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THE TRANSIENT RESPONSE OF A DISK ELECTRODE

Kemal Nişancıoğlu and John Newman

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering; University of California
Berkeley, California

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ABSTRACT

A mathematical model is proposed to treat the transient response of a disk electrode to a change in the applied current. The analysis reduces to a well-defined boundary value problem, which yields solutions in terms of newly defined eigenfunctions. The results allow the determination of time constants characteristic of decay due to an electrode reaction and due to a redistribution of charge within the double layer during the transient process.

Key Words: interrupter, double-layer capacity, time constant,
ideally polarizable electrode

INTRODUCTION

The transient behavior of electrochemical cells has been of interest since the development of the commutator method for the assessment of electrode overpotentials.¹ The subsequent invention of the more accurate interrupter technique² and its perfection in the last couple of decades^{3,4} have provided a reliable tool for the measurement of the uncompensated ohmic drop in the solution. The presence of a non-uniform current distribution at the electrode surface (such as in the case of a disk electrode below the limiting current⁵⁻⁷), however, appears to complicate the interpretation of interrupter data, as this subject has already received ample thought and experimentation.^{4,8-12}

Newman⁸ has shown that the step change in potential at interruption corresponds to the primary current distribution⁵ and discussed the time constants for decay of the double layer capacity due to a Faradaic reaction and redistribution of charge within the double layer. A more complete mathematical study will be presented here in order to determine the transient response of a disk electrode to step changes in the cell current.

The problem was originally conceived for an ideally polarizable electrode with the purpose of calculating the transients one would observe during the charging and decay of the double layer capacity. However, the effect of a Faradaic reaction can be incorporated into the formulation without any added difficulty in the analysis. The more general case will therefore be analyzed with due notice of the

mathematical subtleties relevant to an ideally polarizable electrode.

The following assumptions are made in the treatment of the problem:

1. The disk electrode is embedded in an infinite, insulating plane, and the counter-electrode is placed at infinity.

2. The diffusion layer is neglected. This is a fairly good assumption when the rate of stirring is high (high rotation speeds), and the current density at the electrode surface is considerably below the limiting current.¹³

3. Linear kinetic relationships govern the electrode reaction. This situation is encountered for high reaction rate constants and sufficiently small current densities such that $|i| \ll i_0$, where i_0 is the exchange current density.⁶

The last two assumptions are stated for the sake of simplicity so that the phenomena which directly influence the transient behavior of an electrode can be singled out for investigation with a minimum number of complicating factors. The effect of steady state mass transfer on the current distribution below the limiting current has been discussed elsewhere for various geometries with the consideration of nonlinear electrode kinetics.^{6,7,14,15} Newman has treated the mass transfer problem in rapid double layer charging at an ideally polarizable electrode.¹⁶

MATHEMATICAL MODEL

The potential in the solution satisfies Laplace's equation

$$\nabla^2 \phi = 0 \quad (1)$$

The boundary conditions are

$$\frac{\partial \phi}{\partial z} = 0 \quad \text{at } z = 0, r > r_0 \quad (2)$$

$$\phi \rightarrow 0 \quad \text{as } r^2 + z^2 \rightarrow \infty \quad (3)$$

and the potential is well behaved on the axis of the disk. Furthermore, the normal component of the current density at the electrode surface is given by¹³

$$i_z = C \frac{\partial \eta_s}{\partial t} + (\alpha_a + \alpha_c) \frac{i_0 F}{RT} \eta_s = -\kappa \frac{\partial \phi}{\partial z} \quad \text{at } z = 0, r \leq r_0 \quad (4)$$

where

$$\eta_s = V - \phi_0 \quad (5)$$

is the surface overpotential associated with the Faradaic reaction, V is the electrode potential, ϕ_0 is the potential in the solution adjacent to the electrode, κ is the conductivity of the solution, C is the double layer capacity, and $(\alpha_a + \alpha_c) i_0 F/RT$ is the kinetic

coefficient for the Faradaic reaction.

We would like to have our model simulate the transient response of a disk electrode for the charging or decay of the double layer capacity immediately after the current is turned on or off respectively. The potential in solution for the charging period can then be represented as the difference of a steady state and a transient contribution

$$\phi = \phi^{ss} - \phi^t \quad (6)$$

such that each part satisfies Laplace's equation by itself. The electrode potential V can similarly be expressed as the difference of a steady state and a transient part. The steady state part of the potential includes the contribution of the total cell current, while the transient part contains no net current. Once the current is turned off, therefore, the steady state part vanishes, and the decay period is represented by only the transient part: $\phi = \phi^t$.

STEADY STATE PART OF THE POTENTIAL

The solution of Laplace's equation for the potential distribution in a disk electrode system is well known for various steady state boundary conditions at the electrode surface.^{5,6,9} A solution for the steady state part of the potential will be presented here to meet the purposes of this analysis.

