

DIFFUSION OF NEUTRAL AND CHARGED SPECIES UNDER SMALL-SIGNAL A.C. CONDITIONS *

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ABSTRACT

Several of the ways in which diffusion of an electroactive species may affect the small-signal response of an electrochemical system are examined, with particular attention to cases in which the electrode reaction produces or consumes a neutral species whose concentration at the electrode surface is determined by diffusion through the electrode. The conventional (time domain) rate and diffusion equations may be expressed in the frequency domain through the use of complex, frequency-dependent rate constants, whose form reflects the sequence of events in the overall reaction, including possible adsorption steps, and leads directly to equivalent-circuit representations of the pertinent parts of the system response. The complex rate constant formalism also allows the immediate generalization of existing exact treatments of unsupported systems to include such diffusion effects.

(I) INTRODUCTION

The diffusion of reactant or product species to or from the electrode/electrolyte interface is often the rate controlling step of an electrochemical reaction. The effects of diffusion-controlled reaction on the small-signal impedance of electrochemical systems have been studied by Warburg [1], Randles [2], Ershler [3], and others. For the most part, the classic papers of these authors examined the diffusion of an electroactive species in a supported electrolyte. The diffusion of species through a metallic electrode may, however, also play an important role in determining the rate of an electrode reaction, as is often the case in polarography [4]. Recently, attention has been given to the diffusion of gaseous species through solid electrodes, and along the electrode/electrolyte interface [5–7], processes of technological importance in connection with fuel cells and gas sensing devices [5]. A novel possibility also involving the diffusion of atoms along the interface or through a solid electrode arises from the work of Lányi [8–11] who suggests that the ions of alkali halide crystals may, in some cases, discharge at an interface with a non-parent metal electrode under small-signal conditions. Further, from a mathematical standpoint, the behavior of ions in a supported, or (within limits) an unsupported [12], electrolyte solution which bathes a planar membrane can be treated as involving the diffusion of an effectively uncharged species through an “electrode”.

In many situations the effect of diffusion on the small-signal response of an

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electrochemical system is representable by the inclusion in an equivalent circuit for the system of a Warburg impedance, often given in Warburg's original form, appropriate for diffusion in a semi-infinite space. A Warburg-like impedance, appropriate for finite length, arises in exact treatments of the small-signal response of unsupported binary electrolytes unless one of the charge species is strictly immobile or both species have the same mobility and the identical reaction rate at the electrodes [13,14]. The appearance of the Warburg-like impedance in the general unsupported case can be attributed to the action of the more mobile or more-reactive species in screening the applied electric field, allowing diffusion to dominate the motion of the remaining species. The diffusion of neutral species has thus far not been considered in treatments of unsupported systems under small-signal conditions.

In the present work we focus on the diffusion of gas or metal species through a metallic electrode or along the electrode/electrolyte interface. Our treatment of diffusion through an electrode is also applicable in the case of a membrane bathed in electrolyte solution as described above and, with an appropriate choice of parameters, to the diffusion of charged and uncharged electroactive species in a supported electrolyte (or of neutral species in an unsupported electrolyte) in contact with a metal electrode. A unified treatment of these different cases is afforded by the formalism of complex, frequency-dependent rate constants [15–18], which amounts to a frequency-domain representation of the reaction, adsorption, and diffusion processes characterized in the time domain by the usual real rate and diffusion constants. Although the results to be presented for the unsupported case are original, our discussion of supported systems recapitulates the results of other workers. The latter discussion is, however, included to demonstrate the applicability of the complex rate constant formalism in the supported case and to provide a more unified treatment of diffusive processes in general.

