

COMPLEX RATE CONSTANT FOR AN ELECTROCHEMICAL SYSTEM INVOLVING AN ADSORBED INTERMEDIATE *

J. ROSS MACDONALD

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

(Received 27th August 1975; in revised form 1st October 1975)

ABSTRACT

Two different methods of obtaining the impedance of a system involving an electrochemical reaction with an adsorbed intermediate are compared. The earlier method combines in parallel an impedance derived separately for the overall reaction with that for the rest of the system. It is appropriate for a fully supported electrolyte system but seems much less applicable to the unsupported situation. In contrast, the method derived and discussed herein involves complex reaction rate constants which may be directly incorporated in expressions for the total system impedance. This method may, therefore, be applied to either supported or unsupported situations. Several specific cases of the general complex rate constant results are discussed, particularly, various frequency dependencies possible. The overall small-signal impedance may be inductive in some parts of the frequency range and the low frequency limiting differential resistance negative, zero, or positive under various conditions.

INTRODUCTION

Numerous authors have described the impedances associated with complex electrochemical reactions for which the simple Randles–Ershler [1,2] equivalent circuit is inapplicable. These calculations are formally exemplified by the very general treatment of a reaction with an adsorbed intermediate by Armstrong and Henderson [3] (abbreviated hereafter as AH). These authors employ a Taylor series expansion to avoid the need of specific assumptions concerning adsorption isotherm, reaction orders, and the necessity of operation around the equilibrium potential of the overall reaction.

Consider the reaction [3]



where A and C are assumed by AH to be species in solution and B an adsorbed intermediate. Let e be the proton charge, z_1 the number of electrons trans-

* Work supported by U.S. National Science Foundation (Grant No. DMR 75-10739).

ferred from A to the electrode in the formation of one unit of B, and z_2 the number of electrons transferred from B to the electrode in the formation of one unit of species C. For simplicity, take the stoichiometric coefficients ν_A and ν_C unity in the following. The processes of eqn. (1) may alternatively occur in a solid rather than a liquid electrolyte.

There are several costs implicit in the AH type of approach. First, it leads to an expression for the admittance arising from the overall reaction which is insufficiently coupled to associated electrical processes occurring in the double layer adjacent to the electrode and in the bulk of the solution, at least in the unsupported electrolyte case. It is therefore necessary in a treatment of this kind to account separately in a somewhat ad hoc way for such quantities as C_{dl} , the double layer capacitance, C_g , the geometric capacitance, and R_∞ , the undisturbed bulk (solution) resistance. In addition, in some of their work AH also add in infinite-length Warburg terms in a heuristic effort to account for the diffusion of the A and C species in solution. Such addition seems satisfactory for the supported but not the unsupported case.

In their calculations, AH add to their general reaction admittance another admittance, that associated with the admittance of the "infinite-frequency" double layer capacitance. Even with the implicit assumption that this capacitance is independent of frequency in the range of interest, the assumption of additivity is often dubious. The reactions of eqn. (1) occur on or within about one molecular or ionic radius of the electrode, but the double layer capacitance may be associated with a possibly much larger finite region located within two or three Debye lengths of the electrode, particularly if C_{dl} is primarily a diffuse double layer capacitance. The above admittance additivity implicitly assumes that the same p.d. which powers the electrode reactions also spans the region which contributes to C_{dl} . This parallel assumption should only be accepted if it is verified by analysis of a model which treats electrode reactions and processes near and away from the electrode in a detailed and unified way. Under some circumstances, it may even be appropriate for the electrode impedance and double layer impedance to be taken in series. Further, the micro-potential at the position of species B is not likely to be exactly that at the position of species C.

