamma}^{-1} \equiv \left(\frac{\partial (v_2 - v_1)}{\partial \Gamma}\right)_0 \tag{51}$$

and

$$\tau_{\rm c}^{-1} \equiv -\left(\frac{\partial v_2}{\partial \,{\rm c}}\right)_0 \tag{52}$$

If (49) and (50) are used to eliminate  $\Gamma_1$  and  $c_1$  from (48), one obtains an expression for the boundary condition (44) of the form

$$I_{n1R} = -z_n e[k_n^*(\omega)n_{1R} + (z_n e\eta_1/kT)\gamma_n^*(\omega)n_e]$$
(53)

where  $k_n^*$  and  $\gamma_n^*$  are complex, frequency-dependent rate constants. If  $\eta_1 = 0$ , the boundary condition reduces to the Chang-Jaffé form (27). Expressions for  $k_n^*$  and  $\gamma_n^*$  will not be given here for the case in which both  $c_1$  and  $\Gamma_1$  are non-

zero; however, it should be noted that  $k_n^*$  and  $\gamma_n^*$  then involve the two relaxation times  $\tau_{\Gamma}$  and  $\tau_c$  and are expected to lead to more complex equivalent circuits than in the single-time-constant case. For the simple case treated by Macdonald [19] in which c is held constant, one obtains

$$k_{n}^{*}(\omega) = \left[ \left( \frac{\partial v_{1}}{\partial n_{R}} \right)_{0} - \left( \frac{\partial v_{1}}{\partial \Gamma} \right)_{0} \alpha_{\Gamma n} \tau_{\Gamma} + i\omega \left( \frac{\partial v_{1}}{\partial n_{R}} \right)_{0} \tau_{\Gamma} \right] / (1 + i\omega\tau_{\Gamma})$$
$$\equiv [k_{n0} + i\omega\tau_{\Gamma} k_{n\infty}] / (1 + i\omega\tau_{\Gamma})$$
(54)

and

- .

$$\gamma_{n}^{*}(\omega) = (kT/z_{n}en_{e}) \left[ \left( \frac{\partial v_{1}}{\partial \eta} \right)_{0} - \left( \frac{\partial v_{1}}{\partial \Gamma} \right)_{0} \alpha_{\Gamma\eta}\tau_{\Gamma} + i\omega \left( \frac{\partial v_{1}}{\partial \eta} \right)_{0}\tau_{\Gamma} \right] / (1 + i\omega\tau_{\Gamma})$$

$$\equiv [\gamma_{n0} + i\omega\tau_{\Gamma}\gamma_{n\infty}] / (1 + i\omega\tau_{\Gamma})$$
(55)

The quantity  $\tau_{na}$  defined in section II may thus be set equal to  $\tau_{\Gamma}$ . The expression for  $k_n^*$  originally obtained by Macdonald [19] was based on the assumption  $I_{n1R} = i_f$  (47), valid only in certain special cases, and is superseded by the more general (54). Complex rate constants for simple adsorption ( $v_2 = 0$ ) are obtained by eliminating the derivatives of  $v_2$  from  $\alpha_{\Gamma n}$ ,  $\alpha_{\Gamma \eta}$ , and  $\tau_{\Gamma}$ . It then follows from (54) and (55) that  $k_{n0} = \gamma_{n0} = 0$ .

Thus far, we have not placed any restrictions on  $v_1$  and  $v_2$  aside from the functional dependencies indicated in (44)–(46). We note here that a logical extension of the Butler-Volmer relation (25) to the reaction sequence  $n \rightarrow \Gamma \rightarrow c$ , with c held at constant concentration, is given by

$$v_1 = f_{11}(n_R, \Gamma) \exp\{\beta_1 \lambda_1 z_n e\eta/kT\} - f_{12}(n_R, \Gamma) \exp\{-(1-\beta_1)\lambda_1 z_n e\eta/kT\}$$
(56)

$$v_2 = \mathbf{f}_{21}(\Gamma) \exp\{\beta_2 \lambda_2 z_n e\eta/kT\} - \mathbf{f}_{22}(\Gamma) \exp\{-(1-\beta_2)\lambda_2 z_n e\eta/kT\}$$
(57)

where  $\beta_1$  and  $\beta_2$  are transfer coefficients for the two steps of the reaction sequence and the coefficients  $\lambda_1$  and  $\lambda_2$  are determined by the details of the adsorption and reaction mechanisms. Since c is assumed to be a neutral species, or one that passes into the electrode, the total charge transferred to the electrode in the reaction sequence is  $-z_n e$ , and it is most consistent with the original Butler-Volmer relation (25) to have  $\lambda_1 + \lambda_2 = 1$ . If the only charged species which move during the sequence are electrons, one has  $\lambda_1 = z_1/z_n$  and  $\lambda_2 = z_2/z_n$ . As was stated earlier, discreteness effects, associated with the micropotential, have been omitted from the present discussion. To some extent, these effects might be subsumed into the present treatment by altering the values of  $\lambda_1$  and  $\lambda_2$ .