(II) DIFFUSION OF REACTANT THROUGH ELECTRODE

Consider a uniform planar electrode, one surface of which lies in the yz plane at $x = 0$; the second surface lies at $x = l_e$. The electrolyte (solid or liquid) extends to the left of the electrode ($x < 0$), and it will be assumed that the outer Helmholtz plane lies at $x = -d$. We assume that positive ions of charge $z_p e$ and concentration $p(x)$ react at the electrode to form a neutral adsorbed species whose surface concentration is Γ , and that the adsorbed species may diffuse into the electrode where its concentration is denoted as $b(x)$. We let η denote the potential drop between the electrode and the outer Helmholtz plane. Let the net rate of formation of the adsorbed species per unit area be given by

$$v_1(p_R, \Gamma, \eta) \quad (1)$$

and the net rate at which the adsorbed species enters the electrode be

$$v_2(\Gamma, b_L) \quad (2)$$

where p_R is the concentration of positive ions at the outer Helmholtz plane and b_L is the concentration of neutral species just inside the left edge of the electrode.

The equations governing the behavior of the reactant species at the electrode/electrolyte interface may be written

$$I_{pR} = z_p e v_1(p_R, \Gamma, \eta) \quad (3)$$

$$d\Gamma/dt = v_1(p_R, \Gamma, \eta) - v_2(\Gamma, b_L) \quad (4)$$

and

$$J_{bL} = v_2(\Gamma, b_L) \quad (5)$$

where I_{pR} is the faradaic current of the positive carriers per unit area evaluated at the outer Helmholtz plane and J_{bL} is the flux of neutral species into the electrode.

Under small-signal a.c. conditions we may separate each quantity into a steady-state part and a sinusoidal perturbation: $p_R = p_{0R} + p_{1R} e^{i\omega t}$, $\Gamma = \Gamma_0 + \Gamma_1 e^{i\omega t}$, etc. On making an appropriate Taylor series expansion of the reaction rates about the steady-state values, we obtain

$$I_{p1R} = z_p e [k_{1f} p_{1R} - k_{1b} \Gamma_1 + (z_p e \eta_1 / kT) \gamma_{1f} p_{0R}] \quad (6)$$

$$i\omega \Gamma_1 = I_{p1R} / z_p e - k_{3f} \Gamma_1 + k_{3b} b_{1L} \quad (7)$$

and

$$J_{b1L} = k_{3f} \Gamma_1 - k_{3b} b_{1L} \quad (8)$$

Each of the "rate constants" appearing in eqns. (6)–(8) represents a partial derivative. Thus

$$k_{1f} \equiv (\partial v_1 / \partial p_R)_0 \quad (9)$$

$$k_{3f} \equiv (\partial v_2 / \partial \Gamma)_0 \quad (10)$$

and so on, where the subscript zero indicates that the derivative is evaluated for steady-state conditions and the subscript f indicates the "forward" direction of the reaction. The overpotential-dependent term involves the quantity

$$\gamma_{1f} \equiv (kT / z_p e p_{0R}) (\partial v_1 / \partial \eta)_0 \quad (11)$$

which has the same dimensions as k_{1f} .

We shall assume that within the electrode diffusion is governed by the Fick equations, with the small-signal forms

$$J_{b1} = -D_{1e} db_1/dx \quad (12)$$

and

$$i\omega b_1 = D_{1e} d^2 b_1 / dx^2 \quad (13)$$

Equation (8) provides one boundary condition for the diffusion equation. As a second condition we take

$$J_b = k_{1ef} b_1 \quad (14)$$

at $x = l_e$. For $k_{1ef} = 0$, the exchange of neutral species with the ambient atmosphere or adjoining material is effectively blocked, while for $k_{1ef} \rightarrow \infty$ the exchange is infinitely rapid.

