

Chronopotentiometry with Spherical Electrodes—Sphericity Correction to Sand's Equation

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Sand's Equation can be used to calculate chronopotentiometric diffusion coefficients using spherical electrodes, provided appropriate corrections are made; alternatively care should be taken to control experimental conditions relating to electrode diameter, current-density and transition time. Deviations have been calculated and summarized in terms of a convenient correction factor for a wide range of experimental variables.

ELECTROLYSIS at constant current density with mass transfer partially or totally controlled by diffusion, involving reversible and irreversible electrode processes, with and without kinetic complications, has been widely studied¹⁻⁴. Sand's equation (1)⁵ is applicable for mass transfer conditions, approaching those for semi-infinite linear diffusion, in absence of convective and migrational transport, and for a reversible electrochemical process, uncomplicated by kinetic or catalytic effect.

$$\frac{i_0 \tau^{1/2}}{C^0} = \frac{\pi^{1/2} n F D^{1/2}}{2} \quad \dots(1)$$

where i_0 is the constant current-density (amp. cm⁻²), τ the transition time (sec), C^0 , the bulk concentration (moles cm⁻³), D , the diffusion coefficient (cm² sec⁻¹) of the electroactive species and nF , the number of Faradays per mole of electrode reaction. For cylindrical diffusion, the corresponding equation correlating τ with other parameters has been given by Peters and Lingane⁶ in terms of Eq. (1) and a correction factor R'

$$\frac{i_0 \tau^{1/2}}{C^0} = \frac{\pi^{1/2} n F D^{1/2}}{2} \times R' \quad \dots(2)$$

where,

$$\begin{aligned} \frac{1}{R'} = 1 - \frac{\pi^{1/2} (D^{1/2} \tau^{1/2})}{4 (r'_0)} + \frac{1 (D^{1/2} \tau^{1/2})^2}{4 (r'_0)^2} - \frac{3\pi^{1/2}}{32} \\ \times \frac{(D^{1/2} \tau^{1/2})^3}{(r'_0)^3} + \frac{21 (D^{1/2} \tau^{1/2})^4}{160 (r'_0)^4} - \frac{9\pi^{1/2} (D^{1/2} \tau^{1/2})^5}{128 (r'_0)^5} + \dots \end{aligned} \quad \dots(2a)$$

where r'_0 is the radius of the cylindrical electrode. The values of the correction factor have been evaluated by Evans and Price⁷.

Comparing Eqs. (1) and (2) it is seen that Sand's equation (for linear diffusion) can be used for a

cylindrical electrode only under the restrictive condition that correction factor (R') is not far from unity. This situation applies only for specific combinations of D , r_0 and τ . In spite of this, several workers have neglected the difference in diffusion fields and have evaluated D 's, based on strict adherence of Sand's equation when a cylindrical diffusion field applies.

Hanging drop⁸ and dropping metal electrodes⁹ with large drop times are frequently used in electro-analytical and diffusion measurements, for which spherical diffusion conditions apply. In this study we have used the basic relationship for spherical diffusion¹⁰ and have obtained a relationship for the transition time in terms of the Sand's equation (for linear diffusion) and a correction factor R due to sphericity of the diffusion field, in a manner similar to that for cylindrical diffusion.

Due to rapid advances in instrumentation and experimental simplicity, chronopotentiometry has been widely used as an electroanalytical technique, and since the chronopotentiometric diffusion coefficients agree substantially with those evaluated using the tracer technique^{11,12}, computed values of R should be of interest.

