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**POLAROGRAPHIC KINETIC CURRENTS FOR THE FIRST-ORDER,
ONE-HALF REGENERATION MECHANISM
AT SPHERICAL ELECTRODES**

J. R. Delmastro and G. L. Booman

IDAHO NUCLEAR CORPORATION
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ABSTRACT

The analytical solution for the large potential-step electrode response at a stationary spherical electrode with the first-order, one-half regeneration mechanism is derived by a non-routine application of the Laplace transformation method. The form of the resulting solution depends on the value of the effective electrode sphericity.

SUMMARY

An analytical solution for the first-order, one-half regeneration mechanism with large potential-step electrolysis at a stationary spherical electrode is derived by the method of Laplace Transformation. A non-routine application of this method is employed in evaluating inverse Laplace transforms of the general form $[\sqrt{s} (\sqrt{s + \beta + \gamma})]^{-1}$. The resulting solution, depending on the value of the effective electrode sphericity Q , appears in three different forms.

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INTRODUCTION

A theoretical analysis of polarographic kinetic currents for first-order preceding⁽¹⁾ and first- and second-order⁽²⁾ regeneration reactions at spherical electrodes has already been presented. Such theory is of interest because most large potential-step investigations of the kinetics of electrode processes are performed at hanging drop electrodes. A significant influence of spherical diffusion at normal measurement times, for electrode reaction mechanisms which involve homogeneous chemical reactions coupled to the charge-transfer step, has already been demonstrated⁽¹⁻⁴⁾. Therefore, the solution of spherical diffusion boundary value problems for electrode reaction mechanisms which involve coupled chemical reactions is of interest. Sometimes the analytical solutions of such problems can be obtained by application of the method of Laplace Transformation. These analytical solutions are valuable not only because they permit rapid calculation of electrode response curves to be used in data analysis for a given mechanism, but because they also permit evaluation of various numerical methods which can be developed to treat mechanisms which cannot be solved analytically.

An electrode reaction mechanism which can be solved for the general analytical solution in spherical geometry is the first-order, one-half regeneration mechanism⁽¹⁾.

Mechanism I.

This mechanism involves a first-order or pseudo first-order homogeneous chemical reaction which regenerates half the depolarizer from the product of the electrode reaction. Mechanism I is the first-order analog of the electrode reaction mechanism which describes the reduction of hexavalent uranium in acid solution. The analytical solution for Mechanism I is of interest because it permits an evaluation of numerical methods which were used in treating regeneration mechanisms^(1,3,4) and predicts qualitatively the behavior to be expected with the second-order, one-half regeneration mechanism. This analytical solution is also of special interest because it corresponds to the case of a preceding reaction mechanism with an equilibrium constant of unity⁽¹⁾. Because the derivation of the analytical solution involves a non-routine application of the Laplace transformation method for inversion of some of the transforms, it is presented herein. The derivation is restricted to an expression for the limiting current region for large potential-step electrochemical experiments at stationary spherical electrodes. The analytical solution for the entire polarographic "wave", after invoking Nernstian charge transfer or the absolute rate equation, could not be obtained by a simple extension of the method outlined in the next section. However, for both the preceding and regeneration reaction mechanisms, the electrode response is most sensitive to the kinetics of the coupled reaction in the limiting current region.

DERIVATION OF THE ANALYTICAL SOLUTION FOR THE FIRST-ORDER,
ONE-HALF REGENERATION MECHANISM WITH DIFFUSION TO
A STATIONARY SPHERICAL ELECTRODE

The analytical solution for Mechanism I and large potential-step electrolysis is obtained by application of the method of Laplace Transformation to the integral equation

$$\frac{1}{2nFAD^{1/2}C_o^*} \int_0^t i(t-u) [1 + e^{-ku}] \left[\frac{1}{\sqrt{\pi u}} - D^{1/2} r_o^{-1} E(D^{1/2} r_o^{-1} u^{1/2}) \right] du = 1. \quad (1)$$