The diffusion equation (13) has the general solution

$$b_1 = b_I \exp(Q_1 x) + b_{II} \exp(-Q_1 x) \quad (15)$$

where

$$Q_1 \equiv (1 + \iota)(\omega/2D_{1e})^{1/2} = \sqrt{i\omega/D_{1e}} \quad (16)$$

Thus b_1 is the superposition of two damped oscillations. On imposing the boundary conditions (8) and (14), one readily evaluates the constants b_I and b_{II} and obtains an expression for b_1 in terms of Γ_1 . This expression can be inserted in eqn. (7) to provide a relation between Γ_1 and I_{p1R} . On substituting this expression for Γ_1 in eqn. (6) and rearranging, we finally obtain

$$I_{p1R} = z_p e [k_1^* p_{1R} + (z_p e \eta_1 / kT) \gamma_1^* p_{0R}] \quad (17)$$

where $k_1^* \equiv f_1 k_{1f}$ and $\gamma_1^* \equiv f_1 \gamma_{1f}$, with

$$f_1 \equiv \{1 + k_{1b} / [i\omega + k_{3f} / (1 + F_1(\omega))]\}^{-1} \quad (18)$$

and

$$F_1(\omega) \equiv \frac{k_{3b}}{\sqrt{i\omega D_{1e}}} \frac{[(k_{1ef}/\sqrt{D_{1e}}) + \sqrt{i\omega} \operatorname{ctnh}(l_e \sqrt{i\omega/D_{1e}})]}{[(k_{1ef}/\sqrt{D_{1e}}) \operatorname{ctnh}(l_e \sqrt{i\omega/D_{1e}}) + \sqrt{i\omega}]} \quad (19)$$

The rate constants have a continued fraction form which reflects their sequential nature.

Equation (17) may be used as a boundary condition with the equations of continuity and charge transport to determine an expression for the system impedance. The form of eqn. (17) indicates that k_1^* and γ_1^* will lead to admittance contributions in the equivalent circuit [19]. Equation (18) then implies that $F_1(\omega)$ has the character of an impedance. Indeed, if R_C is a constant normalizing resistance, it may readily be shown that $R_C F_1(\omega)$ is the impedance of a length l_e of distributed transmission line [20] of characteristic impedance $R_C k_{3b} / \sqrt{i\omega D_{1e}}$, with series resistance per unit length $R_{ser} \equiv R_C k_{3b} / D_{1e}$ and shunt admittance per unit length $i\omega C_{sh} \equiv i\omega / k_{3b} R_C$, terminated by an impedance $R_C k_{3b} / k_{1ef}$. Note that $D_{1e} = (R_{ser} C_{sh})^{-1}$. The $l_e \rightarrow \infty$ limit of $F_1(\omega)$ has been discussed by Barker [21]. The quantity f_1 is determined by five independent parameters: k_{1b} , k_{3f} , $k_{3b} / \sqrt{D_{1e}}$, $k_{1ef} / \sqrt{D_{1e}}$ and $l_e / \sqrt{D_{1e}}$.

A number of limiting forms of $F_1(\omega)$ should be examined. When $k_{1ef} > 0$ and $l_e / \sqrt{D_{1e}} \rightarrow 0$, as for a very thin electrode or very rapid diffusion of the product species, one has $F_1(\omega) \rightarrow k_{3b} / k_{1ef}$ and

$$k_1^* \rightarrow (k_{10} + i\omega \tau_{1a} k_{1\infty}) / (1 + i\omega \tau_{1a}) \quad (20)$$

where $k_{10} \equiv k_{3f} k_{1f} / [k_{3f} + k_{1b} / k_{1ef}]$, $k_{1\infty} \equiv k_{1f}$, and $\tau_{1a} \equiv (1 + k_{3b} / k_{1ef}) / [k_{3f} + k_{1b} (1 + k_{3b} / k_{1ef})]$. Equation (20) has the precise form of the complex rate constant derived earlier [16,18] for an adsorption/reaction sequence in which the concentration of the final product is held constant. The complex rate constant, k_1^* , will be non-zero at $\omega = 0$ (and thus a direct current can flow) unless $k_{1f} \rightarrow 0$, or $k_{3f} \rightarrow 0$, for which k_{10} will vanish. When $l_e / \sqrt{D_{1e}} \rightarrow \infty$, as for a very thick electrode and/or very slow diffusion, $F_1(\omega)$ takes on the standard Warburg [1] form $k_{3b} / \sqrt{i\omega D_{1e}}$. In this case k_1^* vanishes as $\omega \rightarrow 0$ and no steady direct current is possible. For $k_{1ef} / \sqrt{D_{1e}} \rightarrow 0$, $F_1(\omega)$ takes on the form $(k_{3b} / \sqrt{i\omega D_{1e}}) \times$