The above problems are immediately evident in the AH type of approach through the introduction of a sinusoidal perturbation of potential, $\Delta E \exp(i\omega t)$, as part of the calculation of the admittance of the electrode reactions, without discussion of the region in space over which any actual time-varying potential difference applies. Because of phase shift of the inner a.c. potential with position, the same potential or p.d. should not in general be associated with two different processes such as electrode reactions and double layer capacitance unless they are completely associated with the same point in space or, if distributed over a region of space, respond to the local micropotential at each point in the region in the same way. These stringent requirements are not generally met exactly in actual experimental situations but will again be better satisfied for supported than for unsupported systems.

One way of approaching the present difficult problem is through the solution of the detailed microscopic equations of motion and chemical reaction of all species of interest, in the bulk, in the interphase, and in/on the electrode. It is not proposed to assay all aspects of this ferocious task herein. Instead, a less ambitious alternative approach to a somewhat simpler problem will be described. First, a general, complex reaction rate constant will be derived which enters directly into an expression for the faradaic current at the electrode. In the supported case, this current may be added to the displacement current at the electrode appropriate for the situation, and a total impedance then obtained in much the same somewhat approximate way as that used by AH. Results of the two approaches are likely to be essentially equivalent when this procedure is followed. Therefore, the main emphasis of the present work will be on the application of the complex rate constant approach to the unsupported electrolyte situation where the AH type of approach seems much less appropriate.

Consider the following unsupported model [4], which can apply to either liquid or solid electrolytes. Let l be the separation length of two identical, plane parallel electrodes. In the bulk assume that there is present a single positively charged mobile species, of equilibrium concentration $p = p_0$ and diffusion coefficient D_p , and a single negatively charged mobile species, of equilibrium concentration $n = n_0$ and diffusion coefficient D_n . Assume no recombination of these charges and that their valence numbers are z_p and z_n . Also assume that the positive species does not react at the electrodes and is thus completely blocked. On the other hand, assume that the negative species can react at the electrodes forming an adsorbed intermediate, B. Let z_1 and z_2 be defined as above. Note that when $z_1 + z_2 = z_n$, species C is neutral and B is not unless $z_2 = 0$. Because of the presence of two reactions, two rate constants must be introduced rather than the conventional one. Further, account must be taken in an a.c. treatment of the phase shift between the z_1 and z_2 processes.

The above situation will be treated under the following conditions: (a) The motion of the mobile charged species in the bulk and interphase will be accounted for exactly except for neglect of the finite size and mass of the charge carriers. Thus, diffusion effects of these species will be fully taken into account without the assumption of electroneutrality anywhere. (b) Electrode reaction effects will be treated by introducing a composite, complex rate constant, and any diffusion of the final species in/on either the electrode or away from it in the material of interest will be neglected for simplicity unless it is identical with the original negative species. Further, the reactions of eqn. (1) may be reversible. An a.c.-only treatment will be considered with the a.c. applied around the equilibrium potential, and the effect of any Frenkel layers and diffusion potentials neglected [4,5]. It seems likely that the approach described above will provide a more satisfactory solution of the overall unsupported electrolyte complex reaction problem than will the AH type of solution.

ANALYSIS

Armstrong and Henderson [3] have shown how the time-varying current associated with the electrode reactions of eqn. (1) may be expressed (to first order) in terms of their perturbation potential $\Delta E \exp(i\omega t)$. An alternative, and conceptually quite different, approach is to express the conductive current at a phase boundary where reactions occur in terms of the perturbed concentration of the reacting species at the boundary and a reaction rate constant. This is the procedure followed by Chang and Jaffé [6] and results, for a negative mobile charge reacting at an electrode and becoming fully neutralized in a single step, in an expression for the boundary conduction current of the following form [4,6]

$$\begin{aligned} I_{ns} &= -ez_n \xi_n (n_s - n_{s0}) \\ &= -r_n (ez_n D_n / \ell) (n_s - n_{s0}) \end{aligned} \quad (2)$$

where n_{s0} is the equilibrium, zero-current value of the volume concentration n_s at the reacting surface, ξ_n is a heterogeneous reaction rate constant, and [6,7] $r_n \equiv (\ell/D_n)\xi_n$ is the related dimensionless reaction rate parameter. The a.c. component of I_n , I_{n1} , will be proportional to just n_{s1} , the amplitude of the a.c. component of n_s . When $\xi_n = 0$, there is complete blocking (no reaction) of negative charge carriers at the electrode. In the limit of a very fast reaction, $\xi_n \rightarrow \infty$, $n_s \rightarrow n_{s0}$, and the conduction current remains finite and non-zero.