For illustrative purposes, in subsequent sections we shall give particular attention to simple specific adsorption, for which  $v_2 = 0$ , and shall set  $\lambda_1 = 1$  in that case. According to the microscopic model usually employed in derivations of the Butler-Volmer equation [30], the latter assumption is most appropriate when  $\Gamma$  is a neutral species or when the plane of centroids of the adsorbed ions is essentially coincident with the effective electrode surface plane. As a special case of simple specific adsorption we shall focus on a Langmuir type isotherm [33], obtained by setting

$$f_{11}(n_{\rm R}, \Gamma) = k_{\rm na1} n_{\rm R} \left[ 1 - (\Gamma/\Gamma_{\rm max}) \right]$$
(58)

and

$$f_{12}(n_{\rm R},\Gamma) = k_{\rm na2}\Gamma/\Gamma_{\rm max}$$
<sup>(59)</sup>

where  $\Gamma_{\max}$  is the number of adsorption sites per unit area. In the Langmuir case we then have from (51), (54), and (55),  $k_{n\infty} = \gamma_{n\infty} = k_{na1} [1 - (\Gamma_e / \Gamma_{\max})]$  and  $\tau_{na} \equiv \tau_{\Gamma} = \Gamma_e / k_{na1} n_e$ , where  $\Gamma_e$  is the value of  $\Gamma$  at equilibrium.

## (VI) STEADY-STATE, SMALL-SIGNAL D.C.

In this section we examine the effect of a supporting electrolyte and the choice of boundary conditions on the d.c.  $(\omega \rightarrow 0)$  circuit parameters. We assume ions of a supporting electrolyte may be present and blocked at the electrodes, as well as the ions of interest which obey eqns. (14)–(19) and the boundary conditions (22) and (23), or (44)–(46). We first obtain an expression for the small-signal d.c. resistance in the absence of specific adsorption. By formally integrating the small-signal Nernst-Planck equations (30) and (31), with constant  $I_{p1}$  and  $I_{p1}$ , one obtains

$$p_{1R} = \frac{-z_{p}ep_{e}\zeta_{1}}{kT} - \frac{I_{p1}l_{h}}{\mu_{p}kT}$$
(60)

and

$$n_{1R} = \frac{z_{n}en_{e}\zeta_{1}}{kT} + \frac{I_{n1}l_{h}}{\mu_{n}kT}$$
(61)

The substitution of eqns. (60) and (61) into the small-signal boundary conditions (34) and (35) yields

$$I_{\rm p1} = -z_{\rm p}^2 e^2 \mu_{\rm p} p_{\rm e} (k_{\rm p} \zeta_1 - \gamma_{\rm p} \eta_1) / (\mu_{\rm p} k T + z_{\rm p} e l_{\rm h} k_{\rm p})$$
(62)

and

$$I_{n1} = -z_n^2 e^2 \mu_n n_e (k_n \zeta_1 + \gamma_n \eta_1) / (\mu_n k T + z_n e l_h k_n)$$
(63)

Evaluating  $1/R_{D1} = -d(I_{p1} + I_{n1})/dV_{ah1}$ , equal to the integral resistance at zero bias, and making use of the identity

$$\frac{\mathrm{d}\zeta_1}{\mathrm{d}V_{\mathrm{ah}1}} + \frac{\mathrm{d}\eta_1}{\mathrm{d}V_{\mathrm{ah}1}} \equiv 1 \tag{64}$$

one obtains

$$\frac{1}{R_{\rm D1}} = z_{\rm p}^2 e^2 \mu_{\rm p} p_{\rm e} [(k_{\rm p} + \gamma_{\rm p}) \frac{\mathrm{d}\zeta_1}{\mathrm{d}V_{\rm ah1}} - \gamma_{\rm p}] / (\mu_{\rm p} kT + z_{\rm p} e l_{\rm h}) + z_{\rm n}^2 e^2 \mu_{\rm n} n_{\rm e} [(k_{\rm n} - \gamma_{\rm n}) \frac{\mathrm{d}\zeta_1}{\mathrm{d}V_{\rm ah1}} + \gamma_{\rm n}] / (\mu_{\rm n} kT + z_{\rm n} e l_{\rm h})$$
(65)

The concentration of supporting electrolyte enters into (65) only through  $d\zeta_1/dV_{ahl}$ , which is largest in the unsupported case (for given  $n_e$  and  $p_e$ ) and decreases as the support concentration increases. From (65) it then follows that the d.c. resistance will be independent of the concentration of the supporting electrolyte if (a) the quantity multiplying  $d\zeta_1/dV_{ahl}$  vanishes, as is the case if

the Butler-Volmer boundary conditions, eqns. (24) and (25), are appropriate [32], or (b) if the overpotential is taken to be zero so that  $d\zeta_1/dV_{ah1} = 1$ , in which case the Butler-Volmer conditions reduce to the Chang-Jaffé forms (26) and (27). In both these situations, one obtains, regardless of the concentration of supporting electrolyte:

$$R_{\rm D1} = \left[ (R_{\rm bp} + R_{\theta \rm p})^{-1} + (R_{\rm bn} + R_{\theta \rm n})^{-1} \right]^{-1} \tag{66}$$

where  $R_{\rm bp} \equiv l_{\rm h}/\mu_{\rm p}p_e z_{\rm p}e$  and  $R_{\rm bn} \equiv l_{\rm h}/\mu_{\rm n}n_e z_{\rm n}e$  are the bulk resistances associated with the positive and negative carriers, respectively, and  $R_{\theta \rm p} \equiv kT/k_{\rm p}p_e z_{\rm p}^2 e^2$  and  $R_{\theta \rm n} \equiv kT/k_{\rm n}n_e z_{\rm n}^2 e^2$  are the charge transfer, or reaction, resistances for the positive and negative carriers, respectively, at the single polarizable electrode.

