Syracuse University

SURFACE

Chemistry - Faculty Scholarship   College of Arts and Sciences

2-10-1983

General Correction for Electrode Sphericity in Voltammetry of Nernstian Systems

Jerry Goodisman
Syracuse University

Follow this and additional works at: https://surface.syr.edu/che

Part of the Chemistry Commons

General Correction for Electrode Sphericity in Voltammetry of Nernstian Systems

Jerry Goodisman, Syracuse University

Abstract

The current is considered at a stationary reversible spherical electrode whose potential $E(t)$ as a function of time is given, such that $E(t)$ determines the ratio of oxidized to reduced species at the electrode surface. Writing the current as that for planar geometry, I_0, plus corrections for sphericity, we derive formulae for the corrections. The first two are expressed as integrals over I_0, with no explicit dependence on the potential, for any form of $E(t)$, and whether the reduced species diffuses into the electrode or into the solution. If the ratio of diffusion constants for oxidized and reduced species is taken as unity, and if oxidized and reduced species are both in the solution, the corrections become extremely simple (no integrations or differentiations), regardless of the form of $E(t)$. The first correction is evaluated in several cases where this does not obtain.

Introduction

To compute the current at a reversible stationary spherical microelectrode with changing potential $E(t)$, one must solve the diffusion equation for oxidized and reduced species in the solution, coupled by the Nernst equilibrium conditions on the concentrations at the electrode surface. The equations for linear diffusion (planar symmetry), being simpler than those for other geometries, an often used strategy [1-5] is to solve the linear diffusion problem and then generate corrections to the current for deviations of the electrode from planarity. However, some authors [2,6] have solved the problem for spherical diffusion directly in certain cases, and the diffusion problems themselves have been studied in detail [4,7,8].

We present here a general procedure for obtaining the leading corrections to the planar result for any variation of electrode potential E with time, for any ratio of diffusion coefficients of oxidized and reduced species, and for diffusion of reduced species into the electrode or into the solution. In all cases, the corrections are expressed as integrals over the current corresponding to planar symmetry (eqns. 24 and 29). If oxidized and reduced species have equal diffusion coefficients, the integrals can be evaluated explicitly (eqn. 30). A numerical evaluation is necessary otherwise, and this is done for one case, to check results of other authors.

The basic idea is a perturbative approach with the perturbation parameter being **[End of page 33]** $1/r_0$, where r_0 is the radius of the spherical microelectrode. The planar electrode corresponds to infinitely large r_0. After reviewing the background and the equation to be solved in section (I), we introduce the perturbation procedure in section (II). Several special cases and illustrative applications are discussed in section (Ill).

(I) Theory

We consider first a reduction of species O to species R, both present in solution. (Amalgam formation, with R diffusing into the electrode, is considered later.) The diffusion equation [1,7,8] for the oxidized species is

$$\frac{\partial c_O}{\partial t} = D_O\left[\left(\frac{\partial^2 c_O}{\partial r^2}\right) + \frac{2}{r}\left(\frac{\partial c_O}{\partial r}\right)\right] \tag{1}$$

where $c_o = c_o(r, t)$ is the concentration of this species and D_O its diffusion coefficient. The boundary conditions are

$$c_O(r, t=0) = c_O^*, \qquad r \geq r_0 \tag{2}$$

$$c_O(\infty, t) = c_O^*, \qquad t \geq 0 \tag{3}$$

where c_O^* is the bulk concentration. The manipulations which follow, through eqn. (14), are fairly standard. The corresponding treatment for the amalgamation case, eqns. (15)-(19), occupies the remainder of this Section, the new work beginning in section (II).