The situation is more complicated when reactions of the type of eqn. (1) occur at the electrode. Then it well may be somewhat of an approximation to represent the overall reaction process by a composite, complex rate parameter. Nevertheless, here any such approximation will be accepted and the consequences of the complex rate constant approach investigated. A first step in such a program has been made by Lányi [8], who showed how a complex rate constant could be derived for a special electrode reaction situation. Some of Lányi's results have been generalized and corrected and their implications discussed elsewhere [9]. Lányi's complex rate constant leads [9] to a complex r_n which goes to zero as $\omega \rightarrow 0$ and to the real value $r_{n\infty}$ as $\omega \rightarrow \infty$. Lányi applied his treatment only to a situation where there was no static direct current. Further, his rate constants are not defined in terms of more basic properties of the system.

By modifying the Taylor series approach of AH, one can readily derive an expression for a frequency-dependent, composite, complex, heterogeneous rate constant, ξ_n^* , better defined and more general than that of Lányi. This composite rate constant, applicable to the overall reaction of eqn. (1), may then be combined with earlier work of the author [4] which deals with unsupported bulk and interphase behavior exactly (within the limitations already stated) and involves reaction rate constants explicitly. Since there is no assumption in the earlier work [4] which prevents the rate constants present from being complex and frequency dependent, the r_n and r_p boundary param-

eters of ref. 4, assumed real and frequency independent there, may be directly replaced at the proper stage by complex parameters, r_n^* and r_p^* , of the form derived below. Such replacement in the Y_{2N} admittance formula of ref. 4 immediately generalizes the earlier work to apply to eqn. (1)-type reactions of both n and p simultaneously. Here for simplicity, it will be assumed that only the negative mobile species reacts at the electrodes according to eqn. (1); thus $r_p^* = 0$. The general form derived for r_n^* will, however, be appropriate for r_p^* as well whenever it is non-zero.

Since the present treatment will apply for small perturbations around equilibrium, the applied p.d. may be written $V_a = V_1 \exp(i\omega t)$, where $V_1 \ll kT/e$. Here k is Boltzmann's constant and T is the absolute temperature. Then if Γ is defined as the surface concentration on the electrode of the adsorbed intermediate species B, one may write $\Gamma \cong \Gamma_0 + \Gamma_1 \exp(i\omega t)$ and $n_s \cong n_{s0} + n_{s1} \exp(i\omega t)$, where "s" denotes the value of the quantity at the reaction surface or plane; "0" here denotes an equilibrium quantity; and "1" here denotes a perturbation amplitude. Further, let the net rate of formation of B from A be denoted v_1 and that of C from B be denoted v_2 . Then

$$d\Gamma/dt = i\omega\Gamma_1 \exp(i\omega t) = v_1 - v_2 \quad (3)$$

Now the conduction component of the total current, the faradaic current, may be written at the reacting surface to first order in $\exp(i\omega t)$ as

$$i = i_n \equiv i_0 + i_1 \exp(i\omega t) = -e(z_1 v_1 + z_2 v_2) \quad (4)$$

for $r_p = 0$. To make contact with the earlier work [4], one may write, following eqn. (2),

$$I_{ns1} = i_1 = -e z_n \xi_n^* n_{s1} \quad (5)$$

When v_1 and v_2 are expressed in terms of $n_{s1} \exp(i\omega t)$, eqns. (4) and (5) will immediately yield expressions for ξ_n^* and $r_n^* \equiv (\ell/D_n)\xi_n^*$.