Theoretical

Spherical diffusion—Starting with Fick's second law of diffusion (Eq. 3) in spherical coordinates and

$$\frac{\partial C(r, t)}{\partial t} = D \left[\frac{\partial^2 C(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r, t)}{\partial r} \right] \quad \dots(3)$$

(i) introducing the initial boundary conditions:

$$C(r, 0) = C^0, \left(\frac{\partial C(r, t)}{\partial r} \right)_{r=r_0} = \frac{i_0}{nFD},$$

$$C(r, t) \rightarrow C^0 \text{ for } r \rightarrow \infty$$

where r is the distance from the centre of the

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spherical electrode of radius r_0 , (ii) transforming Eq. (3) into the form

$$\partial \chi(r, t) / \partial t = D [\partial^2 \chi(r, t) / \partial r^2]$$

by setting $\chi(r, t) = rC(r, t)$ and (iii) solving for the above initial and boundary conditions, the concentration at $r = r_0$ is given¹⁰ by Eq. (4)

$$C(r_0, t) = C^\circ - \frac{i_0 r_0}{nFD} \left[1 - \exp\left(\frac{Dt}{r_0^2}\right) \operatorname{erfc}\left(\frac{(Dt)^{1/2}}{r_0}\right) \right] \quad \dots(4)$$

where

$$\operatorname{erfc}(\lambda) = 1 - \operatorname{erf}(\lambda); \operatorname{erf}(\lambda) = \frac{2}{\pi^{1/2}} \int_0^\lambda \exp(-z^2) dz$$

The transition-time, τ defined by the condition $C(r_0, t) = 0$ would be given by Eq. (5)

$$\frac{C^\circ nFD}{i_0 r_0} = 1 - \exp\left(\frac{D\tau}{r_0^2}\right) \operatorname{erfc}\left(\frac{(\tau D)^{1/2}}{r_0}\right) \quad \dots(5)$$

When τ is very small (or i_0 is large), $(D\tau/r_0^2) \ll 1$, and $\exp\left(\frac{D\tau}{r_0^2}\right) \simeq 1$ and $\operatorname{erfc}(\tau D)^{1/2}/r_0 \simeq 1 - 2D^{1/2}\tau^{1/2}/\pi^{1/2}r_0$,

Eq. (5) then approximates to the same form as Eq. (1) for linear-diffusion. Thus the product $i_0\tau/C^\circ$ for spherical diffusion would also approach the value for linear diffusion. For other conditions, expanding the exponential and error function in Eq. (5), the resulting equation can be put in form similar to Eqs. (2) and (2a),

$$\frac{i_0\tau^{1/2}}{C^\circ} = \frac{\pi^{1/2} nFD^{1/2}}{2} \cdot R \quad \dots(6)$$

where

$$\frac{1}{R} = 1 - \frac{\pi^{1/2} (D^{1/2} \tau^{1/2})}{2 r_0} + \frac{2 (D^{1/2} \tau^{1/2})^2}{3 r_0^2} - \frac{\pi^{1/2} (D^{1/2} \tau^{1/2})^3}{4 r_0^3} + \frac{4 (D^{1/2} \tau^{1/2})^4}{15 r_0^4} - \frac{\pi^{1/2} (D^{1/2} \tau^{1/2})^5}{12 r_0} \quad \dots(6a)$$

Results and Discussion

Influence of experimental variables—The correction factor, R for spherical diffusion is seen to be dependent on the diffusivity of the species, the radius of the electrode and the measured transition time. The trends of each of these variables on R for typical values of D as 10^{-4} and 10^{-6} $\text{cm}^2 \text{sec}^{-1}$, r as 0.25 and 1.0 mm and for τ of 5 and 20 sec, are illustrated in Figs. 1 to 3 and provide a useful guide for design of the appropriate chronopotentiometric experiment.

Fig. 1 shows that R tends to unity as τ tends to zero for both the values of diffusion coefficients and both the electrode radii selected. Therefore, for short transition times (i.e. in the range of milliseconds) Sand's equation will apply. Irrespective of electrode radius and diffusion coefficient, the curves show two characteristic zones as the transition time increases from zero. Initially, the increase from unity is rapid, and more pronounced for small electrodes and high diffusion coefficients. For longer transition times the rate of change is much less but tends to a linear value.