In rotational elliptic coordinates⁵ η and ξ , the solution for the steady state part of the potential satisfying the conditions (2) and (3)

can be expressed as⁶

$$\frac{\phi^{ss}}{\phi_o^p} = \sum_{n=0}^{\infty} B_n^{ss} P_{2n}(\eta) M_{2n}(\xi) \quad (7)$$

where $P_{2n}(\eta)$ is the Legendre polynomial of order $2n$, $M_{2n}(\xi)$ is a Legendre function with known properties,⁷ and ϕ_o^p is the uniform potential in the solution just outside the double layer corresponding to the primary current distribution.⁵ This quantity, in fact, is the ohmic drop which is normally measured by interrupter methods⁸ and is identical to $I/4\kappa r_o$ in this work. The choice of ϕ_o^p as the scaling factor in Eq. (7) is mathematically convenient since this normalizes the numerical value of B_o^{ss} to unity regardless of the electrode conditions.

Substitution into the boundary condition (4) yields

$$-\frac{1}{\eta} \left. \frac{\partial \phi^{ss}}{\partial \xi} \right|_{\xi=0} = J \left(v^{ss} - \phi_o^{ss} \right) \quad (8)$$

where J is the dimensionless exchange current density given by

$$J = \frac{i_o r_o F}{RT\kappa} (\alpha_a + \alpha_c) \quad (9)$$

Combining Eqs. (7) and (8) and employing the orthogonality property of the Legendre polynomials⁶ gives

$$\frac{v^{ss}}{\phi_o^p} = 1 + \frac{4}{\pi J} + 2 \sum_{n=1}^{\infty} a_{o,n} B_n^{ss} \quad (10)$$

and

$$\sum_{n=1}^{n_{\max}} \left[a_{m,n} - 2a_{o,m} a_{o,n} - \delta_{m,n} \frac{M'_{2m}(0)}{(4m+1)J} \right] B_n^{ss} = \frac{4}{\pi J} a_{o,m} \quad (m = 1, 2, \dots, n_{\max}) \quad (11)$$

where

$$a_{m,n} = \int_0^1 \eta P_{2m}(\eta) P_{2n}(\eta) d\eta \quad (12)$$

$$a_{o,m} = \int_0^1 \eta P_{2m}(\eta) d\eta = - \frac{P_{2m}(0)}{2(2m-1)(m+1)} \quad (13)$$

$$\delta_{m,n} = \begin{cases} 0 & \text{if } m \neq n \\ 1 & \text{if } m = n \end{cases} \quad (14)$$

The series in Eqs. (10) and (11) are truncated at n_{\max} for the purposes of numerical calculation. The accuracy of calculation hence depends on the number of terms taken into consideration. The coefficients B_n^{ss} for the first 10 terms in the series are listed in Table I for various J values. The quantity V^{ss}/ϕ_o^D , which can directly be calculated from Eq. (10) once B_n^{ss} are obtained from Eq. (11), is identified as the dimensionless effective direct-current resistance¹⁷ $4r_o \ll R_{\text{eff}}$ for the disk system with the reference electrode at infinity.

Table I. Direct-current resistance V^{ss}/ϕ_0^p and coefficients in the series for the steady state potential

n	J = 0	J = 0.1	J = 1	J = 10
0	1.00000	1.00000	1.00000	1.00000
1	0.31250	0.30731	0.26863	0.13306
2	-0.05273	-0.05446	-0.06568	-0.07356
3	0.01984	0.02040	0.02491	0.04037
4	-0.00993	-0.01019	-0.01232	-0.02324
5	0.00580	0.00594	0.00713	0.01423
6	-0.00373	-0.00382	-0.00455	-0.00926
7	0.00256	0.00262	0.00312	0.00636
8	-0.00185	-0.00189	-0.00224	-0.00456
9	0.00139	0.00142	0.00168	0.00339
10	-0.00107	-0.00110	-0.00130	-0.00260
V^{ss}/ϕ_0^p	-	13.81194	2.34368	1.16459

The solution can therefore be given by

$$U_i = \sum_{n=1}^{\infty} B_{n,i} P_{2n}(\eta) M_{2n}(\xi) \quad (24)$$

The zeroeth term is excluded from the summation since U_i includes no contribution to the net current. The boundary condition (4) now reduces to

$$\left. \frac{\partial U_i}{\partial \xi} \right|_{\xi=0} = \Lambda_i \eta (1 - U_{i,0}) \quad (25)$$

Combining Eqs. (24) and (25) and invoking the orthogonality property of the Legendre polynomials yield

$$\sum_{n=1}^{n_{\max}} a_{0,n} B_{n,i} = \frac{1}{2} \quad (26)$$

$$\sum_{n=1}^{n_{\max}} \left[a_{m,n} + \frac{\delta_{m,n}}{\Lambda_i} \frac{M'_{2m}(0)}{4m+1} \right] B_{n,i} = a_{0,m} \quad (m = 1, 2, \dots, n_{\max}) \quad (27)$$