Equation (1) may be subjected to Laplace transformation in time and the resulting equation solved to give

$$s\bar{c}_O - c_O^* = ar^{-1} \exp\left[-r(s/D_O)^{1/2}\right] \tag{4}$$

where $\bar{c}_O = \bar{c}_O(r, s)$ is the transform of c_O and a is a constant. In order to introduce the current, which is [9]

$$I = nFAD_O(\partial c_O/\partial r)_{r=r_0} = -nFAD_R(\partial c_R/\partial r)_{r=r_0} \tag{5}$$

where F is the Faraday constant and A the electrode area, we differentiate eqn. (4) to obtain

$$\bar{c}_O - c_O^*/s = -\frac{r}{1 + r(s/D_O)^{1/2}} \frac{\partial \bar{c}_O}{\partial r} \tag{6}$$

and then invert the Laplace transform. Using the inversion formula

$$L^{-1}\left(\frac{r}{1 + r(s/D_O)^{1/2}}\right) = \left(\frac{D_O}{\pi t}\right)^{1/2} - \frac{D_O}{r} \exp(D_O t/r^2)\, \mathrm{erfc}(D_O t/r^2)^{1/2}$$

we find **[End of 34]**

$$c_O(r_0, t) - c_O^* = -\int_0^t d\tau \left(\frac{\partial c_O(r, t)}{\partial r}\right)_{r=r_0} \left[\left(\frac{D_O}{\pi(t-\tau)}\right)^{1/2} - \frac{D_O}{r_0} \exp\left[D_O(t-\tau)/r_0^2\right]\right.$$

$$\left. \times \mathrm{erfc}\left(\frac{D_O^{1/2}(t-\tau)^{1/2}}{r_0}\right)\right] \tag{7}$$

Similarly,

$$c_R(r_0, t) - c_R^* = -\int_0^t d\tau \left(\frac{\partial c_R(r, \tau)}{\partial r}\right)_{r=r_0} \left[\left(\frac{D_R}{\pi(t-\tau)}\right)^{1/2} - \frac{D_R}{r_0} \exp\left[D_R(t-\tau)/r_0^2\right]\right.$$

$$\left. \times \mathrm{erfc}\left(\frac{D_R^{1/2}(t-\tau)^{1/2}}{r_0}\right)\right] \tag{8}$$

for the reduced species.

The Nernst condition relates the concentrations of oxidized and reduced species on the electrode surface at each instant of time, if the system is reversible:

$$\frac{c_O(r_0, t)}{c_R(r_0, t)} = \exp\{nF[E(t) - E_0]/RT\} = f(t) \tag{9}$$

where E_0 is the formal potential and $E(t)$ the electrode potential at any time. On substituting $c_O(r_0, t)$ and $C_R(r_0, t)$ from eqns. (7) and (8), and the gradients of these quantities in terms of the current from eqn. (5), we obtain

$$nFA[c_O^* - c_R^* f(t)]$$

$$= \int_0^t d\tau I(\tau)\left[\frac{1}{[\pi D_R(t-\tau)]^{1/2}} - \frac{\exp\left[D_R(t-\tau)/r_0^2\right]}{r_0}\, \mathrm{erfc}\left(\frac{D_R^{1/2}(t-\tau)^{1/2}}{r_0}\right)\right] f(t)$$

$$+ \int_0^t d\tau I(\tau)\left[\frac{1}{[\pi D_O(t-\tau)]^{1/2}} - \frac{\exp\left[D_O(t-\tau)/r_0^2\right]}{r_0}\, \mathrm{erfc}\left(\frac{D_O^{1/2}(t-\tau)^{1/2}}{r_0}\right)\right] \tag{10}$$

For r_0 infinite, terms in erfc disappear and eqn. (10) becomes the planar diffusion equation which may be written [10] in the Abel form

$$\int_0^t d\tau (t-\tau)^{-1/2} I_0(\tau) = Q(t) \tag{11}$$

with

$$Q(t) = nFA(\pi D_O)^{1/2} \frac{c_O^* - c_R^* f(t)}{1 + \gamma f(t)} \tag{12}$$

where $\gamma^2 = D_O/D_R$. Here, the subscript on I_0 identifies it as the current for planar diffusion ($1/r_0 \to 0$). The general solution [11] to eqn. (11) is **[End of page 35]**

$$I_0(t) = \frac{Q(0)}{\pi\sqrt{t}} + \frac{1}{\pi} \int_0^t d\tau \frac{Q'(\tau)}{(t-\tau)^{1/2}} \tag{13}$$

For instance, the current for the linear sweep potential $E = E_i - \upsilon t$ is

$$I_0(t) = nFA\left(\frac{D_O}{\pi t}\right)^{1/2}\left[\frac{c_O^* - c_R^* B}{1 + \gamma B} + \frac{nF\upsilon}{RT}\int_0^t d\tau \left(\frac{t}{t-\tau}\right)^{1/2} \frac{(c_R^* + c_{OY}^*)B\, e^{-nF\upsilon\tau/RT}}{\left(1 + \gamma B\, e^{-nF\upsilon\tau/RT}\right)^2}\right] \tag{14}$$

where In $B = nF(E_i - E_0)/RT$, as shown by other authors [1,9].