The derivation of Equation (1) from the original boundary value problem is presented elsewhere⁽¹⁾. In Equation (1), $E(X)$ denotes the exponential error function complement

$$E(X) = \exp(X^2) \operatorname{erfc}(X) \quad (2)$$

and other notation is presented in the NOTATION DEFINITIONS. Equation (1) can be expressed in Laplace transform space as

$$\psi(s) = \frac{(\sqrt{s+k} + c)(\sqrt{s} + c)}{s(\sqrt{s} + 2c + \sqrt{s+k})} \quad (3)$$

where

$$i(s) = 2nFAD^{1/2} C_o^* \psi(s) \quad (4)$$

and

$$c = D^{1/2}/r_o. \quad (5)$$

The solution of Equation (3) for the special case where $c/\sqrt{k} = 1/2$ may be obtained after partial rationalization of the denominator by the factor $(\sqrt{s} + 2c - \sqrt{s+k})$. This operation yields

$$\psi(s) = [s\sqrt{s+k} - s\sqrt{s} + 2c\sqrt{s}\sqrt{s+k} + c^2\sqrt{s+k} + (3c^2 - k)\sqrt{s} + c(2c^2 - k)][4cs\sqrt{s} + 4c^2 - k]^{-1}. \quad (6)$$

It is convenient to denote $c/\sqrt{k}$ as the effective electrode sphericity Q . For $Q = 0.5$ Equation (6) reduces to

$$\psi(s) = \frac{1}{2} \left[\frac{\sqrt{s+k} - \sqrt{s}}{\sqrt{ks}} + \frac{\sqrt{s+k}}{s} + \frac{\sqrt{k(s+k)}}{4s\sqrt{s}} - \frac{\sqrt{k}}{4s} - \frac{k}{4s\sqrt{s}} \right]. \quad (7)$$

Term-by-term inverse transformation and algebraic rearrangement yield

$$\psi(t) = \frac{\sqrt{k}}{2} \left[\frac{e^{-T}}{\sqrt{\pi T}} - \frac{1}{4} + \operatorname{erf}(\sqrt{T}) + \frac{e^{-T/2}}{4} \left[(T+3)I_0(T/2) + (T+2)I_1(T/2) \right] - \frac{1}{2} \sqrt{\frac{T}{\pi}} \right] \quad (8)$$

where

$$T = kt. \quad (9)$$

The expression for the current ratio is obtained after combining Equation (4) with (8) and the definition of the diffusion current at a stationary spherical electrode⁽⁵⁾.

$$i_D = nFAD^{1/2} C_o^* \left[\frac{1}{\sqrt{\pi t}} + \frac{D^{1/2}}{r_o} \right] \quad (10)$$

These operations yield for the ratio of kinetic-to-diffusion current

$$\frac{i_k}{i_D} = \left[e^{-T} - \sqrt{\pi T} [0.25 - \operatorname{erf}(\sqrt{T})] + 0.25e^{-T/2} \sqrt{\pi T} [(T+3)I_0(T/2) + (T+2)I_1(T/2)] - 0.5T \right] (1 + 0.5 \sqrt{\pi T})^{-1}. \quad (11)$$

The general analytical solution ($Q \neq 0.5$) may be obtained after partial rationalization of Equation (3) by the factor $(\sqrt{s+k+2c} - \sqrt{s})$ upon algebraic rearrangement to

$$\psi(s) = \frac{\sqrt{s} + c}{s} - \frac{(s + 2c\sqrt{s} + c^2)}{s(\sqrt{s+k} + 2c + \sqrt{s})}. \quad (12)$$

Partial rationalization and routine algebraic rearrangement of Equation (12) yields

$$\psi(s) = \frac{\sqrt{s} + c}{s} - \left\{ \frac{\sqrt{s+k} - \sqrt{s}}{4c \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} + \frac{\sqrt{s+k} + 3/2c}{2\sqrt{s} \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} + \frac{c\sqrt{s+k} + 2c^2}{4s \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \right\}. \quad (13)$$

Because of the algebraic complexity of Equation (13), it is convenient to introduce the following simplified notation for each of the terms in braces.

$$f_1(s) = \frac{\sqrt{s+k}}{4c \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (14)$$

$$f_2(s) = \frac{-\sqrt{s}}{4c \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (15)$$

$$f_3(s) = \frac{\sqrt{s+k}}{2\sqrt{s} \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (16)$$

$$f_4(s) = \frac{3c}{4\sqrt{s} \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (17)$$

$$f_5(s) = \frac{c\sqrt{s+k}}{4s \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (18)$$

$$f_6(s) = \frac{c^2}{2s \left[\sqrt{s+k} + \frac{4c^2+k}{4c} \right]} \quad (19)$$