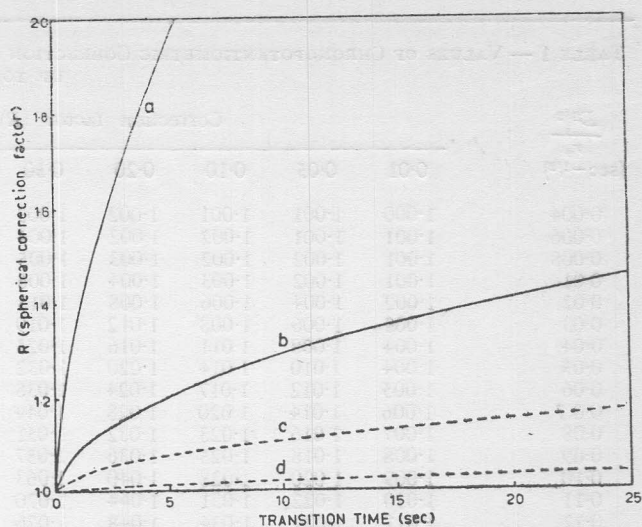


Fig. 1 — Variation of spherical correction factor (R) with transition time [—, $D=10^{-4} \text{ cm}^2 \text{sec}^{-1}$; ----, $D=10^{-6} \text{ cm}^2 \text{sec}^{-1}$] a, radius=0.25 mm ($D=10^{-4}$); b, radius=1.0 mm ($D=10^{-4}$); c, radius=0.25 mm ($D=10^{-6}$); d, radius=1.0 mm ($D=10^{-6}$)

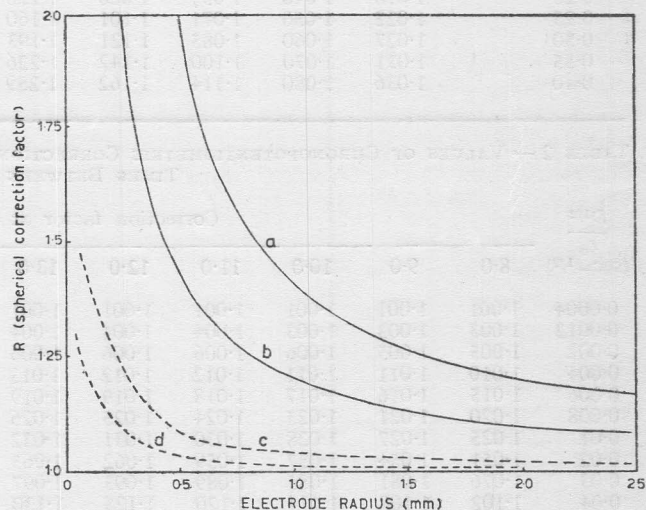


Fig. 2 — Influence of electrode radius on spherical correction factor [—, $D=10^{-4} \text{ cm}^2 \text{sec}^{-1}$; ----, $D=10^{-6} \text{ cm}^2 \text{sec}^{-1}$] a, $\tau=20$ sec ($D=10^{-4}$); b, $\tau=5$ sec ($D=10^{-4}$); c, $\tau=20$ sec ($D=10^{-6}$); d, $\tau=5$ sec ($D=10^{-6}$)

For fixed values of diffusion coefficient and transition time, R is seen (Fig. 2) to increase rapidly as the drop radius tends to zero. Within the usual range of diffusion coefficients (i.e. 10^{-4} to 10^{-6}) it is seen that it is important to have a large electrode diameter (e.g. >1 mm), unless very short transition times are used. The rapid increase in the value of the spherical correction factor for smaller electrode diameters defines the minimum diameter that should be used. Otherwise the drop size would have to be known with a higher precision than it could be measured in order to apply the appropriate correction factor.

Fig. 3 illustrates the effect of varying diffusion coefficient in the range 10^{-8} to $10^{-4} \text{ cm}^2 \text{sec}^{-1}$ on R . Deviation from Sand's equation becomes marked at