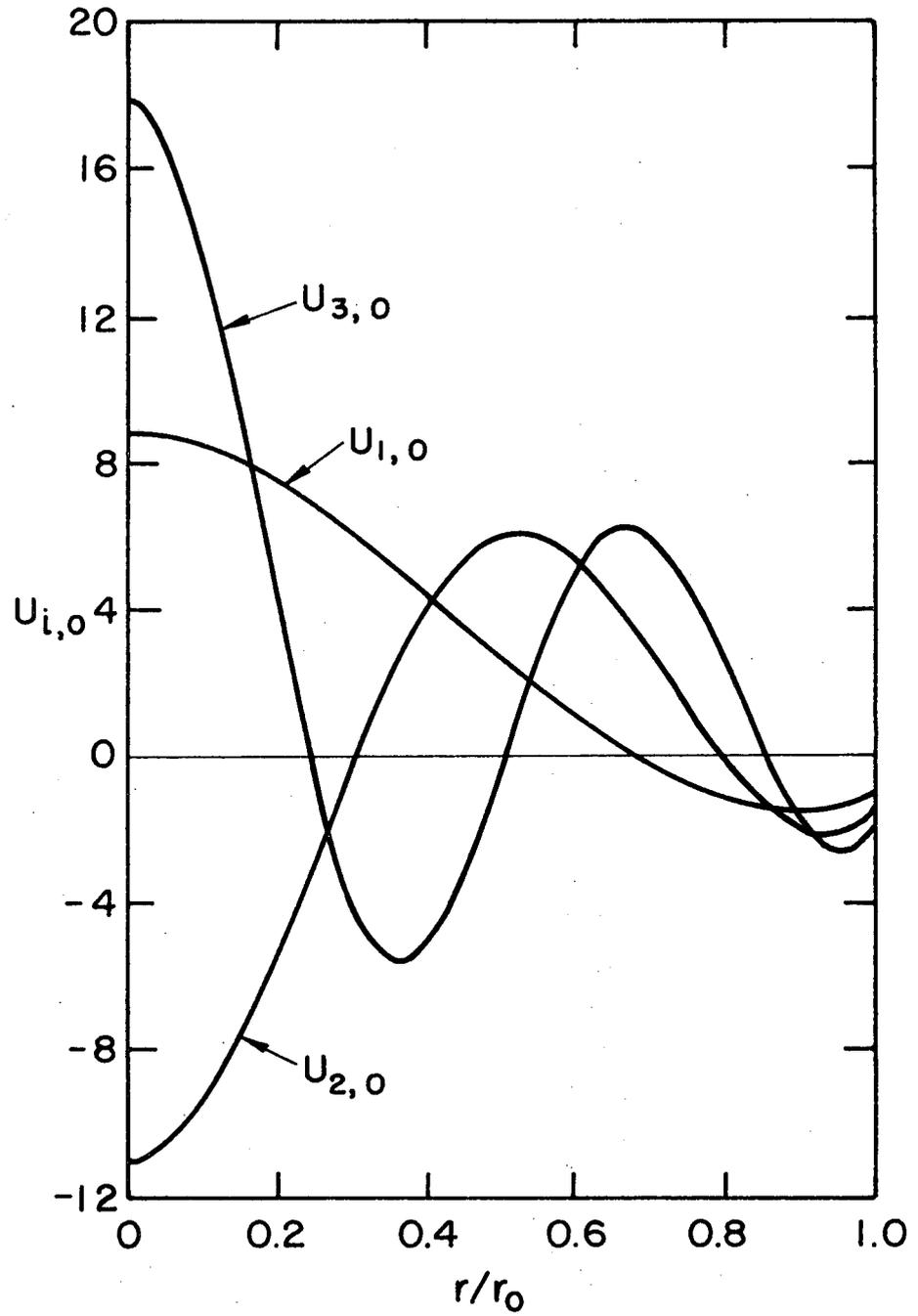
The above set of equations can be solved simultaneously for Λ_i and $B_{n,i}$. Some results are given in Table II, and the first three eigenfunctions are plotted in Fig. 1.

Each term in Eq. (17), and the corresponding term in Eq. (21), describes a potential distribution and a state of charge in the electric double layer which can decay with a single time constant and

Table II. The first five eigenvalues and the related coefficients

$B_{n,i}$ of the eigenfunctions

n	Λ_1	Λ_2	Λ_3	Λ_4	Λ_5
	4.12130	7.34208	10.5171	13.6773	16.8308
	i = 1	i = 2	i = 3	i = 4	i = 5
1	4.56973	3.77404	3.44402	3.25859	3.13834
2	3.58511	-3.70786	-4.65162	-4.79052	-4.75588
3	0.51738	-7.51662	-0.26797	2.76522	4.12690
4	0.10883	-2.89555	9.61986	5.38653	1.50542
5	-0.03143	-0.67828	6.80911	-8.19367	-8.96691
6	0.02275	-0.02899	2.44681	-10.7732	3.13085
7	-0.01587	-0.03992	0.44950	-5.76319	12.7102
8	0.01161	0.02428	0.11318	-1.72888	10.1186
9	-0.00879	-0.01883	-0.02226	-0.42937	4.33793
10	0.00684	0.01470	0.02445	-0.02853	1.34844



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Fig. 1. The first three eigenfunctions for the transient solution.

involves no net current flow to the counter electrode at infinity. The state of charge is proportional to $V - \Phi_0$ or to $1 - U_{i,0}$ for a particular eigenfunction. If this state of charge is non-uniform, it will have associated with it a flow of current through the solution in a direction which tends to make even the charge distribution across the electrode. At the same time, the double layer charge may be decaying through the Faradaic reaction (if $J > 0$).

