

Chronopotentiometry with Spherical Electrodes: Consecutive Electrochemical Reactions

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Theoretical transition-time equations for successive electrochemical reactions, using a constant electrolysis current impulse, for spherical diffusion have been derived. Current reversals at and before transition-time are also considered. Equations are expressed in terms of the equations for linear diffusion and a correction factor due to sphericity of the electrode surface.

HANGING drop electrode has been widely used as an indicator electrode for analytical work and diffusion coefficient measurements¹. It has an advantage over a solid electrode in as much as the surface is smooth and can be conveniently renewed. Also, it eliminates the problem arising from the periodic growth and fall of the drop as in a dropping mercury electrode. Chronopotentiometry is an important electroanalytical technique. Its theory has been recently reviewed by Jain *et al.*² In an earlier publication chronopotentiometric transition time constant for the reduction of a single electroactive species on spherical electrodes³ was obtained and expressed in terms of Sand's equation⁴ for linear diffusion and a correction⁵ factor for the sphericity of the electrode surface. In this paper, theoretical equations for consecutive electrochemical reactions, on a spherical electrode have been developed; similar equations for planar⁶ and cylindrical electrodes are available⁷⁻⁹.

THEORETICAL ANALYSIS

For the electrode reaction (i), $O + ne = R$, flux at the electrode surface for constant electrolysis current is given by Eq. 1,

$$\frac{I}{nFA} = D_O \left\{ \frac{\partial C_O(r,t)}{\partial r} \right\}_{r=r_0} \quad \dots(1)$$

Concentrations of species O and R are obtained by solving Fick's equation for spherical diffusion (Eq. 2),

$$\frac{\partial C(r,t)}{\partial t} = D \left\{ \frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right\} \quad \dots(2)$$

Under the following initial and boundary conditions

$$C_O(r, 0) = C_O^0; C_R(r, 0) = 0 \quad \dots(3)$$

$$C_O(\infty, t) = C_O^0; C_R(\infty, t) = 0$$

and

$$D_O \left\{ \frac{\partial C_O(r,t)}{\partial r} \right\}_{r=r_0} + D_R \left\{ \frac{\partial C_R(r,t)}{\partial r} \right\}_{r=r_0} = 0 \quad \dots(4)$$

The resulting solution for $C_O(r, t)$ is,

$$C_O(r,t) = C_O^0 - \frac{I r_0}{n F D_O A r} \left\{ \operatorname{erfc} \left(\frac{r-r_0}{2D_O t} \right) - \exp \left(\frac{r-r_0}{r_0} \right) \exp \left(\frac{D_O t}{r_0^2} \right) \operatorname{erfc} \left(\sqrt{\frac{D_O t}{r_0^2}} - \frac{r-r_0}{2D_O t} \right) \right\}$$

At the electrode surface¹¹ i.e., $r = r_0$, the concentration of O is,

$$C_O(r,t) = C_O^0 - \frac{I r_0}{n F A D_O} \left\{ 1 - \exp \left(\frac{D_O t}{r_0^2} \right) \operatorname{erfc} \left(\sqrt{\frac{D_O t}{r_0^2}} \right) \right\} \quad \dots(5)$$

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Under the limiting condition $D_0^{1/2} t^{1/2}/r_0 \ll 1$, the term within the bracket can be expanded⁵, neglecting higher order terms, as follows,

$$C_0^0 - C_0(r_0, t) = \frac{2I^{1/2}}{nFA D_0^{1/2} \pi^{1/2}} \left\{ 1 - \frac{\pi^{1/2}}{2} \left(\frac{D_0 t}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_0 t}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_0 t}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_0 t}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_0 t}{r_0^2} \right)^{5/2} \right\} \quad \dots(6)$$

At $t = \tau$, $C_0(r_0, t) = 0$, Eq. (6) reduces to,

$$I \tau^{1/2}/C_0^0 = \frac{nFA \pi^{1/2} D_0^{1/2}}{2S_1} \quad \dots(7)$$

Where

$$S_1 = 1 - \frac{\pi^{1/2}}{2} \left(\frac{D_0 \tau}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_0 \tau}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_0 \tau}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_0 \tau}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_0 \tau}{r_0^2} \right)^{5/2}$$