We now consider the case of diffusion of the reduced species into the electrode.

The condition on $c_R(\infty, t)$, analogous to eqn. (3), is no longer relevant, and is replaced by a condition at the origin

$$c_R(0, t) = \text{finite}, \qquad t \geqslant 0 \tag{15}$$

The Laplace transformation of the equations and boundary conditions proceeds as before. The difference is that a solution such as eqn. (4) is not acceptable for $\bar{c}_R$, the Laplace transform in time of c_R. The proper solution, satisfying eqn. (15), is

$$s\bar{c}_R - c_R^* = 2\alpha_R r^{-1} \sinh\left[-r(s/D_R)^{1/2}\right] \tag{16}$$

where α_R is a constant.

We differentiate as previously to introduce the current, now equal to $nFAD_R(\partial c_R/\partial r)_{r=r_0}$. Replacing eqn. (8) we find

$$c_R(r_0, t) - c_R^* = -\int_0^t d\tau \left(\frac{\partial c_R(r,\tau)}{\partial r}\right)_{r=r_0} L(r_0, t-\tau) \tag{17}$$

where $L(r, t)$ is the inverse Laplace transform of

$$\frac{r}{1 - r\sqrt{\dfrac{s}{D_R}}\coth\left(r\sqrt{\dfrac{s}{D_R}}\right)} \sim r\left[-\frac{1}{r\sqrt{\dfrac{s}{D_R}}} - \frac{1}{\left(r\sqrt{\dfrac{s}{D_R}}\right)^2} - \frac{1}{\left(r\sqrt{\dfrac{s}{D_R}}\right)^3}\cdots\right]$$

The expansion on the right, although it may be obtained by successive differentiation of the function on the left with respect to $x = r^{-1}s^{-1/2}D_R^{1/2}$ and evaluation of derivatives at $x = 0$, is not a true power series expansion. In fact, it corresponds to replacing the hyperbolic cotangent by unity, which is valid for a large argument. It has been noted previously [12] that there are two kinds of spherical corrections in the case of diffusion into the electrode: the correction for the shape of the electrode and the correction for its finite size. For most applications [12,13], the latter us much less important. The replacement of the cotangent by unity corresponds to neglecting this correction.

The inverse Laplace transform of the series is readily performed and leads to **[End of page 36]**

$$c_R(r_0, t) - c_R^* = \int_0^t d\tau \left(\frac{\partial c_R(r,\tau)}{\partial r}\right)_{r=r_0}\left[\left(\frac{D_R}{\pi(t-\tau)}\right)^{1/2} + \frac{D_R}{r_0}\right.$$
$$\left. + \frac{2D_R^{3/2}(t-\tau)^{1/2}}{r_0^2 \pi^{1/2}}\cdots\right] \tag{18}$$

A similar equation for the oxidized species would be obtained if the power series for $[1 + r(s/D_O)^{1/2}]^{-1}$ (see eqn. 6) were introduced before inverting the Laplace transformation, or if the series for $e^{x^2} \text{erfc}(x)$ (see below) were inserted into eqn. (7). It differs from eqn. (18) in the sign of D_R/r_0 and other odd-power terms. The Nernst condition (eqn. 9) may now be used to combine the equations for oxidized and reduced species.