$\text{ctnh}(l_e \sqrt{i\omega D_{1e}})$ and again a steady direct current is not allowed. If, further, $l_e/\sqrt{D_{1e}} \rightarrow 0$ one has $F_1(\omega) \rightarrow k_{3b}/i\omega l_e$ and k_1^* takes on the form appropriate to a two-stage adsorption-desorption sequence. For $k_{1ef}/\sqrt{D_{1e}} \rightarrow \infty$ (equivalent, when $D_{1e} > 0$, to terminating the transmission line with a short), however, $F_1(\omega)$ assumes the finite-length Warburg form $(k_{3b}/\sqrt{i\omega D_{1e}}) \times \tanh(l_e \sqrt{i\omega/D_{1e}})$ and a steady direct current is possible [22].

(a) *Fully supported electrolyte*

In the presence of an excess of supporting electrolyte the motion of the electroactive species is governed entirely by diffusion. It is then possible to treat the quantity p_1 in a similar manner to that in which b_1 was treated so that a relation between I_{p1f} and η_1 is found directly. Our consideration of supported systems will be restricted here to a special case, that in which the positive species of interest diffuses extremely rapidly, so that we may take p_{1R} to be zero. One then has for the admittance of the interface (assuming no other electroactive species present) from eqn. (17)

$$Y \equiv I_{p1R}/\eta_1 = (z_p^2 e^2 p_{0R}/kT) \gamma_1^* \quad (21)$$

which is a generalization of the familiar charge-transfer conductance of supported electrolyte theory. This admittance is represented by the equivalent circuit of Fig. 1, in which R_R has the form of a charge transfer resistance, C_A is an adsorption capacitance, R_A the associated adsorption resistance, and Z_D a diffusion impedance.

It is appropriate to comment on the relationship of the admittance given by eqn. (21) to the results obtained in earlier work by other authors. Although it has been assumed here that the product species diffuses through the electrode, the same mathematical formulation applies to a product species which diffuses into the electrolyte provided that an appropriate value is assigned to l_e . In the limit as $l_e/\sqrt{D_{1e}} \rightarrow \infty$, our result becomes a special case of the admittance derived by Armstrong and Henderson [23] for a system in which both reactant and product species diffuse through an essentially infinite electrolyte. By taking the limit $k_{1b} \rightarrow \infty$, $k_{3f} \rightarrow \infty$, with (k_{1b}/k_{3f}) finite, in essence assigning a vanishingly small lifetime to the adsorbed intermediate, one obtains the results appropriate to a one-step electrode reaction without intermediate species. Then eqn. (18) becomes

$$f_1 \rightarrow [1 + (k_{1b}/k_{3f})(1 + F_1(\omega))]^{-1} \quad (22)$$

An important subcase is that in which no intermediate is formed and the elec-

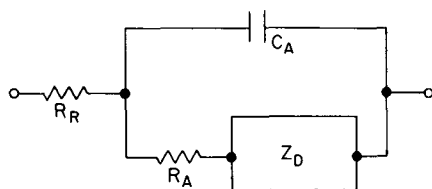


Fig. 1. Equivalent circuit representing the interfacial impedance in the fully supported case of Section II(a). $R_R \equiv kT/(z_p^2 e^2 p_{0R} \gamma_{1f})$, $C_A \equiv 1/(R_R k_{1b})$, $R_A \equiv R_R k_{1b}/k_{3f}$, and $Z_D \equiv R_R k_{1b} F_1(\omega)/k_{3f}$.