To obtain the needed expressions for v_1 and v_2 , we may carry out a Taylor series expansion to first order as did AH but using the natural perturbation variable $n_{s1} \exp(i\omega t)$ rather than the somewhat ill-defined variable $\Delta E \exp(i\omega t)$ employed by AH. One obtains

$$v_1 = v_0 + (\partial v_1/\partial \Gamma)_{n_s} \Gamma_1 \exp(i\omega t) + (\partial v_1/\partial n_s)_{\Gamma} n_{s1} \exp(i\omega t) + \dots \quad (6)$$

and

$$v_2 = v_0 + (\partial v_2/\partial \Gamma)_{n_s} \Gamma_1 \exp(i\omega t) + (\partial v_2/\partial n_s)_{\Gamma} n_{s1} \exp(i\omega t) + \dots \quad (7)$$

In the static steady state, $v_1 = v_2 = v_0$ and Γ remains constant. Here, there is no static potential difference applied and $v_0 = 0$. The combination of eqns. (3), (6), and (7) yields

$$\Gamma_1 = (-\alpha \tau n_{s1}) / (1 + i\omega \tau) \quad (8)$$

where

$$\alpha \equiv [(\partial v_2/\partial n_s)_{\Gamma} - (\partial v_1/\partial n_s)_{\Gamma}] \quad (9)$$

$$\tau \equiv [(\partial v_2/\partial \Gamma)_{n_s} - (\partial v_1/\partial \Gamma)_{n_s}]^{-1} \quad (10)$$

and

$$-\alpha\tau \equiv \ell_0 \quad (11)$$

The time constant τ is related to but different from one formed by AH; it must be ≥ 0 for stability. Finally, combination of eqns. (4)–(8) yields

$$\xi_n^* = \xi_{n\infty} - \xi_{na}/(1 + i\omega\tau) = (\xi_{n0} + i\omega\tau\xi_{n\infty})/(1 + i\omega\tau) \quad (12)$$

where

$$\xi_{n\infty} \equiv [(z_1/z_n)(\partial v_1/\partial n_s)_\Gamma + (z_2/z_n)(\partial v_2/\partial n_s)_\Gamma] \equiv -(ez_n)^{-1}(\partial i/\partial n_s)_\Gamma \quad (13)$$

$$\xi_{na} \equiv \alpha\tau[(z_1/z_n)(\partial v_1/\partial \Gamma)_{n_s} + (z_2/z_n)(\partial v_2/\partial \Gamma)_{n_s}] \equiv (\ell_0/ez_n)(\partial i/\partial \Gamma)_{n_s} \quad (14)$$

and

$$\xi_{n0} \equiv (\xi_{n\infty} - \xi_{na}) \equiv \tau z_r [(\partial v_1/\partial n_s)_\Gamma(\partial v_2/\partial \Gamma)_{n_s} - (\partial v_1/\partial \Gamma)_{n_s}(\partial v_2/\partial n_s)_\Gamma] \quad (15)$$

with

$$z_r \equiv (z_1 + z_2)/z_n \quad (16)$$

The general relation $(\partial i/\partial \Gamma)_{n_s}(\partial n_s/\partial i)_\Gamma \equiv -(\partial n_s/\partial \Gamma)_i$ allows us to write

$$(\xi_{na}/\xi_{n\infty}) \equiv \ell_0(\partial n_s/\partial \Gamma)_i \quad (17)$$

on using the above results.