The resulting equation is

$$nFA[c_O^* - c_R^* f(t)] = \int_0^t d\tau I(\tau)\{\pi^{-1/2}(t-\tau)^{-1/2}[D_O^{-1/2} + f(t)D_R^{-1/2}]$$
$$+ [f(t)-1]r_0^{-1} + 2\pi^{-1/2}(t-\tau)^{1/2}[D_O^{1/2} + f(t)D_R^{1/2}]r_0^{-2}...\}$$

(19)

This becomes the equation for planar diffusion if $r_0 \to \infty$. The corresponding equation when diffusion of reduced species is into the solution may be obtained from eqn. (10) by the use of the series

$$e^{x^2}\,\text{erfc}\,x \approx 1 - 2x/\sqrt{\pi} + 2x^2/\sqrt{\pi} ...$$

We now turn to the calculation of corrections to the planar current (for infinite r_0). Calculation of the planar current is supposed to have been accomplished according to eqn. (13).

(II) The Perturbation Expansion

In seeking a solution for non-infinite values of r_o, we note that the reciprocal of r_o is a natural parameter for a perturbation expansion of the current. We write

$$I(t) = I_0(t) + \frac{I_1(t)}{r_0} + \frac{I_2(t)}{r_0^2} + ...$$

(20)

and substitute into eqns. (10) or (19). The results, on grouping together terms in each power of $1/r_o$, is

$$0 = -nFA[c_O^* - c_R^* f(t)] + \int_0^t d\tau I_0(\tau)\{f(t)[\pi D_R(t-\tau)]^{-1/2} + [\pi D_O(t-\tau)]^{-1/2}\}$$
$$+ \frac{1}{r_0}\int_0^t d\tau I_1(\tau)\{f(t)[\pi D_R(t-\tau)]^{-1/2}$$
$$+ [\pi D_O(t-\tau)]^{-1/2}\} - \frac{1}{r_0}\int_0^t d\tau I_0(\tau)[\pm f(t) + 1]$$

(21)

[End of page 37]

and terms in $1/r_0^2$ and higher powers. The positive sign results from eqn. (10) (diffusion into the solution) and the negative sign from eqn. (19) (diffusion into the electrode). For the expansion (eqn. 20) to hold for all r_o, terms in each power of $1/r_o$ in eqn. (21) must vanish separately. The zeroth power terms vanish, since I_o is supposed to solve the planar diffusion problem, eqns. (11) and (12).

We now turn to the terms in $1/r_o$, which give the first spherical correction I_1. Setting the coefficient of $1/r_o$ in eqn. (21) equal to zero, we have

$$\left(\frac{f(t)}{(\pi D_R)^{1/2}} + \frac{1}{(\pi D_O)^{1/2}}\right)\int_0^t dw \frac{I_1(w)}{(t-w)^{1/2}} = (\pm f(t) + 1)\int_0^t ds I_0(s)$$

(22)

Since $I_0(s)$ is known, this may be rearranged into an equation of the Abel form, like eqn. (11), except that the unknown function is $I_1(t)$ and Q is replaced by

$$P(t) = [\pm f(t) + 1][\gamma f(t) + 1]^{-1}(\pi D_O)^{1/2}\int_0^t ds I_0(s)$$

(23)

Note that $P(0) = 0$; thus the solution according to the formula (13) is

$$I_1(t) = \left(\frac{D_O}{\pi}\right)^{1/2}\int_0^t d\tau(t-\tau)^{-1/2}\frac{d}{d\tau}\left[F(\tau)\int_0^\tau ds I_0(s)\right]$$

(24)

where I_0 is given by eqn. (13) and

$$F(t) = [\pm f(t) + 1][\gamma f(t) + 1]^{-1}$$

The first correction for sphericity is thus calculable, regardless of the form of $E(t)$, in terms of the current for a planar electrode I_0. If I_0 is known either analytically or numerically for the problem of interest, I_1 and hence the current corrected for the sphericity of the electrode may be obtained by a single integration.

Some simplification is possible; after introduction of eqn. (13), the integration over s may be performed, giving

$$I_1(t) - \left(\frac{D_O}{\pi^3}\right)^{1/2} \int_0^t d\tau (t-\tau)^{-1/2} \frac{d}{d\tau}\left[F(\tau)\int_0^\tau du\, Q(u)(\tau-u)^{-1/2}\right] \tag{25}$$

$$= \frac{nFAD_O}{\pi} \int_0^t d\tau (t-\tau)^{-1/2} \frac{d}{d\tau}\left[\frac{1\pm f(\tau)}{1+\gamma f(\tau)} \int_0^\tau du\, \frac{c_O^* - c_R^* f(u)}{1+\gamma f(u)}(\tau-u)^{-1/2}\right]$$

where the upper sign is for diffusion of the reduced species into the solution and the lower sign for diffusion into the electrode (amalgamation).