Thus, the expression for the kinetic current may be written formally as

$$i_k = 2nFAD^{1/2}C_0^* \left[\frac{1}{\sqrt{\pi t}} + c - \sum_{n=1}^6 F_n(t) \right] \quad (20)$$

where $F_1(t) - F_6(t)$ denote the inverse transforms of Equations (14-19), respectively. The inverse transforms of $f_5(s)$ and $f_6(s)$ may be evaluated from standard tables of Laplace transforms⁽⁶⁾ after routine algebraic rearrangement. The inverse of $f_1(s)$ is evaluated by using the relationship between $f_1(s)$ and $f_5(s)$

$$f_1(s) = c^{-2} s f_5(s). \quad (21)$$

Hence, when $F_5(t)$ is known, $F_1(t)$ may be evaluated by using the general property of the Laplace Transformation⁽⁶⁾

$$F^{(1)}(t) = L^{-1} [s f(s) - F(+0)] \quad (22)$$

or

$$F_1(t) = c^{-2} F_5^{(1)}(t) + c^{-2} \delta(t) F_5(+0). \quad (23)$$

Performing the above-mentioned operations and algebraic rearrangement yields for the sum of F_1 , F_5 , and F_6

$$F_1(t) + F_5(t) + F_6(t) = \frac{cQ}{1-4Q^2} \left[\operatorname{erf}(\sqrt{T}) - 2Q + \frac{(16Q^4-1)e^{-T}}{16Q^4\sqrt{\pi T}} \right. \\ \left. + \frac{(4Q^2-1)e^{-T}}{64Q^5} E \left[\left(\frac{4Q^2+1}{4Q} \right) \sqrt{T} \right] \right] + \frac{\delta(t)}{4c}. \quad (24)$$

The inverse transforms of f_2 , f_3 and f_4 could not be evaluated by routine methods. However, if $F_4(t)$ can be obtained, $F_2(t)$ can be evaluated from Equation 22 because F_2 and F_4 are simply related.

$$f_2(s) = \frac{-s}{3c^2} f_4(s) \quad (25)$$

$F_4(t)$ may be evaluated by employing the relationship

$$sf_4(s) - \left[\frac{k-4c^2}{4c} \right]^2 f_4(s) = \frac{3c}{4\sqrt{s}} \left[\sqrt{s+k} - \frac{(4c^2+k)}{4c} \right]. \quad (26)$$

Inverse transformation of (26) yields a first-order linear differential equation in $F_4(t)$.

$$F_4^{(1)}(t) - \left[\frac{k-4c^2}{4c} \right]^2 F_4(t) = \frac{3c}{4} \left[\frac{k}{2} \exp(-kt/2) [I_0(kt/2) + I_1(kt/2)] - \frac{(4c^2+k)}{4c\sqrt{\pi t}} \right] \quad (27)$$

Although the formal solution to Equation (27) may easily be written, it involves an integral which cannot be expressed in terms of known functions. A series solution for $F_4(t)$ can be obtained upon successive differentiation of Equation (27). This solution may be written

$$F_4(t) = -d[\alpha(t) + d^1\alpha^{(1)}(t) + d^2\alpha^{(2)} + \dots + d^n\alpha^{(n)}(t) + \dots] \quad (28)$$

where

$$d = \left[\frac{4c}{k-4c^2} \right]^2 \quad (29)$$

and $\alpha^{(n)}(t)$ denotes the n th derivative of the right-hand side of Equation (27). The contribution of the term $-3(4c^2+k)/(16\sqrt{\pi t})$ in Equation (27) to the series solution for $F_4(t)$ [Equation (28)] is readily identified as the asymptotic expansion for $E(X)$ after successive differentiation, substitution in Equation (28), and algebraic rearrangement. This result may be written in two different forms, depending on whether $c/\sqrt{k} \equiv Q$ is less than, or greater than one-half.