In Stackelberg model¹⁰, a diffusion layer δ for spherical diffusion is given by Eq. 8,

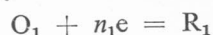
$$\delta = \frac{C_0^0 - C_0(r_0, t)}{[\partial c(r, t) / \partial r]_{r=r_0}} \quad \dots(8)$$

using Eqs (4), (6) and (8), δ for a spherical electrode is given by Eq. (9),

$$\delta = \frac{2D_0^{1/2} t^{1/2}}{\pi^{1/2}} \left\{ 1 - \frac{\pi^{1/2}}{2} \left(\frac{Dt}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{Dt}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{Dt}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{Dt}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{Dt}{r_0^2} \right)^{5/2} \right\} \quad \dots(9)$$

Using expression (9) for diffusion layer δ , transition time equations for consecutive reactions at spherical electrodes can be easily derived.

(a) *Consecutive reactions involving two or more species* — Consider the following electrode process in which the species O_1 and O_2 are reduced to R_1 and R_2 respectively at potentials sufficiently separated to yield two distinct steps in the potential-time curve,



(ii)

Transition-time for the first step (τ_1) is uninfluenced by the presence of O_2 in solution and is still given by Eq. (1). While concentration of O_1 at surface at $t = \tau$ becomes zero, O_1 continues to diffuse towards the electrode so that at $t > \tau_1$, the current through the cell is used in the reduction of both O_1 and O_2 . At $t = t'$ (where $t' = t - \tau_1$), $C_{O_1}(r_0, t') = 0$.

$$\frac{I}{A F} = n_1 D_{O_1} \left\{ \frac{\partial C_{O_1}(r, t)}{\partial r} \right\}_{r=r_0} + n_2 D_{O_2} \left\{ \frac{\partial C_{O_2}(r, t)}{\partial r} \right\}_{r=r_0} \quad \dots(10)$$

Other initial condition (at $t' = 0$) for the reduction of O_2 is,

$$C_{O_2}(r_0, 0) = C_{O_2}^0 \quad \dots(11)$$

Using Eq. (6) for the species O_1 , $C_{O_1}(r_0, 0) = C_{O_1}^0$. Rewriting Eq. (10) in terms of δ and substituting its value from Eq. (9), at $t > \tau$ one obtains,

$$\frac{I}{A F} = \frac{n_1 \pi^{1/2} D_{O_1}^{1/2} C_{O_1}^0}{2t^{1/2} \left[1 - \frac{\pi^{1/2}}{2} \phi^{1/2} + \frac{2}{3} \phi - \frac{\pi^{1/2}}{4} \phi^{3/2} + \frac{4}{15} \phi^2 - \frac{\pi^{1/2}}{12} \phi^{5/2} \right]} + \frac{n_2 \pi^{1/2} D_{O_2}^{1/2} C_{O_2}^0}{2t^{1/2} \left[1 - \frac{\pi^{1/2}}{2} \psi^{1/2} + \frac{2}{3} \psi - \frac{\pi^{1/2}}{4} \psi^{3/2} + \frac{4}{15} \psi^2 - \frac{\pi^{1/2}}{12} \psi^{5/2} \right]} \quad \dots(12)$$

$$\text{where } \phi = \left(\frac{D_{O_1} t}{r_0^2} \right) \text{ and } \psi = \left(\frac{D_{O_2} t}{r_0^2} \right)$$

At $t' = \tau_2$, $C_{O_2}[r_0, (\tau_1 + \tau_2)] = 0$, the equation for transition time for the successive reaction at the spherical electrode, assuming $D = D_{O_1} = D_{O_2}$, is given by Eq. 13,

$$I(\tau_1 + \tau_2)^{1/2} = \frac{I}{R_2} \left[\frac{n_1 \pi^{1/2} D^{1/2} A C_{O_1}^0 F}{2} + \frac{n_2 F A \pi^{1/2} C_{O_2}^0}{2} \right] \quad \dots(13)$$

$$\text{where } R_2 = 1 - \frac{\pi^{1/2}}{2} \left(\frac{D T}{r_0^2} \right) + \frac{2}{3} \left(\frac{D T}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D T}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D T}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D T}{r_0^2} \right)^{5/2}$$

$$\text{and } T = \tau_1 + \tau_2 \quad \dots(14)$$

The terms within square bracket in Eq. (13) are the same as for two successive reactions at a planar electrode. The equation for spherical diffusion is thus written in terms of the equation for linear diffusion and a correction factor R_2 due to sphericity of electrode surface.