trode reaction occurs with infinite speed. This situation may be realized by taking $k_{3b} \rightarrow \infty$, $\gamma_{1f} \rightarrow \infty$ with k_{3b}/γ_{1f} finite. The resulting impedance is

$$Z = (kT/z_p^2 e^2 p_{OR})(k_{1b} F_1(\omega)/k_{3f} \gamma_{1f}) \quad (23)$$

On further specializing to the case in which $k_{1ef}/D_{10} \rightarrow \infty$, one finds

$$Z = (kT/z_p^2 e^2 p_{OR})(k_{1b} k_{3b}/k_{3f} \gamma_{1f} \sqrt{i\omega D_{1e}}) \tanh(l_e \sqrt{i\omega D_{1e}}) \quad (24)$$

which has the finite-length Warburg form obtained by Drossbach and Schultz [24] and Sluyters [25] for systems in which diffusion occurs over a small distance.

(b) Unsupported binary electrolyte

A systematic procedure has been given by the authors [18] for the determination of the small-signal impedance of an unsupported binary electrolyte with compact layers of finite extent subject to electrode kinetics which can be expressed in terms of complex, frequency-dependent boundary parameters. We consider first the case in which the thickness of the compact layers can be neglected so that one may take η_1 and γ_1 as zero. In this case, eqn. (17) takes on the form of a complex Chang-Jaffé boundary condition. An exact expression has been given [26] for the impedance of a binary electrolyte with generation/recombination and possible immobile background charge subject to complex Chang-Jaffé boundary conditions. The impedance (and corresponding admittance) depend on the electrode reaction kinetics only through the normalized boundary value parameters $\rho_1^* \equiv (k_1^* l/2D_1)$ and $\rho_2^* \equiv (k_2^* l/2D_2)$ (for negative charges), where l is length of material between the electrode and D_1 is the diffusion coefficient of the charged species. By employing rate constants k_1^* and k_2^* of the form obtained in the present work, one immediately generalizes the earlier results to include possible diffusion of the product species of the assumed reaction/adsorption sequence.

An important feature of the unsupported cases treated in earlier work [13, 14, 18] is that the response of the system can often be represented by an equivalent circuit of frequency-independent elements and sometimes a Warburg impedance. Prior to a survey of representative instances it is difficult to prescribe a form of equivalent circuit which is appropriate for the general situation in which diffusive behavior of the electrode reaction product occurs together with Warburg-like response due to unequal charge carrier mobilities or electrode reaction rates. For simpler cases, e.g. the case of a single mobile charge carrier species, the equivalent circuit of Fig. 2, in which the geometric capacitance C_g and bulk resistance R_∞ have been added to the circuit of Fig. 1, should suffice. For the rate laws assumed here, the resistances and capacitances appearing in the circuit will always have positive values. Since an exact treatment of the unsupported case is only possible in the case of a flat-band system one must set $p_{OR} = p_0$ here, where p_0 is the bulk equilibrium positive charge carrier density. A related result was found for the case in which no electrode diffusion effects are present but finite-length Warburg effects arise from processes in the electrolyte [18, 22].

For the case in which the compact layer cannot be neglected, we have given

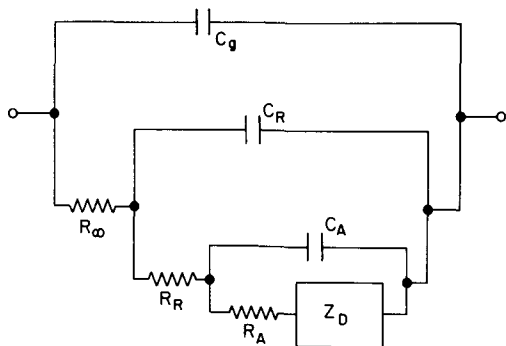


Fig. 2. Equivalent circuit for simple unsupported case of Section II(b). $C_g \equiv$ geometric capacitance, $R_\infty \equiv$ bulk resistance, $C_R \equiv$ (diffuse double layer capacitance $- C_g$), $R_R \equiv 2kT/(z_p^2 e^2 p_0 k_{1f})$; $C_A \equiv 1/(R_R k_{1b})$, $R_A \equiv R_R k_{1b}/k_{3f}$, and $Z_D \equiv R_R k_{1b} F_1(\omega)/k_{3f}$.

an exact expression for the impedance of a system with a single species of mobile charge [18,26] which may be extended to the case of a neutral product diffusing through the electrode by setting $\rho_1 \rightarrow \rho_1^*$ as above and by an appropriate choice of the parameter $\nu_1 = \gamma_1^*/k_1^* \equiv \gamma_{1f}/k_{1f}$.