If each eigenfunction is to represent a single time constant, the amount of current flowing through the solution (related to $\partial U_i / \partial \xi$ at $\xi = 0$) must be proportional, over the surface of the electrode, to the rate of change of the double-layer charge. Equation (25) represents this state of affairs. Only for certain characteristic decay constants Λ_i is it possible to find consonant current and charge distributions which decay with a single time constant, and these eigenvalues are not known in advance. The lowest eigenvalue, either $\Lambda_0 = 0$ or $\Lambda_1 = 4.12130$, is the most important because its effect can most readily be observed experimentally after the other eigenfunctions have decayed to negligible values.

It is a further consequence of boundary condition (25) (current in solution is proportional to surface charge for each eigenfunction) that the eigenfunctions U_i satisfy the unusual orthogonality relationship

$$\int_0^1 U_{i,0} (1 - U_{j,0}) \eta d\eta = \begin{cases} \frac{1}{\Lambda_i} \sum_{n=1}^{\infty} \frac{M'_{2n}(0)}{4n+1} B_{n,i}^2 & \text{if } i=j \\ 0 & \text{if } i \neq j \end{cases} \quad (28)$$

This has much the same meaning; the potential at the surface for one eigenfunction is in a sense orthogonal to the current density for another eigenfunction.

One can study the eigenfunctions in Fig. 1 to visualize how the current flows through the solution. The potential is non-uniform for a given eigenfunction because the state of charge is non-uniform. The current density in the solution is proportional to $1-U_{i,0}$ and flows from a region of high charge to a region of low charge. The higher order eigenfunctions have more minima and maxima in the curves. The current need therefore flow a shorter distance in order to even up the charge, and the time constants are correspondingly shorter.

TRANSIENT POTENTIAL DISTRIBUTION

In order to be able to calculate the values of C_1 and thereby complete the analysis, we need to specify suitable initial conditions for the problem. Let us assume that the current is switched on as a step at $\theta = 0 +$ and kept constant until $\theta = \theta_{ch}$, at which instant it is turned off. The time scale for the decay period can be defined as

$$\theta' = \theta - \theta_{ch} \tag{29}$$

Therefore, for the charging period

$$V = \Phi_0 = \Phi_0^P \text{ at } \theta = 0+, \xi = 0 \tag{30}$$

and for the decay period

$$\left. \begin{aligned} V &= V(\theta_{ch}) - \Phi_o^P \\ \Phi_o &= \Phi_o(\theta_{ch}) - \Phi_o^P \end{aligned} \right\} \text{ at } \theta' = 0+, \quad \xi = 0 \quad (31)$$

Application of the initial condition (30) for the charging period to Eq. (6) gives

$$\frac{\Phi_o^{ss}}{\Phi_o^P} - 1 = \sum_{i=1}^{\infty} C_i U_{i,o} \quad (32)$$

Multiplication by $(1-U_{j,o})\eta$ and integration with respect to η yields

$$C_j = \frac{\int_0^1 \frac{\Phi_o^{ss}}{\Phi_o^P} (1-U_{j,o}) \eta d\eta}{\int_0^1 U_{j,o} (1-U_{j,o}) \eta d\eta} = \frac{\sum_{n=1}^{\infty} \frac{M'_{2n}(0)}{4n+1} B_n^{ss} B_{n,j}}{\sum_{n=1}^{\infty} \frac{M'_{2n}(0)}{4n+1} B_{n,j}^2} \quad (33)$$

Application of the corresponding initial condition for the electrode potential gives

$$C_o = \frac{V^{ss}}{\Phi_o^P} - 1 - \sum_{i=1}^{\infty} C_i = \frac{4}{\pi J} \quad (34)$$

For the decay period where $\Phi = \Phi^t$ (the negative of the transient part for charging), the same results, summarized by Eqs. (32) through (34), also apply as long as θ_{ch} is large enough so that the steady state

has been reached right before interruption. If this is not the case, the equations for decay become

$$\frac{\Phi}{\Phi_0 P} = \sum_{i=1}^{\infty} C_i \left[1 - e^{-\theta_{ch}(\Lambda_i + J)} \right] e^{-\theta'(\Lambda_i + J)} U_i \quad (35)$$

for the potential in the solution, and

$$\frac{V}{\Phi_0 P} = C_0 \left(1 - e^{-\theta_{ch} J} \right) e^{-\theta' J} + \sum_{i=1}^{\infty} C_i \left[1 - e^{-\theta_{ch}(\Lambda_i + J)} \right] e^{-\theta'(\Lambda_i + J)} \quad (36)$$

for the electrode potential. The coefficients C_i are the same as for the charging period, given by Eqs. (33) and (34).