The results just obtained may readily be compared with those of the preceding discussion. The extensive quantities  $R_{\rm bp}$  and  $R_{\rm bn}$  when normalized with  $R_{\infty 1}^{-1} = R_{\rm bn}^{-1} + R_{\rm bn}^{-1}$  are respectively  $\epsilon_{\rm p}^{-1}$  and  $\epsilon_{\rm n}^{-1}$ ; the same quantities appear in eqn. (1) for  $R_{\rm DN}$  and in Fig. 2. Since we have assumed no adsorption of the carriers  $k_{\rm n\infty} = k_{\rm n0} \equiv k_{\rm n}$ , and  $R_{\theta \rm n}$  is simply the reaction resistance for negative carriers,  $R_{\rm R1}$ , given in eqn. (9).  $R_{\theta \rm p}$  is, by analogy, the reaction resistance for positive carriers.

The identity of the charge transfer or reaction resistance as derived from the Chang-Jaffé conditions with that obtained from the Butler-Volmer relations (with the same rate constants  $k_p$  and  $k_n$ ) has been noted by Macdonald [13]. If one assumes that the Butler-Volmer expressions correctly describe the physical situation, the coincidence of results may be seen to arise from a "cancellation of errors" in neglecting the overpotential, which makes  $\zeta_1$  too large by  $\eta_1$ , in turn making  $p_{R1}$  too small by  $z_p e \eta_1 / kT$  and  $n_{R1}$  too large by  $z_n e \eta_1 / kT$ , with the result that  $I_{pR1}$  and  $I_{nR1}$  computed from the Chang-Jaffé expressions and the "incorrect"  $p_{R1}$  and  $n_{R1}$  are identical with  $I_{pR1}$  and  $I_{nR1}$  computed from the Computed from the correct  $p_{R1}$  and  $n_{R1}$ . Although the Butler-Volmer expressions are usually considered to be correct on theoretical and experimental grounds, an argument similar to the preceding could be advanced assuming the Chang-Jaffé relations to be more physically correct. Experimental determination of the small-signal d.c. resistance thus does not, in itself, distinguish between the two sets of boundary conditions.

A similar coincidence is found when one of the carriers (*n* assumed) is specifically adsorbed at the electrode. We consider only simple specific adsorption, so that  $I_{n1} = 0$  in the steady state and *n* may then be assumed to obey Boltzmann statistics. Setting  $I_{n1R} = 0$  in (48) and solving for  $\Gamma_1$  with  $c_1 = 0$ , yields

$$\Gamma_1 = (n_e z_n e/kT) [k_{n\infty} \zeta_1 + \gamma_{n\infty} \eta_1] \tau_{\Gamma}$$
(67)

where use has been made of the symbols defined in (51), (54) and (55). The adsorption capacitance,  $C_{A1} = z_n e \, d\Gamma_1 / dV_{ah1}$  is thus given by

$$C_{\rm A1} = (n_{\rm e} z_{\rm n}^2 e^2 / kT) [(k_{\rm n\infty} - \gamma_{\rm n\infty}) \frac{\mathrm{d}\zeta_1}{\mathrm{d}V_{\rm ah1}} + \gamma_{\rm n\infty}] \tau_{\Gamma}$$
(68)

As was the case with the half-cell resistance,  $C_{A1}$  will be independent of the concentration of the supporting electrolyte if either the quantity multiplying  $d\zeta_1/dV_{ab1}$  or the overpotential is taken as zero. The former condition requires  $k_{n\infty} =$   $\gamma_{n\infty}$ , the latter condition,  $\gamma_{n\infty} = 0$ . In either case, one obtains

$$C_{\rm A1} = \frac{n_{\rm e} z_{\rm n}^2 e^2}{kT} k_{\rm n\infty} \tau_{\rm \Gamma} \tag{69}$$

a result previously obtained by Macdonald [13], and in full agreement with eqn. (13) as applied to pure specific adsorption. The formal equivalence of the  $k_{n\infty} = \gamma_{n\infty} = 0$  (generalized Chang-Jaffé) case results from the same sort of "cancellation of errors" as discussed in connection with  $R_{D1}$  for non-adsorbed carriers. For  $\gamma_{n\infty} = 0$  one has a larger concentration,  $n_{R1}$ , and a compensatingly smaller reaction probability than for  $\gamma_{n\infty} = k_{n\infty}$ .

The Butler-Volmer-like form (56) for  $v_1$ , with  $\lambda_1 = 1$ , leads to  $\gamma_{n\infty} = k_{n\infty}$  provided that

$$f_{11}(n_e, \Gamma_e) = f_{12}(n_e, \Gamma_e) = n_e \left[ \left( \frac{\partial f_{11}}{\partial n_R} \right)_0 - \left( \frac{\partial f_{12}}{\partial n_R} \right)_0 \right]$$
(70)

as is the case when  $f_{11}$  is proportional to  $n_R$  and  $f_{12}$  is independent of it. This requirement is met by such simple functions as (58) and (59), which give the Langmuir-type isotherm. In this case

$$C_{\rm A1} = (z_{\rm n}^2 e^2 / kT) (\Gamma_{\rm e} / \Gamma_{\rm max}) [1 - (\Gamma_{\rm e} / \Gamma_{\rm max})]$$

$$\tag{71}$$

It should finally be noted that eqn. (69) becomes

$$C_{\rm A1} = \frac{-z_{\rm n}^2 e^2 n_{\rm e}}{kT} \left(\frac{\partial v_{\rm 1}}{\partial n_{\rm R}}\right)_0 / \left(\frac{\partial v_{\rm 1}}{\partial \Gamma}\right)_0 = \frac{z_{\rm n}^2 e^2 n_{\rm e}}{kT} \left(\frac{\partial \Gamma}{\partial n_{\rm R}}\right)_{v_{\rm 1}=0}$$
(72)

when expressed in terms of derivatives. Essentially the latter form was used by de Levie and Vukadin [24] in connection with specific adsorption at a membrane surface.