Tabulated values of R_2 for various transition times (τ_2) as a function of $D^{1/2}/r_0$ values, calculated for single species, can still be used.

The above can be generalized for an arbitrary number of reducible species in solution. An equation for P number of species is given by Eq. 15,

$$I T_p^{1/2} = \frac{1}{S_p} \left[\frac{n_1 F A \pi^{1/2} D^{1/2} C_{O_1}^0}{2} + \frac{n_2 F A \pi^{1/2} D^{1/2} C_{O_2}^0}{2} + \dots + \frac{n_P F A \pi^{1/2} D^{1/2} C_{O_P}^0}{2} \right] \quad \dots(15)$$

where,

$$S_p = I - \frac{\pi^{1/2}}{2} \left(\frac{D T_p}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D T_p}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D T_p}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D T_p}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D T_p}{r_0^2} \right)^{5/2} \quad \dots(16)$$

and $T_p = \sum_{i=1}^P \tau_i \quad \dots(17)$

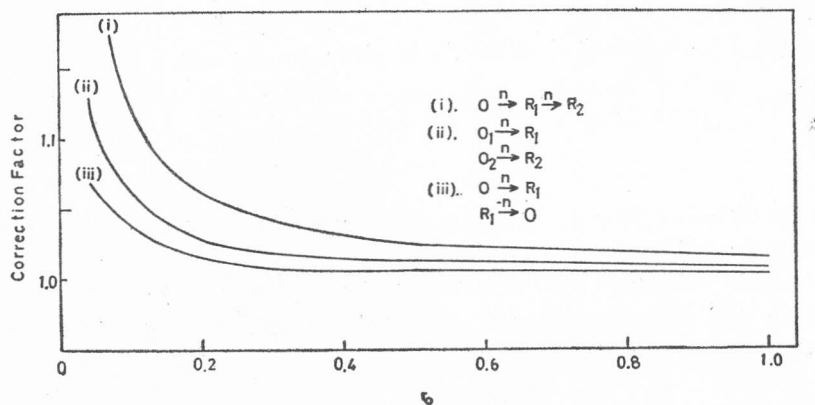


Fig. 1 — Plot of correction factor versus r_0 for reaction (ii) $O_1 \xrightarrow{n} R_1, O \xrightarrow{n} R_2$; (iii) $O \xrightarrow{n} R_1 \xrightarrow{n} R_2$ and (iv) $O \xrightarrow{n} R_1, R_1 \xrightarrow{-n} O$.

TABLE 1 — VALUES OF CORRECTION FACTORS FOR CONSTANT CURRENT CHRONOPOTENTIOMETRY AT SPHERICAL ELECTRODES FOR SECOND STEP OF CONSECUTIVE REACTION (ii) ($\tau = \tau_1 + \tau_2$)

$D^{1/2}/r_0$	τ							
	0.05	0.10	0.50	1.0	2.0	3.0	4.0	5.0
0.004	1.001	1.001	1.003	1.004	1.005	1.006	1.007	1.008
0.006	1.001	1.002	1.004	1.005	1.008	1.009	1.011	1.012
0.008	1.002	1.002	1.005	1.007	1.010	1.012	1.014	1.016
0.01	1.002	1.003	1.006	1.009	1.013	1.015	1.018	1.020
0.02	1.004	1.006	1.013	1.018	1.025	1.031	1.036	1.040
0.04	1.008	1.011	1.025	1.036	1.051	1.062	1.054	1.080
0.06	1.012	1.017	1.038	1.054	1.076	1.093	1.090	1.121
0.08	1.016	1.023	1.051	1.072	1.102	1.125	1.126	1.162
0.10	1.020	1.028	1.063	1.090	1.128	1.157	1.163	1.204
0.11	1.022	1.031	1.070	1.099	1.141	1.173	1.200	1.225
0.12	1.024	1.034	1.076	1.108	1.154	1.189	1.219	1.246
0.13	1.026	1.037	1.082	1.117	1.167	1.205	1.233	1.267
0.14	1.028	1.040	1.089	1.126	1.180	1.227	1.257	1.288
0.15	1.030	1.042	1.095	1.136	1.193	1.238	1.276	1.309
0.16	1.032	1.045	1.102	1.145	1.206	1.254	1.295	1.331
0.17	1.034	1.048	1.108	1.154	1.219	1.270	1.314	1.352
0.18	1.036	1.051	1.115	1.163	1.233	1.287	1.333	1.374
0.20	1.040	1.057	1.128	1.182	1.259	1.320	1.372	1.418
0.25	1.050	1.071	1.160	1.228	1.327	1.404	1.470	1.530
0.30	1.060	1.085	1.193	1.276	1.363	1.450	1.537	1.624
0.35	1.070	1.100	1.226	1.323	1.465	1.580	1.685	1.790
0.40	1.080	1.114	1.259	1.372	1.537	1.676	1.813	1.952