For an ideally polarizable electrode ($J=0$) the same relationships hold to express the potential in the solution, both for charging and for decay. The electrode potential, however, increases indefinitely once the current is turned on and decays to a non-zero value after the interruption of current. This is because of the fact that the net double-layer charge has no means for decay in the absence of an electrode reaction; it can only redistribute by flow of current through the solution in order to attain a final uniform state. Hence, for the charging period we have

$$\frac{V}{\Phi_0 P} = \frac{4}{\pi} \theta + D - \sum_{i=1}^{\infty} C_i e^{-\Lambda_i \theta} \quad (37)$$

The constant term can be obtained by integrating condition (4) over the electrode surface for the total period of charging to obtain the net charge added to the double layer

$$2\pi C \int_0^{r_o} \int_0^{t_{ch}} \frac{\partial(V-\phi_o)}{\partial t} dt dr = 2\pi \int_0^{r_o} \int_0^{t_{ch}} i_z dt dr = It_{ch} \quad (38)$$

Substitution of Eqs. (6) and (37) into the left side and integration lead to the result

$$D = 2 \sum_{n=0}^{\infty} B_n^{ss} a_{o,n} = 1.08076 = 32/3\pi^2 \quad (39)$$

Finally, the electrode potential for the decay period is

$$\frac{V}{\phi_o} = \frac{4}{\pi} \theta_{ch} + \sum_{i=1}^{\infty} U_i e^{-\Lambda_i \theta} \left(1 - e^{-\Lambda_i \theta_{ch}} \right) \quad (40)$$

The analysis at this point can readily be extended to account for arbitrary changes in the cell current by a straight forward application of the superposition integral. If the time dependent cell current is given by $I(\theta)$, the electrode potential can be expressed as

$$4r_o kV = I(\theta) + C_o J e^{-\theta J} \int_0^{\theta} I(\theta) e^{\theta J} d\theta + \sum_{i=1}^{\infty} C_i (\Lambda_i + J) e^{-\theta(\Lambda_i + J)} \int_0^{\theta} I(\theta) e^{\theta(\Lambda_i + J)} d\theta \quad (41)$$

in the presence of an electrode reaction, and

$$4r_0 kV = I(\theta) + \frac{4}{\pi} \int_0^\theta I(\theta) d\theta + \sum_{i=1}^{\infty} C_i \Lambda_i e^{-\Lambda_i \theta} \int_0^\theta I(\theta) e^{\Lambda_i \theta} d\theta \quad (42)$$

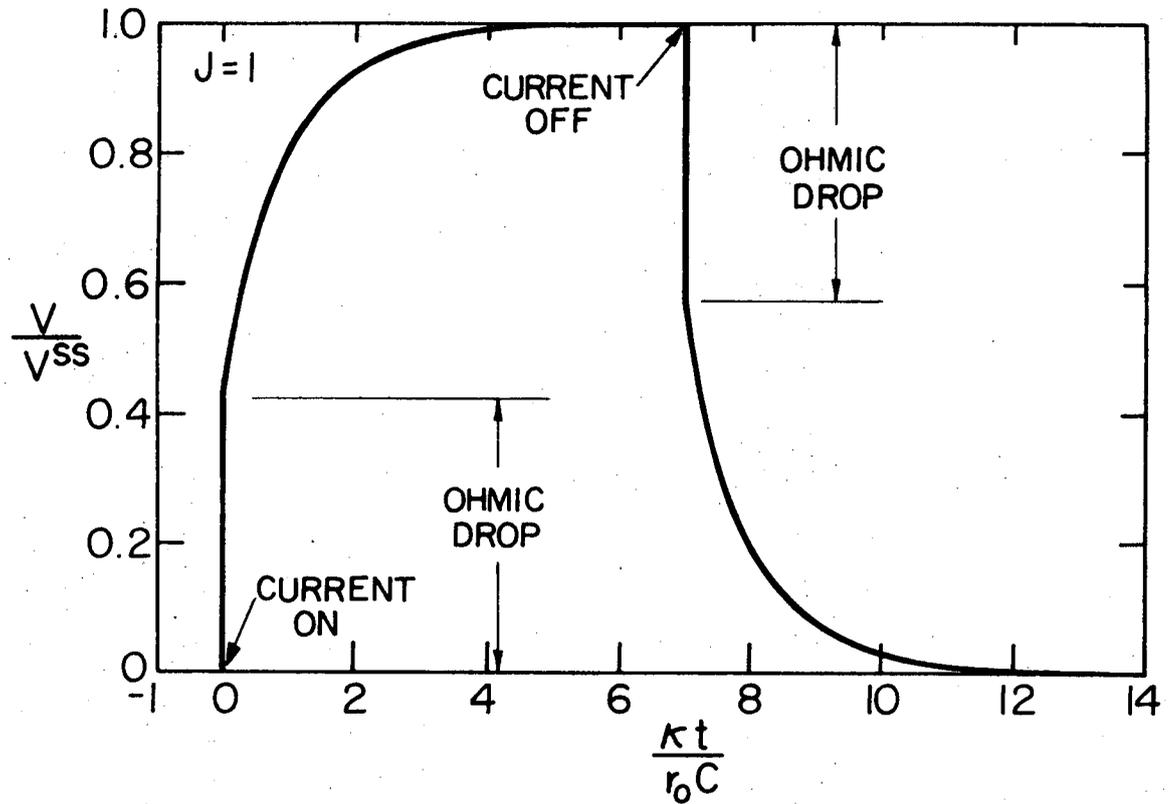
for an ideally polarizable electrode. One application of these equations would be for an alternating current situation, where the frequency dispersion of the measured impedance is of interest. A more rigorous and accurate calculation has been performed by Newman¹⁷ for this particular case. The present equations were used to compute the frequency dispersion in capacity measurements at a disk electrode and compared to Newman's results.¹⁷ The agreement is good for small frequencies, but a large number of terms is required in the series to attain any reasonable accuracy at high frequencies. The same numerical problem is encountered in calculating the short-time response of the potential to a step change in the current since the series do not converge very fast. An asymptotic solution, applicable to small charging and decay periods, may therefore be desirable.