For example, consider a voltage pulse: $E = E_1$ for $t < t_o$ and $E = E_1 + \Delta E$ for $t > t_0$. This has been treated by Birke [5]. First we assume equilibrium at $t = 0$, so that

$$c_O^*/c_R^* = \exp\left[nF(E_1 - E_0)/RT\right] \equiv c_1 \tag{26}$$

and abbreviate $\exp[nF(\Delta E)/RT]$ by d_1. The first spherical correction would be

$$\frac{I_1}{r_0} - \frac{nFAD_O}{\pi r_0} \int_0^t d\tau (t-\tau)^{-1/2} \frac{d}{d\tau}\left[\frac{1\pm f(\tau)}{1+\gamma f(\tau)} S(\tau-t_0)\int_{t_0}^\tau du\, \frac{c_O^* - c_O^* d_1}{1+\gamma c_1 d_1}(\tau-u)^{-1/2}\right]$$

[End of page 38]

where $S(\chi) = 0$ for $\chi < 0$ and 1 for $\chi > 0$. This simplifies to

$$\frac{2nFAD_O c_O^*(1-d_1)(1\pm c_1 d_1)}{\pi(1+\gamma c_1 d_1)^2 r_0} \int_0^t d\tau (t-\tau)^{-1/2}$$

$$\left[\delta(\tau-t_0)(\tau-t_0)^{1/2} + \frac{S(\tau-t_0)(\tau-t_0)^{-1/2}}{2}\right]$$

$$= \frac{nFAD_O c_O^*(1-d_1)(1\pm c_1 d_1)}{(1+\gamma c_1 d_1)^2 r_0}$$

Without assuming equilibrium at $t = 0$, we may consider the current for $c_R^* = 0$. The current I_0 is easily found from eqn. (13), and then the first equality of eqn. (25) gives

$$I_1(t) = \frac{D_O nFAc_O^*}{\pi} \int_0^t d\tau (t-\tau)^{-1/2} \frac{d}{d\tau}\left[\frac{1\pm f(\tau)}{1+\gamma f(\tau)} \int_0^\tau du\, \frac{(1+\gamma f)^{-1}}{(\tau-u)^{1/2}}\right]$$

where $f = c_1$ for $t < t_0$ and $f = c_1 d_1$ for $t > t_0$. (Of course, C_O^*/C_R^* is no longer equal to c_1.) Straightforward manipulations then lead to the result

$$I_1(t) = D_O nFAc_O^*(1\pm c_1)(1+\gamma c_1)^{-2}, \qquad t < t_0$$

$$= D_O nFAc_O^*\left[(1\pm c_1 d_1)(1+\gamma c_1 d_1)^{-2}\right.$$

$$\left. + c_1(1 - (2/\pi)\tan^{-1}K - 2/\pi K)(d_1 - 1)(\gamma \mp 1)(1+\gamma c_1)^{-2}(1+\gamma c_1 d_1)^{-1}\right],$$

$$t \geq t_0 \tag{27a}$$

where $K^2 = (t - t_0)/t_0$. This becomes identical to the previous result, which assumes $C_O^*/C_R^* = c_1$, when one allows c_1, but not $c_1 d_1$, to become infinitely large.

The second-order correction is obtained by setting terms in $1/r_0^2$ in eqn. (10) equal to zero. The equation determining I_2 is

$$\left[f(t)D_R^{-1/2} + D_O^{-1/2}\right]\int_0^t d\tau I_2(\tau)(t-\tau)^{-1/2} = \sqrt{\pi}\left[\pm f(t) + 1\right]\int_0^t d\tau I_1(\tau)$$

$$-2\left[f(t)D_R^{1/2} + D_O^{1/2}\right]\int_0^t d\tau I_0(\tau)(t-\tau)^{1/2} \tag{28}$$