## (VII) SMALL-SIGNAL A.C. RESPONSE

We have seen that in the small-signal d.c. case the d.c. resistance  $R_{D1}$  and the adsorption capacitance  $C_{A1}$ , obtained assuming Butler-Volmer boundary conditions, were identical with those obtained from the Chang-Jaffé conditions. This observation suggests that a frequency-dependent correction might be introduced into the exact small-signal response obtained for an unsupported system obeying Chang-Jaffé boundary conditions to yield the small-signal response appropriate to more general boundary conditions. In this section we shall show that such a correction can in general be found for the overpotential-dependent boundary conditions (34) and (35) with real or complex rate constants and that the smallsignal admittance may be expressed as a sum of the admittance calculated for Chang-Jaffé boundary conditions and a correction dependent on  $\eta_1$ , the smallsignal overpotential. In the following sections  $\eta_1$  and the admittance correction will be evaluated for a simple model.

We begin by assuming that a transformed set of fundamental quantities (indicated by a circumflex) may be defined:  $\hat{p}_1 \equiv p_1 + (\gamma_p z_p e \eta_1 p_e/kTk_p)S_p(x, \omega)$ ;  $\hat{n}_1 \equiv n_1 + (\gamma_n z_n e \eta_1 n_e/kTk_n)S_n(x, \omega)$ ;  $\hat{V}_1 \equiv V_1 + \eta_1 S_v(x, \omega)$ ;  $\hat{I}_p \equiv I_p + (\sigma \eta_1/L_D)S_{I_p}(x, \omega)$ ;  $\hat{I}_n \equiv I_n + (\sigma \eta_1/L_D)S_{I_n}(x, \omega)$ ; and  $\hat{I} \equiv I + (\sigma \eta_1/L_D)S_I(\omega)$ , such that the

$$\hat{I}_{p1R} = z_p e k_p \hat{p}_{1R}$$
(73)  
and

$$\hat{I}_{n1R} = -z_n e k_n \hat{n}_{1R} \tag{74}$$

where  $k_n$  and  $k_p$  may be complex (if specific adsorption occurs), and the smallsignal equations (28)–(33) are satisfied by the circumflexed variables. In the preceding,  $\sigma \equiv (p_e \mu_p z_p + n_e \mu_n z_n)e$  is the bulk conductivity of the electrolyte and  $L_D$  the Debye length. Straightforward substitution reveals that the dimensionless correction factors  $S_p$ ,  $S_n$ , etc. must then satisfy the differential equations

$$\frac{\mathrm{d}S_{\mathrm{I}_{\mathrm{p}}}}{\mathrm{d}x} = -\mathrm{i}\omega\tau_{\mathrm{D}}\nu_{\mathrm{p}}\delta_{\mathrm{p}}S_{\mathrm{p}}/L_{\mathrm{D}}$$
(75)

$$\frac{\mathrm{d}S_{\mathbf{I}_{\mathbf{n}}}}{\mathrm{d}x} = \mathrm{i}\omega\tau_{\mathrm{D}}\nu_{\mathrm{n}}\delta_{\mathrm{n}}S_{\mathrm{n}}/L_{\mathrm{D}}$$
(76)

$$S_{I_p} = -\epsilon_p L_D \left[ \frac{dS_v}{dx} + \nu_p \frac{dS_p}{dx} \right]$$
(77)

$$S_{I_n} = -\epsilon_n L_D \left[ \frac{dS_v}{dx} - \nu_n \frac{dS_n}{dx} \right]$$
(78)

$$\frac{\mathrm{d}S_{\mathrm{v}}}{\mathrm{d}x} = (S_{\mathrm{I}} - S_{\mathrm{I}_{\mathrm{p}}} - S_{\mathrm{I}_{\mathrm{n}}})/(\mathrm{i}\omega\tau_{\mathrm{D}}L_{\mathrm{D}})$$
(79)

and

$$\frac{\mathrm{d}^2 S_{\mathrm{v}}}{\mathrm{d}x^2} = -[\nu_{\mathrm{p}} \delta_{\mathrm{p}} S_{\mathrm{p}} - \nu_{\mathrm{n}} \delta_{\mathrm{n}} S_{\mathrm{n}}]/L_{\mathrm{D}}^2$$
(80)

where  $\nu_{\rm p} \equiv \gamma_{\rm p}/k_{\rm p}$ ,  $\nu_{\rm n} \equiv \gamma_{\rm n}/k_{\rm n}$ , and the dielectric relaxation time  $\tau_{\rm D}$  and the factors  $\delta_{\rm p}$ ,  $\delta_{\rm n}$ ,  $\epsilon_{\rm p}$ , and  $\epsilon_{\rm n}$  were defined in section II.