RESULTS AND DISCUSSION

Figure 2 depicts a typical potential trace for double layer charging and decay in the presence of a Faradaic reaction, and Fig. 3 shows potential decay curves after the interruption of current for various values of the kinetic parameter J . For both representations, the current is interrupted after the double layer is charged to steady state conditions. For large decay periods, the slope of each curve approaches the corresponding J value on a semi-logarithmic scale as can be inferred from Eq. (36). Curves similar to Fig. 1 could be constructed for different J values by making use of the information contained in Fig. 2 and by remembering that the ohmic drop is given by the primary distribution ϕ_o^P , and the charging and decay portions of each curve are symmetric.

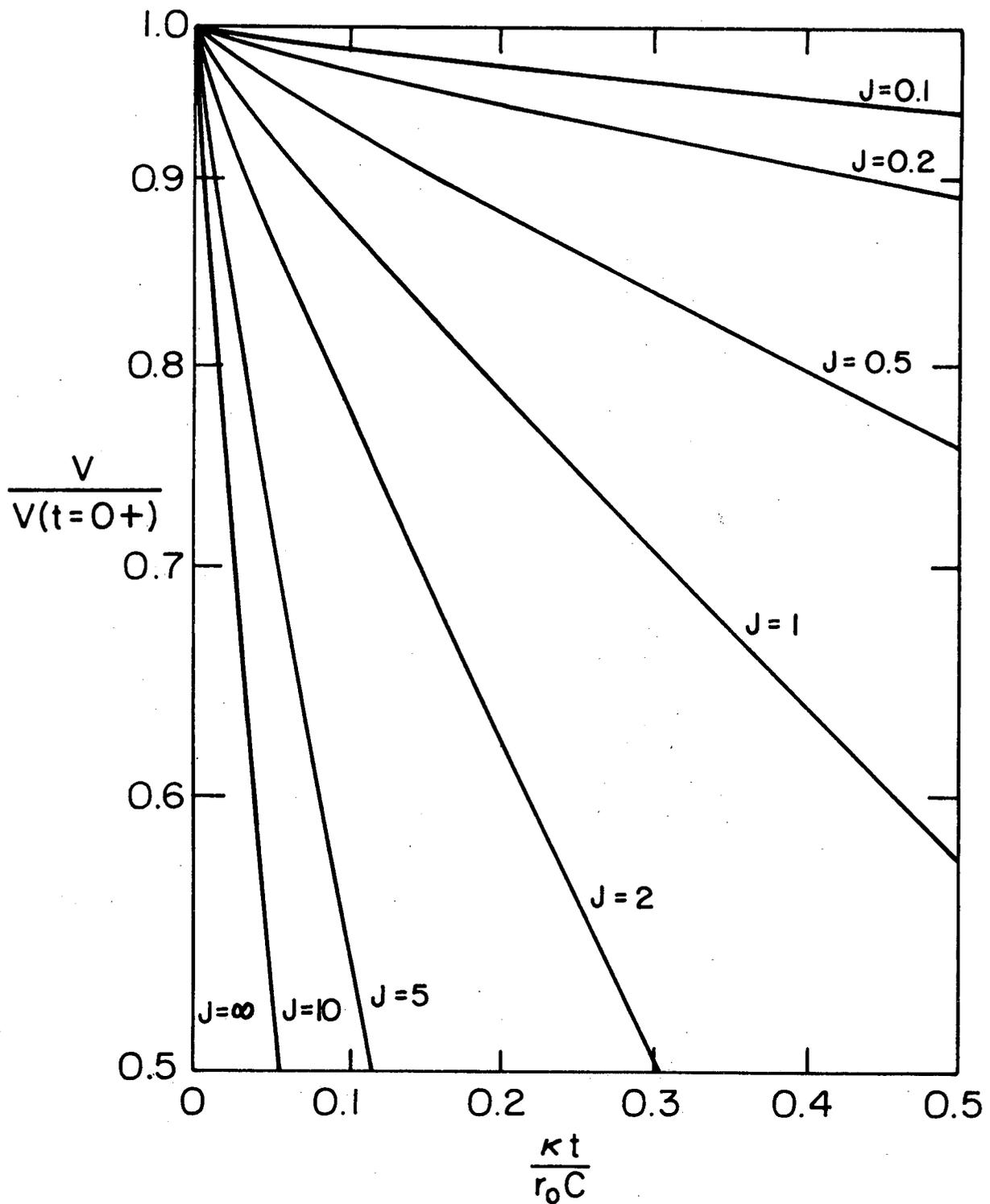
The fact that the instantaneous potential step immediately preceding both the charging and decay portions of Fig. 1 corresponds to the primary current distribution⁸ is implicit in the present analysis by virtue of the particular initial conditions (Eqs. (30) and (31)) employed. Nanis and Kesselman⁹ have expressed the contrary view in this regard. We would like to stress that the same criterion would hold for the ohmic drop even if the diffusion layer were taken into consideration. An experimental verification along these lines has been provided by Miller and Bellavance.¹²