Inserting eqn. (24) for I_1, into the first term on the right-hand side of eqn. (28) and interchanging the order of integrations, we have

$$\sqrt{\pi}\int_0^t d\tau I_1(\tau) = 2D_O^{1/2}\int_0^t du(t-u)^{1/2}\frac{d}{du}\left[F(u)\int_0^u ds I_0(s)\right]$$
$$= D_O^{1/2}\int_0^t du(t-u)^{-1/2}F(u)\int_0^u ds I_0(s)$$

after an integration by parts. The right-hand side of eqn. (28) may then be written as an integral over I_0, i.e.**[End of page 39]**

$$[\pm f(t)+1]D_O^{1/2}\int_0^t ds I_0(s)\int_s^t du F(u)(t-u)^{-1/2}$$
$$-2D_O^{1/2}[1+f(t)/\gamma]\int_0^t d\tau I_0(\tau)(t-\tau)^{1/2}$$
$$= D_O^{1/2}\int_0^t ds I_0(s)\left\{[1\pm f(t)]\int_s^t du F(u)(t-u)^{-1/2}-2[1+f(t)/\gamma](t-s)^{1/2}\right\}$$

$$(29)$$

Equation (28) then becomes an Abel-type integral equation [11] for the second-order correction $I_2(t)$. It may be treated as we did the equation for the first-order correction $I_1(t)$, by comparing with eqns. (11) and (13). Then I_2 may be calculated, if the sizes of I_0 and I_1 indicate it is warranted, as an integral over the zero-order (planar symmetry) current I_0.

(III) Applications

The general problem of calculating spherical corrections to the current for a planar electrode has now been solved. For any particular application, one would have to evaluate an integral, according to eqn. (25), as we illustrate below. There is also one situation for which an extreme simplification occurs.

If we assume with Reinmuth and others [1,6,14] that γ, may be taken as unity for the calculation of the correction when diffusion is into the solution, so $F(t)=1$, the corrections take on an exceedingly simple form. Inserting I_0 from eqn. (13) into eqn. (24),

$$I_1(t) = (D_O/\pi^3)^{1/2}\int_0^t d\tau(t-\tau)^{-1/2}\left[Q(0)\tau^{-1/2}+\int_0^\tau ds Q'(s)(\tau-s)^{-1/2}\right]$$
$$= (D_O/\pi^3)^{1/2}\left[Q(0)\pi+\int_0^t ds Q'(s)\int_s^t d\tau(t-\tau)^{-1/2}(\tau-s)^{-1/2}\right]$$
$$= (D_O/\pi)^{1/2}\left[Q(0)+\int_0^t ds Q'(s)\right] = (D_O/\pi)^{1/2}Q(t)$$

All the integrals have thus been performed, and the correction for sphericity in this case is, on inserting Q according to eqn. (12),

$$\frac{I_1(t)}{r_0} = \left(\frac{nFAD_O}{r_0}\right)\left(\frac{c_O^* - c_R^*\exp(nF[E(t)-E_0]/RT)}{1+\exp(nF[E(t)-E_0]/RT)}\right)$$

$$(30)$$

This is an explicit expression for the correction to the time-dependent current, valid regardless of the dependence of E on t.

The second-order correction simplifies even more drastically. Using eqn. (29) for the right-hand member of eqn. (28), one has

$$[f(t)+1]\int_0^t d\tau I_2(\tau)(t-\tau)^{1/2}$$
$$= -D_O\int_0^t ds I_0(s)\left\{[1+f(t)]\int_s^t du(t-u)^{-1/2}-2[1+f(t)](t-s)^{1/2}\right\} = 0$$

[End of page 40]

The second correction I_2/r_0 vanishes identically, regardless of $f(t)$. Reinmuth [1] has in fact shown that, in this case, the current is exactly equal to $I_0 + I_1/r_0$, where I_1 is given by eqn. (23). Obviously, $\gamma = 1$ leads to no simplification in the amalgamation case, since it does not make F equal to unity.