$Q < 0.5$:

$$F_e(t) = \frac{3c}{4} \left(\frac{1+4Q^2}{1-4Q^2} \right) E \left[\left(\frac{1-4Q^2}{4Q} \right) \sqrt{t} \right] \quad (30)$$

$Q > 0.5$:

$$F_e(t) = \frac{3c}{4} \left(\frac{4Q^2+1}{4Q^2-1} \right) E \left[\left(\frac{4Q^2-1}{4Q} \right) \sqrt{t} \right] \quad (31)$$

Therefore, $F_4(t)$ may be written

$$F_4(t) = -d[B(t) + d^1 B^{(1)}(t) + d^2 B^{(2)}(t) + \dots + d^n B^{(n)}(t) + \dots] + F_e(t) \quad (32)$$

where

$$B(t) = \frac{3ck}{8} \exp(-kt/2) [I_0(kt/2) + I_1(kt/2)] \quad (33)$$

The contribution of the $B(t)$ term to the series solution for $F_4(t)$ is evaluated after successively differentiating Equation (33) and expressing the resulting derivatives in terms of $I_0^{(n)}$ with appropriate coefficients obtained by routine algebraic manipulations. Substitution of these results in Equation (32) and algebraic rearrangement yields

$$F_4(t) = \frac{-6cQ^2 \exp(-kt/2)}{(1+16Q^4)} \left[I_0(kt/2) + \frac{(1+4Q^2)^2}{8Q^2} \sum_{n=1}^{\infty} \left[\frac{8Q^2}{1+16Q^4} \right]^n I_0^{(n)}(kt/2) \right] + F_e(t) \quad (34)$$

The inverse of $f_2(s)$ is evaluated by using Equation (25) or

$$F_2(t) = - \frac{F_4^{(1)}(t)}{3c^2} - \frac{\delta(t)}{3c^2} F_4(+0) \quad (35)$$

Differentiation of Equation (34) and substitution in Equation (35) yields

$$F_2(t) = - \frac{c \exp(-kt/2)}{8Q^2(1+16Q^4)} \left[(1+16Q^4) I_0^{(1)}(kt/2) + 8Q^2 I_0(kt/2) \right. \\ \left. - \frac{(1-16Q^4)^2}{8Q^2} \sum_{n=1}^{\infty} \left[\frac{8Q^2}{1+16Q^4} \right]^n I_0^{(n)}(kt/2) \right] - \frac{F_e^{(1)}(t)}{3c^2} - \frac{\delta(t)}{4c} \quad (36)$$

where

$$F_e^{(1)}(t) = \frac{3ck(1+4Q^2)}{16Q} \left[\left(\frac{1-4Q^2}{4Q} \right) E \left[\left(\frac{1-4Q^2}{4Q} \right) \sqrt{kt} \right] - \frac{1}{\sqrt{\pi kt}} \right] \quad (37)$$

for $Q < 0.5$ or

$$F_e^{(1)}(t) = \frac{3ck(1+4Q^2)}{16Q} \left[\left(\frac{4Q^2-1}{4Q} \right) E \left[\left(\frac{4Q^2-1}{4Q} \right) \sqrt{kt} \right] - \frac{1}{\sqrt{\pi kt}} \right] \quad (38)$$

for $Q > 0.5$. The inverse of f_3 is evaluated by using the relationship between f_3 and f_4

$$f_3(s) = \frac{-(4c^2+k)}{6c^2} f_4(s) + \frac{1}{2\sqrt{s}} \quad (39)$$

$$F_3(t) = \frac{c(1+4Q^2)}{1+16Q^4} \exp(-kt/2) \left[I_0(kt/2) + \frac{(1+4Q^2)^2}{8Q^2} \sum_{n=1}^{\infty} \left[\frac{8Q^2}{1+16Q^4} \right]^n I_0^{(n)}(kt/2) \right] - \left[\frac{4Q^2+1}{6Q^2} \right] F_e(t) + \frac{1}{2\sqrt{\pi t}} \quad (40)$$