(III) DIFFUSION OF REACTANT ALONG ELECTRODE/ELECTROLYTE INTERFACE

One of the most important theoretical problems in electrochemistry at present is the description of the interface between a solid electrode and a liquid or solid electrolyte. Although treatment of electrodes with ruled surfaces and of porous electrodes in contact with a supported electrolyte have been given [27, 28], little has been done in the corresponding case of unsupported electrolytes in which the Debye length may be greater than the average distance between imperfections on the electrode surface. The treatment of the previous Section must be applied with caution in the case of a gas diffusing through metal electrodes since, with the exception of hydrogen, such diffusion through the bulk of a metal is notoriously slow, and even a small density of surface imperfections would be sufficient to dominate motion of atoms within the electrode. If the electrode is characterized by a reasonably uniform distribution of pores or cracks roughly perpendicular to the interface, the treatment of the previous Section may be applicable provided that D_{1e} and l_e are interpreted as an effective diffusion constant and length for atomic motion along the internal surfaces of the electrode. In other cases, however, one must begin to consider the diffusion of atoms along the interface as well as through the electrode. The diffusion of metal adatoms on a solid electrode surface has been considered by Lorenz [29] and others in connection with electrocrystallization processes. A related model for the diffusion of adsorbed oxygen atoms at the interface of platinum electrodes and ceria of zirconia has recently been proposed by Wang [5], who did not, however, explore the consequences of his model for small-signal response, which we shall do in this Section.

In Wang's model the electrode/electrolyte interface is characterized by regions of contact which are long thin rectangles. The appropriateness of this

assumption in a particular experimental case might be tested by electron microscopy [5]. The concentration b of the product species at the interface is assumed to be governed by diffusion of the species along the metal/electrolyte interface. Let the width of the rectangles be 2δ and assume that the short dimension lies along the y -axis. For simplicity we shall in this case assume that an adsorbed intermediate species is not formed and that the rate of formation of the product species is given by

$$v(p_R, \eta, b_L) \quad (25)$$

Then the faradaic current per unit area at the electrode is given by

$$I_p = \frac{z_p e}{2\delta} \int_{-\delta}^{\delta} v[p_R(y), \eta(y), b_L(y)] dy \quad (26)$$

and the equation of continuity for diffusion of the product species is

$$\frac{db}{dt} = D_{1e} \frac{d^2 b}{dy^2} + v[p_R(y), \eta(y), b_L(y)] \quad (27)$$

The corresponding small-signal forms are

$$I_{p1R} = \frac{z_p e}{2\delta} \int_{-\delta}^{\delta} \left[k_{1f} p_{1R} + \left(\frac{z_p e \eta_1}{kT} \right) \gamma_{1f} p_{0R} - k_{1b} b_1 \right] dy \quad (28)$$

and

$$i\omega b_1 = D_{1e} \frac{d^2 b_1}{dy^2} - k_{1b} b_1 + k_{1f} p_{1R} + \left(\frac{z_p e \eta_1}{kT} \right) \gamma_{1f} p_{0R} \quad (29)$$