For a voltage pulse, considered by Birke [5], suppose E is equal to E_1 for $t < \tau$ and equal to $E_1 + \Delta E$ for $t > \tau$. With the previously introduced abbreviations, the spherical correction according to eqn. (30) would be

$$\frac{nFAD_0 c_0^*}{r_0}\left(\frac{1 - c_1 d_1 c_R^*/c_0^*}{1 + c_1 d_1}\right) = \frac{nFAD_0 c_0^*}{r_0}\frac{1 - d_1}{1 + c_1 d_1}$$

This checks the general result of eqn. (27) when γ is taken equal to 1, with the upper sign. If the equilibrium condition (26) does not hold, but $c_R^* = 0$, eqn. (30) makes I_1 equal to $nFAD_0 c_0^*(1 + c_1)$ for $t < t_0$ and $nFAD_0 c_0^*(1 + c_1 d_1)$ for $t > t_0$. The same results follow from eqn. (27a) on inserting $\gamma = 1$ and choosing the upper sign.

It is possible to calculate exactly the second-order spherical correction in this case, according to eqns. (28) and (29). After some algebra and integration we find

$$(D_0 D_R)^{-1/2}\int_0^t d\tau I_2(\tau)(t-\tau)^{-1/2} = nFAc_0^*(\pi D_0)^{1/2} R(t)$$

where

$$R(t) = -f_0(1 \mp \gamma)^2 t/(1 + \gamma f_0)^3, \qquad t < t_0$$

$$= \frac{(\pm\gamma - 1)}{(1 + \gamma f_0)^2(1 + \gamma f_1)^3}\Big\{(2\gamma/\pi)(f_1 - f_0)(f_1 \pm 1)(1 + \gamma f_1)$$

$$\times\left[t\sin^{-1}(t_0/t)^{1/2} - (t_0 t - t_0^2)^{1/2}\right]$$

$$+ (1 + \gamma f_0)f_1(1 \mp \gamma)[(1 + \gamma f_0)t - \gamma(f_0 - f_1)t_0]\Big\}, \qquad t > t_0$$

Then

$$I_2 = \frac{1}{\pi}\int_0^t d\tau R'(\tau)(t-\tau)^{-1/2}$$

and all the integrations may be carried out in closed form to yield, for $t > t_0$,

$$\frac{I_2(1 + \gamma f_0)^2 \pi^{1/2}}{nFAc_0^* D_0 D_R^{1/2}} = -2t^{1/2}f_0\frac{(1 \mp \gamma)^2}{1 + \gamma f_0} + 2(t - t_0)^{1/2}(1 \mp \gamma)^2\left(\frac{f_0}{1 + \gamma f_0} - \frac{f_1(1 + \gamma f_0)^2}{(1 + \gamma f_1)^3}\right)$$

$$+ 2(\pm\gamma - 1)\frac{(f_1 - f_0)\gamma(f_1 \pm 1)}{(1 + \gamma f_1)^2}\left[(t - t_0)^{1/2} - t^{1/2}\right]$$

$$+ \frac{t_0}{(t - t_0)^{1/2}}\left[(\pm\gamma - 1)\frac{f_1 \mp \gamma f_0}{1 + \gamma f_1} + f_0\frac{(1 \mp \gamma)^2}{1 + \gamma f_0}\right] \qquad (31)$$

Of course, only the first term remains for $f_1 = f_0$, and the entire correction vanishes **[End of page 41]** for $\gamma = 1$ with the upper sign (outward diffusion).

The spherical corrections for a potential scan or ramp, $E = E_1 -- \upsilon t$, and for a triangular wave, have been given in a semi-empirical form by Beyerlein and Nicholson [13] for the case of amalgamation. For the potential scan,

$$f(t) = \theta\exp^{-at}$$

where In $\Theta = nF(E_i - E_0)/RT$ and $a = nF\upsilon/RT$. Then eqn. (25) is (with no initial concentration of R)

$$\frac{I_1}{r_0} = \frac{nFAD_0 c_0^*}{\pi r_0}\int_0^t d\tau\frac{d}{d\tau}\left[\frac{1 - \theta e^{-a\tau}}{1 + \gamma\theta e^{-a\tau}}\int_0^\tau du\frac{(\tau - u)^{-1/2}}{1 + \gamma\theta e^{-au}}\right](t - \tau)^{-1/2}$$