TABLE 1 — VALUES OF CHRONOPOTENTIOMETRIC CORRECTION FACTOR (R) FOR SPHERICAL DIFFUSION AT TRANSITION TIMES UP TO 7 SEC

$\frac{D^{1/2}}{r_0}$ (sec ^{-1/2})	Correction factor (R) at designated transition time (sec)											
	0.01	0.05	0.10	0.20	0.50	1.00	2.00	3.00	4.00	5.00	6.00	7.00
0.004	1.000	1.001	1.001	1.002	1.003	1.004	1.005	1.006	1.007	1.008	1.009	1.009
0.006	1.001	1.001	1.002	1.002	1.004	1.005	1.008	1.009	1.011	1.012	1.013	1.014
0.008	1.001	1.002	1.002	1.003	1.005	1.007	1.010	1.012	1.014	1.016	1.017	1.019
0.01	1.001	1.002	1.003	1.004	1.006	1.009	1.013	1.015	1.018	1.020	1.022	1.024
0.02	1.002	1.004	1.006	1.008	1.013	1.018	1.025	1.031	1.036	1.040	1.044	1.047
0.03	1.003	1.006	1.008	1.012	1.019	1.027	1.038	1.046	1.054	1.060	1.066	1.071
0.04	1.004	1.008	1.011	1.016	1.025	1.036	1.051	1.062	1.072	1.080	1.088	1.095
0.05	1.004	1.010	1.014	1.020	1.032	1.045	1.063	1.078	1.090	1.101	1.110	1.119
0.06	1.005	1.012	1.017	1.024	1.038	1.054	1.076	1.093	1.108	1.121	1.133	1.144
0.07	1.006	1.014	1.020	1.028	1.044	1.063	1.089	1.109	1.126	1.142	1.155	1.168
0.08	1.007	1.016	1.023	1.032	1.051	1.072	1.102	1.125	1.145	1.162	1.178	1.193
0.09	1.008	1.018	1.025	1.036	1.057	1.081	1.115	1.141	1.163	1.183	1.201	1.217
0.10	1.009	1.020	1.028	1.040	1.063	1.090	1.128	1.157	1.182	1.204	1.224	1.242
0.11	1.010	1.022	1.031	1.044	1.070	1.099	1.141	1.173	1.200	1.225	1.247	1.267
0.12	1.011	1.024	1.034	1.048	1.076	1.108	1.154	1.189	1.219	1.246	1.270	1.292
0.13	1.012	1.026	1.037	1.052	1.082	1.117	1.167	1.205	1.233	1.267	1.293	1.317
0.14	1.012	1.028	1.040	1.056	1.089	1.126	1.180	1.221	1.257	1.288	1.317	1.343
0.15	1.013	1.030	1.042	1.060	1.095	1.136	1.193	1.238	1.276	1.309	1.340	1.368
0.16	1.014	1.032	1.045	1.064	1.102	1.145	1.206	1.254	1.295	1.331	1.364	1.394
0.17	1.015	1.034	1.048	1.068	1.108	1.154	1.219	1.270	1.314	1.352	1.388	1.420
0.18	1.016	1.036	1.051	1.072	1.115	1.163	1.233	1.287	1.333	1.374	1.411	1.446
0.20	1.018	1.040	1.057	1.080	1.128	1.182	1.259	1.320	1.372	1.418	1.460	1.500
0.25	1.022	1.050	1.071	1.101	1.160	1.228	1.327	1.404	1.470	1.530	1.587	1.640
0.30	1.027	1.060	1.085	1.121	1.193	1.276	1.363	1.450	1.537	1.624	1.711	1.798
0.35	1.031	1.070	1.100	1.142	1.226	1.323	1.465	1.580	1.685	1.789	1.899	2.022
0.40	1.036	1.080	1.114	1.162	1.259	1.372	1.537	1.676	1.813	1.962	2.410	2.370

TABLE 2 — VALUES OF CHRONOPOTENTIOMETRIC CORRECTION FACTOR (R) FOR SPHERICAL DIFFUSION IN THE TRANSITION TIMES BETWEEN 8 AND 20 SEC