The transient response of an ideally polarizable electrode to step changes in the current is depicted in Fig. 4. The step portions again correspond to the primary distribution. The differences in comparison



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Fig. 2. Double layer charging and decay in the presence of a Faradaic reaction.



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Fig. 3. Decay of the electrode potential for various values of the kinetic parameter J . A steady condition was attained before interruption of the current.

to Fig. 2 are obvious. The potential-time relationship becomes linear for sufficiently large charging periods as the surface current density attains a uniform distribution. After the interruption of current, the electrode potential decays to a non-zero value, given by $4\theta_{ch}/\pi$. Decay curves for various charging periods are sketched in Fig. 5 to show the effect of short charging times on the potential decay. The same effect is also discernable when J is greater than zero, but the dependence on the charging period was not of prime interest in constructing Fig. 3 and was suppressed by allowing a steady state to develop before current interruption.

The reference electrode was assumed to be positioned at infinity relative to the working electrode in obtaining all these results. The measurements would be different for other placements, and appropriate corrections would be necessary.^{5,11}

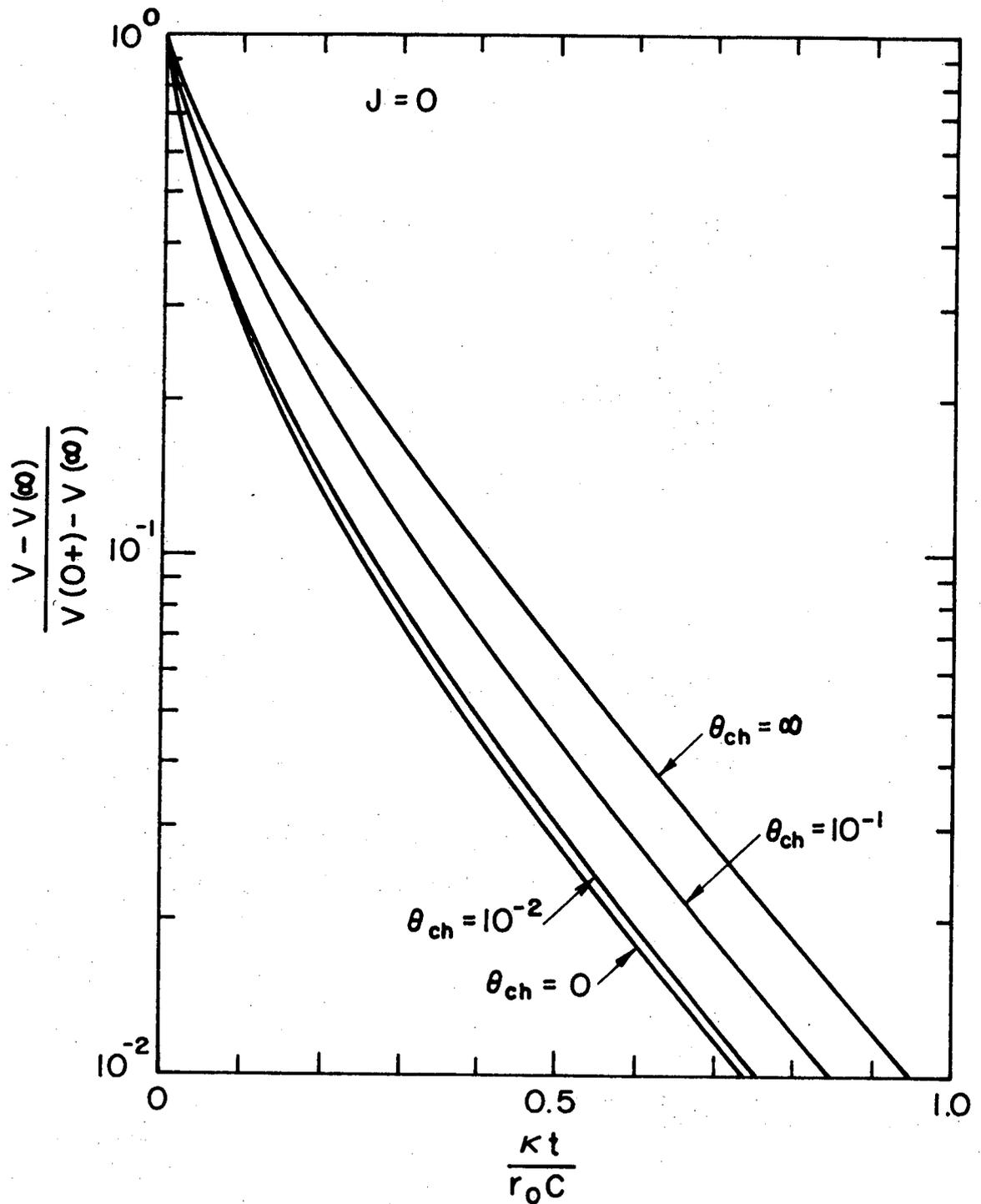
An important result of the present analysis is the assessment of an accurate time constant for the decay of the double layer capacity in the absence of concentration gradients at the electrode surface.