If all the reducible species present have the same concentration, Eq. 15 reduces to a simple form,

$$IT_P^{1/2} = \frac{\pi^{1/2} A D^{1/2} F C^0}{2S_p} (n_1 + n_2 + n_3 + \dots + n_p) \quad \dots(18)$$

Since S_p will be essentially the same for large P , transition-time for the P th wave is given by,

$$I (T_P^{1/2} - T_{P-1}^{1/2}) = \frac{\pi^{1/2} A F D^{1/2} C^0 n_p}{2S_p} \quad \dots(19)$$

For mixtures of several substances the successive inflections are not clearly distinguishable, particularly when the concentrations are too small and/or the potentials for successive electrode processes are close. Transition-times then cannot be accurately determined.

(b) *Stepwise reduction of a single species* — Consider the case, in which O undergoes stepwise reductions,



The transition-time, τ_1 , for the first step is given by eq. (7). At $t > \tau_1$, the concentration of O at the electrode surface is zero, but it continues to diffuse towards the electrode and is reduced directly to R_2 involving $(n_1 + n_2)$ electrons. Simultaneously, R_1 formed in the first step is reduced to R_2 involving n_2 electrons. The current through the cell is a sum of two components. Thus,

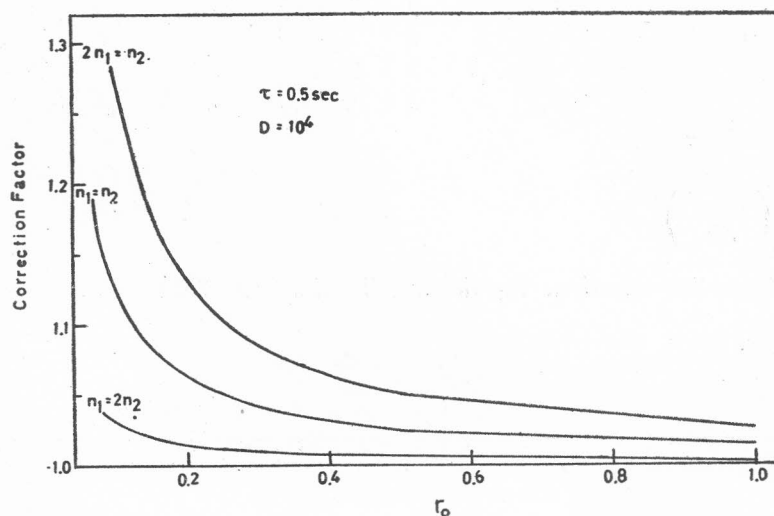


Fig. 2— Plot of correction factor versus r_0 for reaction (iii) when $2n_1 = n_2$; $n_1 = n_2$ and $n_1 = 2n_2$.

TABLE 2 — VALUES OF CORRECTION FACTORS FOR CONSTANT CURRENT CHRONOPOTENTIOMETRY AT SPHERICAL ELECTRODE FOR DIFFERENT TRANSITION TIMES OF THE SECOND STEP OF STEP-WISE REDUCTION OF A SINGLE SPECIES (iii)