Six boundary conditions are required to completely specify a solution. These are taken to be  $S_p(0, \omega) = S_n(0, \omega) = S_v(0, \omega) = 0$ , and  $S_v(l_h, \omega) = 1$ ,  $S_{I_p}(l_h, \omega) = (L_D \gamma_p \epsilon_p / D_p) [S_p(l_h, \omega) - 1]$ , and  $S_{I_n}(l_h, \omega) = (L_d \gamma_n \epsilon_n / D_n) [1 - S_n(l_h, \omega)]$ . so that  $V_{ah_1} = \hat{V}_1(l_h) - \hat{V}_1(0)$ , and the ohmic and general boundary conditions at the left and right electrodes transform into ohmic and Chang-Jaffé boundary conditions, respectively. The admittance  $Y_1 \equiv Z_1^{-1}$  of the halfcell for the general boundary conditions becomes

$$Y_1 = Y_{CJ1} + Y_{\eta 1}$$
(81)

where  $Y_{CJ1}$  is the admittance calculated from the Chang-Jaffé boundary conditions and

$$Y_{\eta 1} \equiv \sigma \eta_1 S_{\rm I} / L_{\rm D} V_{\rm ah\,1} \tag{82}$$

Evaluation of  $\eta_1$ , making possible the evaluation of  $Y_{\eta_1}$ , will be considered in the next section.

Solution of the equations (75)-(80), although straightforward, is rather

296

tedious. We will restrict ourselves here to the special case  $\mu_p = 0$ , so that only the negative carriers are assumed mobile. Such materials may be taken to be completely extrinsic, with  $\chi \to \infty$  and consequently  $\delta_n = \epsilon_n = 1$ , provided  $L_D$  is taken as  $L_{Dn}$ . The correction factors are then given by

$$S_{n} = \frac{(1 + i\Omega)(\nu_{n}r_{n} + 2)\sinh(Qx)/\sinh(Ql_{n})}{\nu_{n}[2 + r_{n}(1 + i\Omega) + 2i\Omega\gamma_{1}]}$$
(83)

$$S_{v} = \frac{(\nu_{n}r_{n} + 2)[\sinh(Qx)/\sinh(Ql_{h})] + (x/l_{h})[r_{n}(1 + i\Omega - \nu_{n}) + 2i\Omega\gamma_{1}]}{2 + r_{n}(1 + i\Omega) + 2i\Omega\gamma_{1}}$$
(84)

$$S_{I_n} = \frac{r_n(\nu_n - 1 - i\Omega) - 2i\Omega\gamma_1 + (\nu_n r_n + 2)i\Omega Ql_h [\cosh(Qx)/\sinh(Ql_h)]}{(l_h/L_{Dn})[2 + r_n(1 + i\Omega) + 2i\Omega\gamma_1]}$$
(85)

and

$$S_{\rm I} = \frac{(1+{\rm i}\Omega)[r_{\rm n}(\nu_{\rm n}-1-{\rm i}\Omega)-2{\rm i}\Omega\gamma_{\rm I}]}{(l_{\rm L}/L_{\rm Dn})[2+r_{\rm n}(1+{\rm i}\Omega)+2{\rm i}\Omega\gamma_{\rm I}]},\tag{86}$$

where  $Q^2 \equiv (1 + i\omega\tau_D)/L_{Dn}^2$  and  $\gamma_1 \equiv (Ql_h) \operatorname{ctnh}(Ql_h)$ . It should be noted that  $S_1$ , and thus  $Y_{\eta 1}$  (for  $\eta_1 \neq 0$ ), do not vanish in the d.c. limit unless  $\nu_n = 1$ , as in the case for the Butler-Volmer equation (25) and for the Butler-Volmer-like equation for specific adsorption (56) when the condition (70) is met. In such cases the admittance correction becomes

$$Y_{\eta 1} = \frac{-\sigma \eta_1 i\Omega(1 + i\Omega)}{l_h V_{ahl}} \frac{(r_n + 2\gamma_1)}{[2 + r_n(1 + i\Omega) + 2i\Omega\gamma_1]}$$
(87)

which may be expressed in normalized form as

$$Y_{\eta 1N} = \frac{-\eta_1 i\Omega(1+i\Omega)}{l_h V_{ahl}} \frac{(r_n + 2\gamma_1)}{[2 + r_n(1+i\Omega) + 2i\Omega\gamma_1]}$$
(88)

## (VIII) A MODEL FOR THE SMALL-SIGNAL OVERPOTENTIAL $\eta_1$

We assume that the potential in the region between  $x = l_h$  and  $x = l_h + d$  obeys the relation (compare eqn. 32)

$$i\omega \frac{dV_1}{dx} = -\frac{4\pi}{\epsilon_1} (I_1 - I_{fi})$$
(89)

where  $\epsilon_1$  is a compact-layer effective dielectric constant and  $I_{f1}$  is the faradaic current, consisting of ions or electrons or both. Upon integration of (89) one obtains

$$\eta_1 = -\frac{4\pi I_1 d}{i\omega\epsilon_1} + \frac{4\pi}{i\omega\epsilon_1} \int_{l_h}^{l_h + d} I_{f_1} dx$$
(90)

since the total current (in one-dimensional flow) is spatially invariant [34]. When no specific adsorption occurs, or only neutral species are adsorbed, or the plane of centroids of the adsorbed ions is essentially coincident with the effective electrode surface plane, we may set  $I_{f1} = I_{p1R} + I_{n1R}$ , so that

$$\eta_1 = -\frac{4\pi d}{i\omega\epsilon_1} [I_1 - I_{\text{p1R}} - I_{\text{n1R}}]$$
(91)