The sum of F_2 , F_3 , and F_4 may be written

$$F_2(t) + F_3(t) + F_4(t) = - \frac{cQ^2 e^{-T/2}}{8(1+16Q^4)} \left[\frac{(1+16Q^4)}{Q^4} I_0^{(1)}(T/2) + 16 I_0(T/2) - \frac{(1+4Q^2)^2}{8Q^6} \sum_{n=1}^{\infty} \left[\frac{8Q^2}{1+16Q^4} \right]^n I_0^{(n)}(T/2) \right] - \frac{F_e(t)}{48Q^4} + \frac{c(1+12Q^2)}{16Q\sqrt{\pi T}} - \frac{\delta(t)}{4c} \quad (41)$$

Upon substitution of Equations (24) and (41) into Equation (20) and division of the result by the expression for the diffusion current at a stationary spherical electrode [Equation (10)], we obtain for the current ratio

$$\frac{i_k}{i_D} = 2 \left[1 + Q\sqrt{\pi T} + \frac{Q^2 \sqrt{\pi T}}{4Q^2-1} \left[\operatorname{erf}(\sqrt{T}) - 2Q + \frac{(16Q^4-1)e^{-T}}{16Q^4} + \frac{(1+4Q^2)e^{-T}}{64Q^5} \right] E \left[\frac{[1+4Q^2]\sqrt{T}}{4Q} \right] + \frac{Q^3 e^{-T/2} \sqrt{\pi T}}{8(1+16Q^4)} \left[\frac{(1+16Q^4)}{Q^4} I_0^{(1)}(T/2) + 16 I_0(T/2) - \frac{(1+4Q^2)^2}{8Q^6} \sum_{n=1}^{\infty} \left[\frac{8Q^2}{1+16Q^4} \right]^n I_0^{(n)}(T/2) \right] + \frac{\sqrt{\pi T}}{48Q^3 c} F_e(t) \right]$$

$$- \frac{(1+12Q^2)}{16Q^2} \left] (1+Q\sqrt{\pi T})^{-1} \right.$$

where $F_e(t)$ is given by Equation (30) for $Q < 0.5$ or Equation (31) for $Q > 0.5$.

In these equations, $I_P^{(n)}(X)$ denotes the n th derivative of the modified Bessel function of order P and Equation (2) defines $E(X)$. Computation procedures for calculating electrode response curves for discrete values of Q from Equations (11) and (42) have already been discussed⁽¹⁾. Electrode response curves of i_k/i_D versus generalized time T for representative values of the effective electrode sphericity Q are presented elsewhere⁽¹⁾. Results predicted by Equations (11) and (42) were employed to evaluate the numerical method and computation procedures which were used in treating the fractional regeneration and preceding reaction mechanisms⁽¹⁾.

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NOTATION DEFINITIONS

A	Electrode area.
c	Spherical geometry constant, $D^{1/2}/r_o$.
C_o^*	Initial concentration of species <u>O</u> .
D	Diffusion coefficient of species <u>O</u> and <u>R</u> .
$\delta(t)$	Dirac delta function.
e	Electron.
$E(X)$	Exponential error function complement. $E(X) = \exp(X^2)\text{erfc}(X)$.
$\text{erf}(X)$	Error function.
$\text{erfc}(X)$	Error function complement. $\text{erfc}(X) = 1 - \text{erf}(X)$.
F	Value of the Faraday.
$F_n^{(1)}(t)$	First derivative of a given function with respect to time.
$f_n(s)$	Laplace transform of $F_n(t)$.
$F_e(t)$	Time-dependent terms defined by Equations (30) and (31).
$i(t)$	Electrode current.
i_k	Electrode current in the presence of kinetic complication.
i_D	Electrode current at a stationary spherical electrode controlled completely by diffusion.
$I_P^{(n)}$	<u>n</u> th derivative of the modified Bessel function of order P.
k	Homogeneous rate constant for the first-order, one-half regeneration reaction in Mechanism I.
n	Number of electrons transferred in the heterogeneous charge-transfer step.
O	Oxidized form of the electroactive redox couple.
Q	A constant which reflects the effective electrode sphericity for the one-half regeneration mechanism. $Q = \frac{1}{r_o} \left(\frac{D}{k} \right)^{1/2}$.

r_0 Spherical electrode radius in centimeters.
R Reduced form of the electroactive redox couple.
s Laplace Transform variable.
t Time in seconds.
T Dimensionless time parameter for the one-half regeneration mechanism. $T = kt$.
u Variable of integration.