$D^{1/2}/r_0$	τ	$n_1 = n_2$				$n_1 = 2n_2$				$2n_1 = n_2$			
		0.05	0.5	1.0	2.0	0.05	0.5	1.0	2.0	0.05	0.5	1.0	2.0
0.01		1.004	1.014	1.018	1.051	1.001	1.003	1.004	1.006	1.008	1.026	1.036	1.050
0.02		1.008	1.024	1.036	1.099	1.002	1.006	1.009	1.012	1.018	1.050	1.072	1.102
0.04		1.016	1.051	1.071	1.150	1.004	1.012	1.017	1.024	1.034	1.102	1.144	1.206
0.06		1.024	1.075	1.105	1.174	1.006	1.018	1.026	1.036	1.052	1.154	1.218	1.313
0.08		1.032	1.099	1.141	1.198	1.008	1.024	1.034	1.048	1.070	1.204	1.293	1.420
0.10		1.040	1.126	1.175	1.211	1.010	1.030	1.042	1.058	1.086	1.260	1.370	1.529
0.11		1.044	1.137	1.192	1.246	1.011	1.033	1.046	1.063	1.096	1.284	1.408	1.583
0.12		1.047	1.150	1.210	1.295	1.012	1.036	1.050	1.069	1.104	1.312	1.447	1.646
0.13		1.051	1.163	1.219	1.319	1.013	1.039	1.054	1.074	1.112	1.335	1.487	1.703
0.14		1.055	1.174	1.246	1.344	1.014	1.042	1.057	1.079	1.122	1.365	1.526	1.764
0.15		1.060	1.187	1.262	1.367	1.015	1.044	1.061	1.084	1.130	1.393	1.563	1.828
0.16		1.063	1.198	1.279	1.392	1.016	1.047	1.065	1.089	1.140	1.420	1.604	1.895
0.17		1.067	1.210	1.297	1.417	1.017	1.050	1.069	1.094	1.148	1.558	1.645	1.968
0.18		1.071	1.223	1.314	1.439	1.017	1.053	1.072	1.098	1.158	1.594	1.688	2.047
0.20		1.078	1.246	1.347	1.585	1.019	1.055	1.076	1.108	1.174	1.668	1.771	2.242
0.25		1.100	1.309	1.433	1.628	1.024	1.071	1.097	1.131	1.221	1.672	2.002	3.211
0.30		1.118	1.365	1.451	1.913	1.029	1.084	1.114	1.156	1.267	1.755	2.388	—
0.35		1.139	1.428	1.622	2.184	1.033	1.096	1.130	1.185	1.313	2.007	3.131	—
0.40		1.158	1.490	1.746	3.056	1.038	1.108	1.147	1.226	1.359	2.247	—	—

$$(n_1 + n_2) D_O \left\{ \frac{\partial C_O(r, t)}{\partial r} \right\}_{r=r_0} + n_2 D_{R_1} \left\{ \frac{\partial C_{R_1}(r, t)}{\partial r} \right\}_{r=r_0} = \frac{I}{A F} \quad \dots(20)$$

Using Stackelberg's diffusion layer concept, Eq. (20) can be written as,

$$(n_1 + n_2) D_O \frac{[C_O^0 - C_O(r, t)]}{\delta_1} + n_2 D_{R_1} \frac{[-C_{R_1}(r, t)]}{\delta_2} = \frac{I}{A F} \quad \dots(21)$$

Appropriate substitution of the value of δ from Eq. (9) yields,

$$\begin{aligned} \frac{I}{A F} = & \frac{(n_1 + n_2) D_O^{1/2} \pi^{1/2} [C_O^0 - C_O(r, t)]}{2 t^{1/2} \left[1 - \frac{\pi^{1/2}}{2} \left(\frac{D_O t}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_O t}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_O t}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_O t}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_O t}{r_0^2} \right)^{5/2} \right]} \\ & + \frac{n_2 D_{R_1}^{1/2} \pi^{1/2} [-C_{R_1}(r_0, t)]}{2 t^{1/2} \left[1 - \frac{\pi^{1/2}}{2} \left(\frac{D_{R_1} t}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_{R_1} t}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_{R_1} t}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_{R_1} t}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_{R_1} t}{r_0^2} \right)^{5/2} \right]} \end{aligned} \quad \dots(22)$$