If the currents in eqn. (91) are then expressed in terms of the transformed variables  $\hat{I}_1$ ,  $\hat{I}_{p1}$ ,  $\hat{I}_{n1}$ , and the corresponding correction factors, and eqn. (32) is used to relate the transformed currents to  $d\hat{V}_1/dx$ , one finds

$$\eta_1 = \hat{\eta}_1 / [1 - (d/i\omega\tau_1 L_{\rm Dn})(S_{\rm I} - S_{\rm IpR} - S_{\rm InR})]$$
(92)

where  $\tau_1 \equiv \epsilon_1/4 \pi \sigma$  is an effective dielectric relaxation time for the compact double layer and

$$\hat{\eta}_1 \equiv \frac{\epsilon d}{\epsilon_1} \left( \frac{\mathrm{d} \, \hat{V}_1}{\mathrm{d} x} \right)_{\mathrm{R}} \tag{93}$$

is the overpotential that would be extrapolated from the computed electric field,  $-(d\hat{V}_1/dx)$  to the left of  $x = l_h$ , taking into account the dielectric constant change at  $x = l_h$ , with the field throughout the compact layer assumed constant. Equation (92) may be viewed as the application of a correction to  $\hat{\eta}_1$  which compensates for the original assumption that the total applied potential falls only across the diffuse part of the double layer. For the  $\mu_p = 0$  case considered in the preceding section, we can explicitly write

$$\eta_{1} = \hat{\eta}_{1} \left[ 1 + \left( \frac{\epsilon d}{\epsilon_{1} l_{h}} \right) \frac{\left[ (r_{n} \nu_{n} + 2 + 2i\Omega) \gamma_{1} + r_{n} (1 + i\Omega - \nu_{n}) \right]}{\left[ 2 + r_{n} (1 + i\Omega) + 2i\Omega \gamma_{1} \right]} \right]^{-1}$$
(94)

It should be noted that, if the half-cell considered here is taken as half of a symmetrical cell (as in the earlier sections),  $l_{\rm h}/L_{\rm Dn} \equiv l/2 \ L_{\rm Dn} \equiv M_{\rm n}$ , and  $\omega \tau_{\rm D}$  is the normalized frequency  $\Omega$ . When eqn. (92) is inserted into eqn. (82) an expression is obtained for the admittance correction  $Y_{\eta 1}$  in terms of the solutions of eqns. (75)–(80).

The model for  $\eta_1$  presented here is easily extended to more general adsorption situations. We take as an example the case  $n \rightarrow \Gamma + z_1 e^-$ , considered in section Vb, and suppose that the plane of charge centroids of the adsorbed ions  $\Gamma$  lies a distance  $\beta$  to the right of  $l_{\rm h}$ . Again, considering only the negative species to be mobile in the electrolyte, we have  $I_{\rm f1} = I_{\rm n1R}$  from  $x = l_{\rm h}$  to  $x = l_{\rm h} + \beta$  and  $I_{\rm f1} = (z_1/z_{\rm n})I_{\rm n1R}$  from  $x = l_{\rm h} + \beta$  to  $x = l_{\rm h} + d$ . The adsorption current is carried by electrons in the latter interval. From eqn. (90), and the definitions of transformed currents in section VII, one finds

$$\eta_{1} = \frac{-\frac{4\pi}{i\omega\epsilon_{1}}(\hat{I}_{1}d - \hat{I}_{n1R}\xi)}{1 - (i\omega\tau_{1}L_{Dn})^{-1}(S_{I}d - S_{InR}\xi)}$$
(95)

where  $\xi \equiv \beta + (z_1/z_n)(d-\beta)$ . When specific adsorption of charged species occurs,  $\eta_1$  is not simply proportional to  $\hat{\eta}_1$  as in eqn. (92), and the admittance correction  $Y_{\eta_1}$  takes on a somewhat more complicated form.

### (IX) DISCUSSION

In section VII a method was introduced, based on a transformation of the fundamental variables: currents, concentrations, and potential, which enables

298

one to relate the small-signal response of an unsupported system with overpotential-dependent electrode reaction rates to the response of a similar system obeying Chang-Jaffé boundary conditions. The result is most simply expressed as an addition  $Y_{\eta 1}$  to the Chang-Jaffé small-signal admittance,  $Y_{CJ1} = Z_{CJ1}^{-1}$ . The quantity  $Y_{\eta 1}$  is proportional to the small-signal overpotential  $\eta_1$ , which can be evaluated from a physical model such as that presented in the preceding section.