Since the earlier work [4,7,10] involves r_n explicitly rather than ξ_n , it is worthwhile to give an expression here for r_n^* as well as one for ξ_n^* . The r_n^* which should replace the r_n of earlier work when an adsorbed intermediate is present may be written as

$$r_n^* \equiv r_n' + ir_n'' = r_{n\infty} - (r_{n\infty} - r_{n0})/(1 + i\omega\tau) = (r_{n0} + i\omega\tau r_{n\infty})/(1 + i\omega\tau) \quad (18)$$

where

$$r_{n\infty} \equiv (\ell/D_n)\xi_{n\infty} \quad (19)$$

and

$$r_{n0} \equiv (\ell/D_n)\xi_{n0} \quad (20)$$

Note that $r_n^* \rightarrow r_{n\infty}$ as $\omega \rightarrow \infty$ and it goes to r_{n0} as $\omega \rightarrow 0$. The boundary parameter r_{n0} will usually be ≥ 0 except for inhibition reaction situations [3].

The forms of eqns. (12) and (18) are very general, involving $(i\omega)$ linearly in both numerator and denominator. Any more complicated form would require the presence of $(i\omega)$ to a higher power. When $\xi_{n\infty}$ and ξ_{na} are re-interpreted, this same general form can apply to the situation where some negative charges are neutralized directly in a single step (possibly involving a frequency-independent r_n) and, simultaneously, others which reach the reaction region undergo the two-step discharge process of eqn. (1).

Finally, it should be emphasized that as far as a.c. response is concerned,

the general complex rate constant expressions of eqns. (12) and (18) apply not only at equilibrium but at any stable overpotential, η , for supported or unsupported situations. The v_1 and v_2 derivatives may, in principle, be evaluated at any appropriate η , not just $\eta \equiv 0$. It is the subsequent use of the present general ξ_n^* or r_n^* results in the earlier unsupported impedance expression [4] which limits the overall analysis to small perturbations around $\eta = 0$ since this impedance was derived only for this simplifying condition.

SPECIFIC CASES

Several of the interesting special possibilities contained in eqns. (9)–(17) will be discussed below.

$$(A) \quad v_2 = 0, (\partial v_2 / \partial n_s)_\Gamma = 0, \text{ and } (\partial v_2 / \partial \Gamma)_{n_s} = 0$$

When v_2 and its derivatives are zero, species C drops out of the analysis. In this case one finds

$$\alpha = -(\partial v_1 / \partial n_s)_\Gamma \quad \tau = -(\partial v_1 / \partial \Gamma)_{n_s}^{-1} \quad (21)$$

$$\ell_0 = \ell_1 \equiv (\partial \Gamma / \partial n_s)_{v_1} \quad (22)$$

$$\xi_{n\infty} = \xi_{na} = -(z_1/z_n)\alpha \equiv (z_1/z_n)(\ell_1/\tau) = (z_1/z_n)(\partial v_1 / \partial n_s)_\Gamma \quad (23)$$

and

$$\xi_n^* = \xi_{n\infty} [i\omega\tau / (1 + i\omega\tau)] = [i\omega\ell_1 / (1 + i\omega\tau)] (z_1/z_n) \quad (24)$$

In this limiting case of an adsorbed species, $\xi_{n0} = 0$. When $z_1 = z_n$, species B will be neutral. It is plausible to expect that ℓ_1 and $(\partial v_1 / \partial n_s)_\Gamma$ will both be ≥ 0 ; therefore, for $(z_1/z_n) > 0$ $\xi_{n\infty}$ will be ≥ 0 as well. Since it is necessary that $\tau \geq 0$ for a steady state to be achievable, we require that $-(\partial \Gamma / \partial v_1)_{n_s} \geq 0$, consistent with the above choices.