In general the concentrations, overpotential, and rate constants appearing in these equations are functions of y . For unbiased small-signal measurements, however, the rate constants should be independent of position. Further, for ω^{-1} greater than the dielectric relaxation time one may assume that the distribution of charged species in the y direction and the overpotential will be nearly uniform. Under these conditions it is possible to solve eqn. (29), and one finds as a general solution

$$b_1 = \frac{k_{1f} p_{1R}}{k_{1b} + i\omega} + b_I \cosh Q'y + b_{II} \sinh Q'y \quad (30)$$

where b_I and b_{II} are constants of integration and

$$Q' \equiv \sqrt{(k_{1b} + i\omega)/D_{1e}} \quad (31)$$

If the edges of the regions of contact between electrode and electrolyte are assumed to be in contact with the ambient atmosphere and concentration gradients in the gas phase can be neglected, the appropriate boundary condition at $y = \pm\delta$ is

$$-D_{1e} db_1/dy = \pm k_{1ef} b_1 \quad (32)$$

where k_{1ef} is related to the desorption rate constant for the gas. When these conditions are employed to evaluate b_1 and the result is inserted in eqn. (28), the

integration can be carried out and one finally obtains

$$I_{p1R} = z_p e [k_1^* p_{1R} + (z_p e \eta_1 / kT) \gamma_1^* p_{0R}] \quad (33)$$

as in the case of the previous Section, but where now $k_1^* = f_1' k_{1f}$ and $\gamma_1^* = f_1' \gamma_{1f}$ with

$$f_1' \equiv \left[1 - \frac{k_{1b}}{k_{1b} + i\omega} \left(1 - \frac{k_{1ef}}{(k_{1b} + i\omega)\delta + k_{1ef}(Q_1' \delta) \operatorname{ctnh}(Q_1' \delta)} \right) \right] \quad (34)$$

The $k_{1ef} \rightarrow \infty$ limit of eqn. (34) has the same form as an expression obtained earlier by Lorenz [29] for the admittance associated with the deposition of metal atoms on a metal electrode with evenly spaced steps, a process with many features in common with that considered in this Section. Therefore, electrocrystallization can also be treated within the present complex rate constant formalism which, in allowing a finite value for k_{1ef} affords a minor generalization of the Lorenz result.

Clearly, the set of complex boundary parameters obtained in this Section may be used precisely in the same manner as those of the previous Section. It is noteworthy that in the present case f_1' does not have the continued fraction form since the electrode reaction mechanism involves not a simple sequence of steps but rather a competition between the electrode reaction and diffusion of the product. Further, the frequency dependent factor does not depend simply on $\omega^{1/2}$ but on the more complicated form Q' (eqn. 31).

The quantity f_1' is determined by three independent parameters which may be taken as k_{1b} , k_{1ef} , and $\delta/\sqrt{D_{1e}}$. A number of special cases of f_1' are noteworthy. When $\delta \rightarrow 0$, f_1' becomes unity and one formally obtains the boundary condition considered earlier [13,14,18,22] for a simple first-order electrode reaction with the product concentration held constant. On the other hand, when $D_{1e} \rightarrow \infty$, we obtain $f_1' = [k_{1ef} + i\omega\delta] / [k_{1b}\delta + k_{1ef} + i\omega\delta]$, formally equivalent to earlier reaction/adsorption results [16–18,22]. When $k_{1ef} \rightarrow 0$, so that exchange of the product with the surroundings is forbidden, $f_1' \rightarrow i\omega / (k_{1b} + i\omega)$, a form previously obtained for simple specific adsorption [16–18] and one which vanishes as $\omega \rightarrow 0$. In the opposite extreme when $k_{1ef} \rightarrow \infty$, one obtains $f_1' \rightarrow [k_{1b}(Q_1' \delta)^{-1} \tanh(Q_1' \delta) + i\omega] / (k_{1b} + i\omega)$.

(IV) SUMMARY

The diffusion of an electroactive species through a planar electrode and along a planar electrode/electrolyte interface has been considered. These conditions may be incorporated directly into the present exact treatment of the small-signal response of unsupported systems through the artifice of complex, frequency-dependent rate constants. The authors have incorporated the generalized form of the rate constants into existing computer programs for non-linear least squares analysis of complex data [30] and hope in future work to discuss the treatment of experimental data.

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