The treatment given here has been rather formal in nature; investigation of systems with particular boundary conditions will be the subject of forthcoming work. To conclude the present discussion we will briefly examine the sensitivity of the small-signal response to the choice of boundary conditions. From eqn. (81) it follows that the half-cell small-signal impedance for a given set of boundary conditions is  $Z_1 = Z_{CJ1}/(1 + Y_{\eta 1}Z_{CJ1})$ , where  $Y_{\eta 1}$  is determined by the boundary conditions of interest. It is then a simple matter to show that the normalized impedance of a symmetrical cell,  $Z_N$ , is related to the normalized impedance  $Z_{CJN}$  (denoted  $Z_{TN}$  in earlier sections), determined for Chang-Jaffé boundary conditions by

$$Z_{\rm N}(\Omega) = Z_{\rm CJN}(\Omega) / [1 + \Delta(\Omega)]$$
(96)

where  $\Delta(\Omega) \equiv Y_{\eta 1N}(\Omega) Z_{CJN}(\Omega)$  and  $Y_{\eta 1N}(\Omega) \equiv R_{\infty 1} Y_{\eta 1}(\Omega)$ . If  $|\Delta(\Omega)| << 1$  over the frequency range accessible to measurement, it will not be possible to distinguish between the chosen overpotential-dependent boundary conditions and the Chang-Jaffé conditions.

We restrict ourselves here to systems for which eqn. (91) is valid, i.e. to cells in which there is no build up of charge within the compact layer except at the effective electrode surface and to the  $\mu_p = 0$  case. We may then combine eqns. (92), (93), (85), (86) and (82), to write

$$Y_{\eta \mathbf{1N}} = \left(\frac{\epsilon \mathbf{d}}{\epsilon_1 V_{ahl}}\right) \left(\frac{\mathrm{d}V_1}{\mathrm{d}x}\right)_{\mathbf{R}} \frac{(1 + \mathrm{i}\Omega)[r_n(\nu_n - 1 - \mathrm{i}\Omega) - 2\mathrm{i}\Omega\gamma_1]}{[2(1 + \mathrm{i}\Omega\gamma_1) + r_n(1 + \mathrm{i}\Omega)]} \times \left[1 + \left(\frac{\epsilon \mathbf{d}}{\epsilon_1 l_h}\right) \frac{[(r_n\nu_n + 2 + 2\mathrm{i}\Omega)\gamma_1 + r_n(1 + \mathrm{i}\Omega - \nu_n)]}{[2(1 + \mathrm{i}\Omega\gamma_1) + r_n(1 + \mathrm{i}\Omega)]}\right]^{-1}$$
(97)

From the exact small-signal solution for  $\mu_p = 0$  and Chang-Jaffé boundary conditions we have

$$\left(\frac{\mathrm{d}V_1}{\mathrm{d}x}\right)_{\mathrm{R}} = \frac{V_{\mathrm{ah1}}(1+\mathrm{i}\Omega)[r_{\mathrm{n}}+2(Ql_{\mathrm{h}})\mathrm{ctnh}(Ql_{\mathrm{h}})]}{l_{\mathrm{h}}[2+(1+\mathrm{i}\Omega)r_{\mathrm{n}}+2\,\mathrm{i}\Omega(Ql_{\mathrm{h}})\mathrm{ctnh}(Ql_{\mathrm{h}})]}$$
(98)

and

$$Z_{\rm CJN} = \frac{\left[2 + (1 + i\Omega)r_{\rm n} + 2\,i\Omega(Ql_{\rm h}){\rm ctnh}(Ql_{\rm h})\right]}{(1 + i\Omega)\left[(1 + i\Omega)r_{\rm n} + 2\,i\Omega(Ql_{\rm h}){\rm ctnh}(Ql_{\rm h})\right]}$$
(99)

Combining (97), (98) and (99) then leads to the exact expression

$$\Delta(\Omega) = \left(\frac{\epsilon d}{\epsilon l_{\rm h}}\right) \frac{(1+i\Omega)(r_{\rm h}+2\gamma_1)[r_{\rm n}(\nu_{\rm h}-1-i\Omega)-2i\Omega\gamma_1]}{[r_{\rm n}(1+i\Omega)+2i\Omega\gamma_1][2(1+i\Omega\gamma_1)+r_{\rm n}(1+i\Omega)]} \times \left[1+\left(\frac{\epsilon d}{\epsilon_1 l_{\rm h}}\right) \frac{\nu_{\rm n} r_{\rm n}(\gamma_1-1)+(1+i\Omega)(r_{\rm h}+2\gamma_1)}{[2(1+i\Omega\gamma_1)+r_{\rm n}(1+i\Omega)]}\right]^{-1}$$
(100)

Assume  $0 \le v_n \le 10$  and define  $M_n \equiv l_h/L_{Dn}$ . For  $M_n << 1$  (a dilute or thin cell), eqn. (100) reduces to the form

$$\Delta(\Omega) \approx \frac{\epsilon d}{\epsilon_1 l_h} \frac{\left[r_n(\nu_n - 1 - i\Omega) - 2i\Omega\right]}{\left[(1 + i\Omega)r_n + 2i\Omega\right]} \left[1 + \frac{\epsilon d}{\epsilon_1 l_h}\right]^{-1}$$
(101)

and  $|\Delta| \sim 1$  only if  $(\epsilon d/\epsilon_1 l_n) \sim 1$ , which is likely to occur only in cells of microscopic thickness. At the other extreme,  $M_n >> 1$  (thick or concentrated cell), eqn. (100) reduces to the form

$$\Delta(\Omega) \approx \left(\frac{\epsilon d}{\epsilon_{1}l_{h}}\right) \frac{(1 + i\Omega)(r_{n} + 2Ql_{h})[r_{n}(\nu_{n} - 1 - i\Omega) - 2i\Omega Ql_{h}]}{[r_{n}(1 + i\Omega) + 2i\Omega Ql_{h}][2(1 + i\Omega Ql_{h}) + r_{n}(1 + i\Omega)]} \times \left[1 + \left(\frac{\epsilon d}{\epsilon_{1}l_{h}}\right) \frac{\nu_{n}r_{n}(Ql_{h} - 1) + (1 + i\Omega)(r_{n} + 2Ql_{h})}{[2(1 + i\Omega Ql_{h}) + r_{n}(1 + i\Omega)]}\right]^{-1}$$
(102)