Because of the general relation $(\partial v_1 / \partial n_s)_\Gamma (\partial \Gamma / \partial v_1)_{n_s} \equiv -(\partial \Gamma / \partial n_s)_{v_1}$, which here corresponds to $\alpha\tau = -\ell_1$, the condition $\tau \rightarrow \infty$ requires $\ell_1 \rightarrow \infty$ when $\alpha < 0$. Then except at $\omega = 0$ when $\omega\tau \neq \infty$, $\xi_n^* \rightarrow \xi_{n\infty} > 0$, a finite, real, frequency-independent rate constant, equivalent, except at the point $\omega \equiv 0$, to that employed in earlier work [4,7,10]. When $\omega = 0$ and $\omega\tau \neq \infty$, $\xi_n^* = 0$. These are limiting results, however, since one would not expect the condition $\tau = \infty$ to be physically achievable in this A \rightleftharpoons B case. Equation (24) is of the form found by Lányi [8,9] by a different approach with $z_1 = z_n = 1$ and no species C considered. Note that species A and B are in equilibrium when $(\partial v_1 / \partial n_s)_\Gamma \rightarrow \infty$ and $(\partial v_1 / \partial \Gamma)_{n_s} \rightarrow -\infty$. Then, $\alpha \rightarrow -\infty$, $\tau \rightarrow 0$, and $\xi_n^* \rightarrow (z_1/z_n)(i\omega\ell_1)$, with $\ell_1 \geq 0$ but not necessarily infinite. Since $i = -ez_1 v_1$ in the present case, the v_1 partial derivatives appearing above may, alternatively, be expressed as partial derivatives of i . For example, using $\ell_1 = -\alpha\tau$ allows one to write $\ell_1 = -(\partial i / \partial n_s)_\Gamma (\partial i / \partial \Gamma)_{n_s}^{-1} \equiv (\partial \Gamma / \partial n_s)_i$.

$$(B) \quad z_2 = -z_1$$

Here $z_r = 0$, species C will have the same valence as species A, and species B will be neutral if $z_1 = z_n$. When the v_1 and v_2 derivatives are equal as well, $\xi_n^* = 0$, yielding $i \equiv 0$ and complete blocking at all frequencies. If species C is actually species A, then the forward and reverse rates of the resulting $A \rightleftharpoons B$ reaction will always be the same in this situation.

In general, the $z_2 = -z_1$ condition leads to $\xi_{n0} = 0$ and to

$$\xi_{n\infty} = -(z_1/z_n)\alpha \quad (25)$$

formally the same as the first part of eqn. (23), but here α is given by eqn. (9). When $\alpha = 0$, complete blocking is again found. Alternatively, when $\alpha < 0$, ξ_n^* is given by (24) with $\xi_{n\infty}$ from (25) and $\ell_0 \equiv -\alpha\tau > 0$. Since $i = -ez_1(v_1 - v_2)$ here, we may express α and τ as $(\partial i/\partial n_s)_\Gamma/(ez_1)$ and $(ez_1)/(\partial i/\partial \Gamma)_{n_s}$, respectively. It follows in turn that $\ell_0 = (\partial \Gamma/\partial n_s)_i$ in the present situation. Note that cases A and B are physically, although not mathematically, identical. They become mathematically identical as well if we formally replace the $(v_1 - v_2)$ of case B by v_1 , yielding case A.

$$(C) \quad (\partial v_2/\partial n_s)_\Gamma = 0$$

This condition may be physically plausible when C is a different species from A. The constancy of Γ for the above partial should then tend to decouple changes in v_2 from changes in n_s . This condition also requires that (a) $(\partial v_2/\partial \Gamma)_{n_s} = 0$ unless (b) $(\partial \Gamma/\partial n_s)_{v_2} \equiv \ell_2 = 0$. In case (a), one obtains just the results given in Section A above. Case (b) yields $\alpha = -(\partial v_1/\partial n_s)_\Gamma$, $\xi_{n\infty} = (z_1/z_n)(\partial v_1/\partial n_s)_\Gamma$, and τ and ξ_{na} as given in eqns. (10) and (14). Thus $\xi_{n\infty}$ and ξ_{na} will not generally be equal in this situation and ξ_n^* will not be zero at $\omega = 0$.