At $t > \tau_1$; $C_O(r_0, t) = 0$ and at $t = \tau_1 + \tau_2$, $C_{R_1}(r_0, t) = 0$, and rearranging,

$$\begin{aligned} \left(\frac{\tau_1 + \tau_2}{\tau_1} \right)^{1/2} = & \frac{n_1 + n_2}{n_1} \frac{1 - \frac{\pi^{1/2}}{2} \left(\frac{D_O \tau_1}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_O \tau_1}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_O \tau_1}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_O \tau_1}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_O \tau_1}{r_0^2} \right)^{5/2}}{1 - \frac{\pi^{1/2}}{2} \left(\frac{D_O T}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_O T}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_O T}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_O T}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_O T}{r_0^2} \right)^{5/2}} \end{aligned} \quad \dots(23)$$

Again comparing with similar equations for linear diffusion, Eq. (23) may be put in the form,

$$\frac{\tau_2}{\tau_1} = S' \left(\frac{n_1 + n_2}{n_1} \right)^2 - 1 \quad \dots(24)$$

TABLE 3 — VALUES OF CORRECTION FACTORS FOR CONSTANT CURRENT CHRONOPOTENTIOMETRY AT SPHERICAL ELECTRODES FOR CURRENT REVERSED STEP (iv)

$D^{1/2}/r_0$	τ							
	0.01	0.10	0.50	1.00	3.00	5.00	7.00	10.00
0.004	1.000	1.001	1.001	1.002	1.004	1.005	1.005	1.006
0.006	1.000	1.001	1.002	1.003	1.005	1.007	1.008	1.010
0.008	1.000	1.001	1.003	1.004	1.007	1.009	1.011	1.013
0.010	1.001	1.002	1.004	1.005	1.009	1.011	1.013	1.016
0.020	1.001	1.003	1.007	1.010	1.018	1.023	1.027	1.032
0.040	1.002	1.006	1.014	1.020	1.035	1.045	1.053	1.062
0.060	1.003	1.010	1.021	1.030	1.052	1.066	1.078	1.092
0.080	1.004	1.013	1.028	1.040	1.068	1.087	1.102	1.120
0.100	1.005	1.016	1.035	1.050	1.084	1.107	1.125	1.148
0.110	1.006	1.018	1.039	1.055	1.092	1.117	1.137	1.161
0.120	1.006	1.019	1.042	1.059	1.100	1.127	1.148	1.175
0.130	1.007	1.021	1.046	1.064	1.108	1.137	1.160	1.188
0.140	1.007	1.022	1.049	1.069	1.116	1.146	1.171	1.201
0.150	1.008	1.024	1.053	1.074	1.123	1.156	1.182	1.214
0.160	1.008	1.026	1.056	1.078	1.131	1.165	1.193	1.227
0.170	1.009	1.027	1.059	1.083	1.138	1.175	1.204	1.241
0.180	1.009	1.029	1.063	1.087	1.146	1.184	1.215	1.256
0.200	1.010	1.032	1.069	1.097	1.161	1.203	1.238	1.287
0.250	1.013	1.040	1.086	1.119	1.197	1.251	1.303	1.397
0.300	1.015	1.047	1.102	1.141	1.233	1.308	1.402	1.656

where,

$$S' = \left[\frac{1 - \frac{\pi^{1/2}}{2} \left(\frac{D_O \tau_1}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_O \tau_1}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_O \tau_1}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_O \tau_1}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_O \tau_1}{r_0^2} \right)^{5/2}}{1 - \frac{\pi^{1/2}}{2} \left(\frac{D_O T}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D_O T}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D_O T}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D_O T}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D_O T}{r_0^2} \right)^{5/2}} \right]^2 \quad \dots(25)$$

(c) *Cathodic process followed by reoxidation due to current reversal* — The process, $O + ne = R$ at $0 < t < \tau'$,

is followed by the reoxidation,

$R - ne = O$ at $\tau < t < \tau'$

Transition, time for the forward step is still defined by Eq. (5), that for the reverse step is evaluated using the current excitation function,

$$i(t) = I t + I_1 (t - t_f) \quad \dots(26)$$

where I and I_1 determine the magnitude of current for forward and reverse steps respectively. Time t is considered from the start of electrolysis and t_f is the time after the current is reversed.