For  $r_n >> M_n$  (rapid electrode reaction), it is readily found that  $|\Delta|$  again approaches unity only when  $(\epsilon d/\epsilon_1 l_h) \sim 1$ , which in the present case is physically unrealizable. On the other hand, for  $r_n < M_n$  (slow electrode reaction) and  $\Omega \sim r_n/M_n$ , one finds that  $|\Delta|$  may approach unity when the Debye length becomes comparable to the compact layer thickness so that  $(\epsilon d/\epsilon_1 l_h) \sim 1$ . As  $\Omega \rightarrow 0$ ,  $|\Delta|$  approaches a finite value for non-Butler-Volmer kinetics but vanishes as expected in the Butler-Volmer case  $(\nu_n \equiv 1)$ .

#### ACKNOWLEDGMENTS

We are grateful to Dr. J.A. Garber for computational assistance and to Mr. T.R. Brumleve for helpful discussion.

#### REFERENCES

- 1 V.G. Levich, Advan. Electrochem. Electrochem. Eng., 4 (1966) 249.
- 2 H. Gerischer, Advan. Electrochem. Electrochem. Eng., 1 (1962) 139.
- 3 V.G. Levich and V.S. Krylov, Dokl. Akad. Nauk SSSR, 142 (1962) 123.
- 4 E. Gileadi and B.E. Conway in J.O'M. Bockris and B.E. Conway (Eds.), Modern Aspects of Electrochemistry, Vol. 3, Butterworths, London, 1964, pp. 347-442.
- 5 I. Epelboin and M. Keddam, J. Electrochem. Soc., 117 (1970) 1052.
- 6 I. Epelboin et al., Discuss. Faraday Soc., 56 (1974) 264.
- 7 R.D. Armstrong and M. Henderson, J. Electroanal. Chem., 39 (1972) 81.
- 8 Ref. 1, p. 326.
- 9 H. Chang and G. Jaffé, J. Chem. Phys., 20 (1952) 1071.
- 10 J.R. Macdonald, J. Chem. Phys., 58 (1973) 4982.
- 11 J.R. Macdonald, J. Electroanal. Chem., 47 (1973) 182; 49 (1974) 160.
- 12 J.R. Macdonald, J. Electroanal. Chem., 53 (1974) 1.
- 13 J.R. Macdonald, J. Chem. Phys., 61 (1974) 3977.
- 14 J.R. Macdonald, J. Phys. C, Solid State Phys., 7 (1974) 327; 8 (1975) 63.
- 15 J.R. Macdonald in M. Kleitz and J. Dupuy (Eds.), Electrode Processes in Solid State Ionics, D. Reidel, Dordrecht, Holland, 1976, pp. 149-180.
- 16 J.R. Macdonald in G.D. Mahan and W.L. Roth (Eds.), Superionic Conductors, Plenum, New York, 1976, pp. 81-97.
- 17 J.R. Macdonald, D.R. Franceschetti and R. Meaudre, J. Phys. C, Solid State Phys., to be published.
- 18 J.R. Macdonald and J.A. Garber, J. Electrochem. Soc., 124 (1977) 1022.
- 19 J.R. Macdonald, J. Electroanal. Chem., 70 (1976) 17.
- 20 J.R. Macdonald and P.W.M. Jacobs, J. Phys. Chem. Solids, 37 (1976) 1117.
- 21 S. Lányi, J. Phys. Chem. Solids, 36 (1975) 775.

300

- 22 G. Gabrielli, Ph.D. Thesis, University of Paris, 1973; Métaux, Corrosion, Industrie, Nos. 573, 574, 577, 578, 1973.
- 23 K.S. Cole, Membranes, Ions, and Impulses, University of California Press, Berkeley, 1968, p. 77.
- 24 R. de Levie and D. Vukadin, J. Electroanal. Chem., 62 (1975) 95.
- 25 J.R. Macdonald, J. Electroanal. Chem., 32 (1971) 317.
- 26 J.R. Macdonald, J. Chem. Phys., 22 (1954) 1317.
- 27 K.J. Vetter, Electrochemical Kinetics, Academic Press, New York, 1967, p. 75.
- 28 C.A. Barlow, Jr. and J.R. Macdonald, Advan. Electrochem. Electrochem. Eng., 6 (1967) 1.
- 29 W.R. Fawcett and S. Levine, J. Electroanal. Chem., 65 (1975) 505.
- 30 Ref. 27, p. 107ff.
- 31 R.D. Armstrong, R.E. Firman and H.R. Thirsk, Discuss. Faraday Soc., 56 (1974) 244.
- 32 Ref. 27, p. 154.
- 33 Ref. 4, p. 382.
- 34 J.R. Macdonald, J. Appl. Phys., 46 (1975) 4602.