$$(D) \quad \xi_n^* \text{ real, frequency independent}$$

Although we have found conditions above which lead to real, frequency-independent ξ_n^* except at $\omega = 0$, there are other possibilities which can yield a real ξ_n^* , constant at all frequencies, as in earlier work. When $\xi_{na} = 0$, $\xi_n^* = \xi_{n\infty} = \xi_{n0}$, for example. Now $\xi_{na} = 0$ when either (a) $\alpha = 0$ or (b) $\alpha \neq 0$ and the remainder of the expression for ξ_{na} in eqn. (14) is zero. Case (a) requires only that $(\partial v_2/\partial n_s)_\Gamma = (\partial v_1/\partial n_s)_\Gamma$. Then $\xi_{n\infty} > 0$ if $z_r > 0$. Case (b) requires that $z_1(\partial v_1/\partial \Gamma)_{n_s} = -z_2(\partial v_2/\partial \Gamma)_{n_s}$ and $z_r \neq 0$.

Another possibility for constancy arises when $\tau = 0$. Then $\xi_n^* = \xi_{n0} \neq \xi_{n\infty}$. Two conditions which lead to $\tau = 0$ are (a) $(\partial v_2/\partial \Gamma)_{n_s} = \pm \infty$ and (b) $(\partial v_1/\partial \Gamma)_{n_s} = \pm \infty$. For these cases, one finds $\xi_{n0} = z_r(\partial v_j/\partial n_s)_\Gamma$, where $j = 1$ for case (a) and 2 for case (b). Again for ξ_n^* to be different from zero, one must also require that $z_r \neq 0$. One interesting possibility follows from the choices $z_2 = 0$, $z_1 = z_n$. Then $z_r = 1$ and species B is neutral, as is C, but the v_2 derivatives need not be zero. In this case, species B might be temporarily adsorbed oxygen atoms

and C be oxygen atoms in solution (or bulk) or in the gas phase. The result above for the (b) condition is valid only when $\xi_{n0} = z_r(\partial v_2/\partial n_s)_\Gamma \neq 0$. When it is zero, one reverts to the final equilibrium result found in case A.

A further interesting possibility is that produced by (c) $\alpha = 0$, $\tau = \infty$, and $\ell_0 \equiv -\alpha\tau$ not necessarily zero or infinite. In this case, where $v_2 \neq 0$, in contrast to that of Section A, it is physically allowable for τ to be infinite. It follows that $\xi_{n\infty} = z_r(\partial v_2/\partial n_s)_\Gamma$ and $\xi_{na} = z_r\ell_0(\partial v_2/\partial \Gamma)_{n_s}$. Also, here $v_1 = v_2$ and $(d\Gamma/dt) = 0$. This is the non-adsorbed-intermediate case, and the reaction becomes $\nu_A A \rightleftharpoons \nu_C C$. When $\ell_0 = 0$ and thus $\xi_{na} = 0$, ξ_n^* becomes equal to the above $\xi_{n\infty}$ at all frequencies and is thus real and frequency independent. To avoid reference to z_r , it may be written from eqn. (13) as $\xi_n^* = -(ez_n)^{-1} \cdot (\partial i/\partial n_s)_\Gamma$. Since $\tau = \infty$, $\omega\tau = \infty$ in the present case except at $\omega = 0$. Thus, except at $\omega = 0$, ξ_n^* again equals the present $\xi_{n\infty}$ when $\alpha(\partial v_2/\partial \Gamma)_{n_s} = 0$, consistent with the $\alpha = 0$ choice. If we take $\omega\tau = 0$ at $\omega = 0$, then ξ_n^* may be written generally here as $-(ez_n)^{-1}[(\partial i/\partial n_s)_\Gamma - \{1 - u(\omega+)\}\ell_0(\partial i/\partial \Gamma)_{n_s}]$, where $u(\omega+)$ is the unit step function. The $\omega \equiv 0$ condition is not actually ever physically realizable, however.