In this case, flux of R at the electrode surface is,

$$\left\{ \frac{\partial C_R(r, t)}{\partial r} \right\}_{r=r_0} = \frac{I t + I_1 (t + t_f)}{n F A D} \quad \dots(27)$$

Solution of Fick's spherical diffusion Eq. (2) for R under initial and boundary conditions (3), (4) and (27) is,

$$C_R(r_0, t) = \frac{I r_0}{n F A D_O} \left\{ 1 - \exp\left(\frac{D_O t}{r_0^2}\right) \operatorname{erfc}\left(\sqrt{\frac{D_O t}{r_0^2}}\right) \right\} + \frac{I_1 r_0}{n F A D_O} \left\{ 1 - \exp\left(\frac{D_O(t - t_f)}{r_0^2}\right) \operatorname{erfc}\left(\sqrt{\frac{D_O(t - t_f)}{r_0^2}}\right) \right\} \quad \dots(28)$$

If the magnitude of current for forward and reverse process is equal, I_1 should be equal to $-2I$. Further at $t = t_f + \tau_r$, $C_R(r_0, t_f + \tau_r) = 0$

Hence, on rearrangement, Eq. (28) yields,

$$\frac{t_f}{\tau_r} = (2 S'')^2 - 1 \quad \dots(29)$$

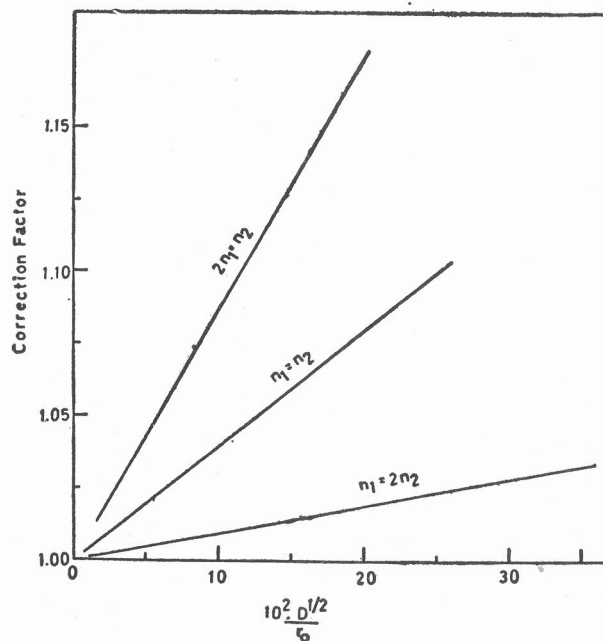


Fig. 3 — Plot of correction factor versus $D^{1/2}/r_0$ for reaction (iii) when $2n_1 = n_2$; $n_1 = n_2$ and $n_1 = 2n_2$

where,

$$S'' = \frac{1 - \frac{\pi^{1/2}}{2} \left(\frac{D\tau_r}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D\tau_r}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D\tau_r}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D\tau_r}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D\tau_r}{r_0^2} \right)^{5/2}}{1 - \frac{\pi^{1/2}}{2} \left(\frac{D(t_f + \tau_r)}{r_0^2} \right)^{1/2} + \frac{2}{3} \left(\frac{D(t_f + \tau_r)}{r_0^2} \right) - \frac{\pi^{1/2}}{4} \left(\frac{D(t_f + \tau_r)}{r_0^2} \right)^{3/2} + \frac{4}{15} \left(\frac{D(t_f + \tau_r)}{r_0^2} \right)^2 - \frac{\pi^{1/2}}{12} \left(\frac{D(t_f + \tau_r)}{r_0^2} \right)^{5/2}} \dots(30)$$

Eqs (7), (19), (24) and (29) are similar to those for planar electrodes except that these involve factor S' s. Factor S can be termed as correction to equations applicable to planar electrodes, due to sphericity of the diffusion field. It depends on various variables e.g., diffusion coefficients of the species, transition time and the radius of the electrode⁴. Variation of S 's with these variables are shown in the Figs. 1, 2 and 3. These figures indicate that values of S are practically unity for small τ (< 1 sec), low diffusion coefficients ($< 10^{-5}$ cm² sec⁻¹) and large electrode radius (> 1 mm).

Under a set of experimental conditions, deviations from planar electrode equations, under spherical diffusion conditions can easily be obtained from tabulated values of S for various values of $D^{1/2}/r_0$ as a function of τ . (Tables 1, 2 and 3) These tabulated values can help in the choice of electrode radius and current densities to keep deviations below 1%.

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