From Eq. (18), we obtain

$$\tau_i = \frac{1}{\Lambda_i + J} \frac{r_o C}{\kappa} \quad (43)$$

When an electrochemical reaction is possible, the dominant time constant at long times is

$$\tau = \frac{r_o C}{\kappa J} \quad (44)$$



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Fig. 5. Decay of the electrode potential for various charging periods in the absence of a reaction. The slope here is related at long times to the first eigenvalue Λ_1 .

as identified by Newman.⁸ When an electrochemical reaction is not possible (the ideally polarizable electrode), this time constant becomes infinite, and the potential decays to a non-zero constant. The dominant time constant then is

$$\tau = \frac{r_o C}{\Lambda_1 \kappa} = \frac{1}{4.12} \frac{r_o C}{\kappa} \quad (45)$$

also suggested in the same context⁸ but without the determination of the numerical factor. The present analysis amplifies the roles and interrelationship of these two quantities and the processes they describe.

A direct experimental test of these time constants may be performed with the utility of an original reference electrode system designed by Miller and Bellavance.¹² This consists of two probes positioned coaxially with the disk in the solution, so that the potential drop between two distinct locations in the solution could be measured. If linear electrode kinetics and finite exchange current densities are ensured, and concentration gradients near the surface of the disk are avoided, the time constant so measured should correspond to Eq. (43) for $i=1$.

CONCLUSIONS

The transient behavior of a disk electrode for a step change in the applied current has been worked out theoretically in the absence of mass transfer effects. The analysis leads to a boundary value problem, which yields analytic solutions in terms of a new set of eigenfunctions U_1 . These equations can be extended to account for arbitrary variations in the applied current by employing the superposition integral.

The results demonstrate a) the effects of a Faradaic reaction and b) the non-uniform primary current distribution on the double layer charging and decay at a disk electrode, and c) the interaction of these phenomena to determine the resultant electrode behavior. The overall treatment of the problem allows the determination of accurate time constants for each of these effects.

ACKNOWLEDGEMENT

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NOMENCLATURE

$a_{o,m}$	see Eq. (12)
$a_{m,n}$	see Eq. (11)
B_n^{ss}	coefficients in series for ϕ^{ss}
$B_{n,i}$	coefficients in series for U_i
C	double layer capacity (f/cm ²)
C_i	coefficients in series for ϕ^t and V^t
D	1.08076
F	Faraday's constant (coulomb/equiv.)
i_z	component of current density normal to the plane of disk (amp/cm ²)
i_o	exchange current density (amp/cm ²)
I	total current (amp)
J	dimensionless exchange current density
M_{2n}	Legendre function discussed in ref. (6)
P_{2n}	Legendre polynomial of order 2n
r	radial position from axis of disk (cm)
r_o	radius of disk (cm)
R	universal gas constant (joule/mole-deg)
R_{eff}	effective D.C. resistance (ohm)
t	time (sec)
t_{ch}	total period of charging (sec)
T	absolute temperature (°K)
U_i	eigenfunctions in series for ϕ^t
$U_{i,o}$	value of U_i at the electrode surface
V	electrode potential (volt)

V^{ss}	steady state part of the electrode potential (volt)
V^t	transient part of the electrode potential (volt)
z	distance from plane of disk (cm)
α_a, α_c	parameters in the kinetic coefficient
$\delta_{m,n}$	Kronecker delta
η	rotational elliptic coordinate
η_s	surface overpotential (volt)
κ	conductivity of the solution ($\text{ohm}^{-1}\text{-cm}^{-1}$)
Λ_i	dimensionless eigenvalue
Φ	potential in the solution (volt)
Φ_o	value of Φ at the electrode surface (volt)
Φ^{ss}	steady state part of potential in the solution (volt)
Φ^t	transient part of potential in the solution (volt)
Φ_o^p	potential in the solution adjacent to the disk corresponding to the primary current distribution (volt)
ξ	rotational elliptic coordinate
τ_i	time constants for decay (sec)
θ	dimensionless time for the charging period
θ'	dimensionless time for the decay period
θ_{ch}	dimensionless total period of charging
U_i	constants in the series for V^t (normalized to unity)

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720