CONCLUSION

In the general case when ξ_n^* is complex but $\xi_{n0} \neq 0$, the system allows a steady direct current to pass. An example is the parent metal electrode case with adsorption, where species A is the ion of the metal making up the electrode, B is this ion in a specifically adsorbed state, and C is an atom of the electrode metal. The conventional situation, the parent metal electrode without adsorption, yields a ξ_n^* which is real and frequency independent and is exemplified by cases discussed in Section D above. In a non-parent-metal case, no steady direct current can flow (unless an alternate reaction path, not considered here, is present) and ξ_{n0} must be zero, as in Section A, B, and C-a above.

In the conventional treatment with ξ_n^* always equal to a real, frequency-independent constant, one obtains [4,7,10] the equivalent circuit of Fig. 1, where $C_g, R_D \equiv G_D^{-1}$, and $R_E \equiv G_E^{-1}$ are frequency independent and $G_D + G_E \equiv G_\infty \equiv R_\infty^{-1}$. The impedance $Z_i \equiv Y_i^{-1} \equiv R_i + (i\omega C_i)^{-1}$ involves the generally frequency-dependent elements R_i and C_i .

The present general ξ_n^* treatment leads to exactly the same equivalent circuit but with modified expressions for various elements. In particular, when $r_p^* = 0$ and the positive species in the bulk is immobile, one finds $G_E = [1 + (r_{n0}/2)]^{-1}G_\infty$ and $G_D = [1 + (2/r_{n0})]^{-1}G_\infty$. Since $G_D = 0$ when $r_{n0} = 0$, the parallel resistive path disappears from the equivalent circuit as it should in such a situation. To obtain the full expressions for Z_i , R_D , and R_E in arbitrary mobility and valence situations, one need only replace r_p and r_n with r_p^* and r_n^* , respectively, in the earlier expressions for these quantities which do not depend, as does eqn. (A49) of Ref. 4, on the assumption of frequency-independent rate constants [4,7,10]. For the $r_p^* = 0, D_p = 0$ situation, some $r_{n0} =$

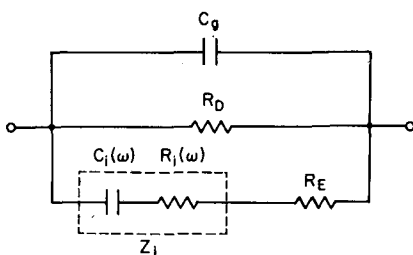


Fig. 1. General equivalent circuit for real or complex rate constants.

0 results have already been obtained [9] for comparison with Lányi's predictions. It is also found that when $r_{n0} \neq 0$ the total impedance of the circuit of Fig. 1 can become inductive at some frequencies, and it is possible for the low-frequency-limiting differential resistance to be negative as well. Generally, impedance plane plots similar to some of those of AH are obtained, but it should be emphasized that in terms of detailed frequency dependence and shape, the present treatment yields appreciably different results. Some of these will be presented in a later paper which will also include $r_{n0} \neq 0$ situations where neither D_n nor D_p are zero.

ACKNOWLEDGMENTS

Valuable comments of Drs. R.D. Armstrong, P.W.M. Jacobs and J.A. Garber are much appreciated.

REFERENCES

- 1 J.E.B. Randles, Discuss. Faraday Soc., 1 (1947) 11.
- 2 B.V. Ershler, Discuss. Faraday Soc., 1 (1947) 269.
- 3 R.D. Armstrong and M. Henderson, J. Electroanal. Chem., 39 (1972) 81.
- 4 J.R. Macdonald, J. Chem. Phys., 58 (1973) 4982.
- 5 J.R. Macdonald, J. Appl. Phys., 45 (1974) 73.
- 6 H. Chang and G. Jaffé, J. Chem. Phys., 20 (1952) 1071.
- 7 J.R. Macdonald, J. Electroanal. Chem., 53 (1974) 1.
- 8 Š. Lányi, J. Phys. Chem. Solids, 36 (1975) 775.
- 9 J.R. Macdonald and P.W.M. Jacobs, submitted to J. Phys. Chem. Solids.
- 10 J.R. Macdonald, J. Chem. Phys., 61 (1974) 3977.