$$= \frac{nFAD_0 c_0^*}{\pi r_0}\int_0^S dT(S - T)^{-1/2}\frac{d}{dT}\left[\frac{1 - \theta e^{-T}}{1 + \gamma\theta e^{-T}}\int_0^T dU\frac{(T - U)^{-1/2}}{1 + \gamma\theta e^{-U}}\right] \qquad (32)$$

where $S = at$. For comparison with the results of ref. 13, we put $\gamma = 1$ and assume the first correction suffices ($\phi < 1$ in the notation of ref. 13). Then ß, tabulated in ref. 13, should be given by

$$\beta = \frac{1}{\pi}\int_0^S dT(S - T)^{-1/2}\frac{d}{dT}\left[\frac{1 - \theta e^{-T}}{1 + \theta e^{-T}}\int_0^T dU\frac{(T - U)^{-1/2}}{1 + \theta e^{-U}}\right]\cdots \qquad (33)$$

For large S, the terms Θe^{-T} and Θe^{-U} may be dropped (because the factor $(S -- T)^{-1/2}$ weights values of S near T heavily), and ß may be directly evaluated to give unity. Otherwise, the singular factor $(T-- U)^{-1/2}$ may be dealt with by the substitution $U = T\sin^2\phi$ so that

TABLE 1

Values for β from ref. 14 and eqn. (33)

ΔE/mV	β (ref. 14)	β (eqn. 33)
120	−0.018	−0.009
100	−0.024	−0.019
80	−0.036	−0.037
60	−0.065	−0.067
40	−0.090	−0.093
20	−0.041	−0.044
0	0.174	0.164
−20	0.520	0.514
−40	0.845	0.837
−60	1.019	1.024
−80	1.098	1.095
−100	1.107	1.107
−120	1.097	1.096

[End of page 42]

$$\frac{d}{dT}\int_0^T dU \frac{(T-U)^{-1/2}}{1+\theta\,e^{-U}}$$

$$=\int_0^{\pi/2}\sin\phi\,d\phi\,\frac{T^{-1/2}\left(1+\theta\,e^{-T\sin^2\phi}\right)+2T^{1/2}\left(\sin^2\phi\right)\theta\,e^{-T\sin^2\phi}}{\left[1+\theta\exp\left(-T\sin^2\phi\right)\right]^2}$$

and ß evaluated by numerical quadratures. Table 1 shows that the results are quite close to those of Beyerlein and Nicholson [12]. Here, $\Delta E = E -- E_0$ and $nF/RT = 38.92$ V^{-1}. The results are independent of Θ for sufficiently large Θ, as should be the case.

Conclusions

The most important results of the present article are given by eqns. (20) and (25) and in the prescription for obtaining the second-order correction I_2. Equation (25) gives a general expression for the first-order correction I_1 for any variation of the potential (see eqn. 9). It is valid whether the reduced species diffuses into the solution or the amalgam, and for all values of the ratio D_0/D_R. In any particular case, specific approximations may be warranted to simplify eqn. (25).

References
1 W.H. Reinmuth, J. Am. Chem. Soc., 79 (1957) 6358.
2 M.L. Olmstead and R.S. Nicholson, J. Electroanal. Chem., 14 (1967 133.
3 H.E. Keller and W.H. Reinmuth, Anal. Chem., 44 (1972) 434.
4 J. Galvez and A. Serna, J. Electroanal. Chem., 69 (1976) 133.
5 R.L. Birke, Anal. Chem., 50 (1978) 1489.
6 R.P. Frankenthal and I. Shaln, J. Am. Chem. Soc., 78 (1956) 2969.
7 R. Guidelli, J. Electroanal. Chem., 33 (1971) 291.
8 K.B. Oldham, J. Electroanal. Chem., 41 (1973) 251.
9 A. Sev~ik, Collect. Czech. Chem. Commun., 13 (1948) 349.
10 R.S. Nicholson and I. Shain, Anal. Chem., 36 (1964) 706.
11 K. Yoshida, Lectures on Differential and Integral Equations, Interscience, New York, 1960, Sect. 41.
12 F.H. Beyerlein and R.S. Nicholson, Anal. Chem., 44 (1972) 1647.
13 M.M. Nicholson, J. Am. Chem. Soc., 76 (1954) 2539.
14 W.H. Reinmuth, Anal. Chem., 33 (1961) 185.