$\frac{D^{1/2}}{r_0}$ (sec ^{-1/2})	Correction factor at designated transition time (sec)												
	8.0	9.0	10.0	11.0	12.0	13.0	14.0	15.0	16.0	17.0	18.0	19.0	20.0
0.0004	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.001	1.002	1.002	1.002	1.002
0.0012	1.003	1.003	1.003	1.004	1.004	1.004	1.004	1.004	1.004	1.004	1.005	1.005	1.005
0.002	1.005	1.005	1.006	1.006	1.006	1.006	1.007	1.007	1.007	1.007	1.008	1.008	1.008
0.004	1.010	1.011	1.011	1.012	1.012	1.013	1.013	1.014	1.014	1.015	1.015	1.016	1.016
0.006	1.015	1.016	1.017	1.018	1.019	1.019	1.020	1.021	1.021	1.022	1.023	1.023	1.024
0.008	1.020	1.021	1.023	1.024	1.025	1.026	1.027	1.028	1.029	1.029	1.030	1.031	1.032
0.01	1.025	1.027	1.028	1.030	1.031	1.032	1.033	1.035	1.036	1.037	1.038	1.039	1.040
0.02	1.051	1.054	1.057	1.059	1.062	1.065	1.067	1.069	1.072	1.074	1.076	1.078	1.080
0.03	1.076	1.081	1.085	1.089	1.093	1.097	1.101	1.105	1.108	1.111	1.115	1.118	1.121
0.04	1.102	1.108	1.114	1.120	1.125	1.130	1.135	1.140	1.145	1.149	1.154	1.158	1.162
0.05	1.128	1.136	1.143	1.150	1.157	1.163	1.170	1.176	1.182	1.187	1.193	1.198	1.204
0.06	1.154	1.163	1.172	1.181	1.189	1.197	1.205	1.212	1.219	1.226	1.233	1.239	1.246
0.07	1.180	1.191	1.202	1.212	1.221	1.231	1.240	1.248	1.257	1.265	1.273	1.280	1.288
0.08	1.206	1.219	1.231	1.243	1.254	1.265	1.275	1.285	1.295	1.304	1.313	1.322	1.331
0.09	1.227	1.247	1.261	1.274	1.287	1.299	1.311	1.322	1.333	1.344	1.354	1.364	1.374
0.10	1.259	1.276	1.291	1.306	1.320	1.333	1.347	1.359	1.372	1.384	1.395	1.407	1.418
0.11	1.286	1.304	1.321	1.338	1.353	1.368	1.383	1.397	1.411	1.424	1.437	1.450	1.462
0.12	1.313	1.333	1.352	1.370	1.387	1.403	1.419	1.435	1.450	1.465	1.479	1.493	1.507
0.13	1.340	1.362	1.382	1.402	1.421	1.439	1.457	1.474	1.490	1.507	1.523	1.538	1.554
0.14	1.368	1.391	1.413	1.435	1.455	1.475	1.494	1.513	1.531	1.549	1.567	1.585	1.601
0.15	1.395	1.420	1.445	1.468	1.490	1.512	1.533	1.553	1.573	1.593	1.613	1.632	1.651
0.16	1.423	1.450	1.476	1.501	1.525	1.549	1.572	1.594	1.617	1.639	1.660	1.682	1.703
0.17	1.451	1.480	1.508	1.535	1.562	1.587	1.612	1.637	1.662	1.686	1.710	1.735	1.759
0.18	1.479	1.511	1.541	1.570	1.599	1.627	1.654	1.682	1.709	1.736	1.764	1.792	1.820
0.20	1.508	1.573	1.608	1.643	1.676	1.710	1.744	1.778	1.813	1.848	1.885	1.923	1.962
0.25	1.693	1.745	1.800	1.855	1.913	1.975	2.041	2.113	2.192	2.280	2.378	2.490	2.619

diffusion rates $>10^{-5}$ cm² sec⁻¹, but the correction factor tends to unity at low diffusion rates. The rapid change for longer transition times or for smaller drop radii again highlights the need to optimize these values.

Generalized correction factor — Whilst the desirability of compensating for sphericity has been clearly

established, experimental conditions will seldom match those used to illustrate the above. The value of R for various values of $D^{1/2}/r_0$, as a function of transition time (the experimentally determined variable) are presented in Tables 1 and 2, the limits of the variables being drop radius within the range 0.2 to 2.0 mm, measured transition times within

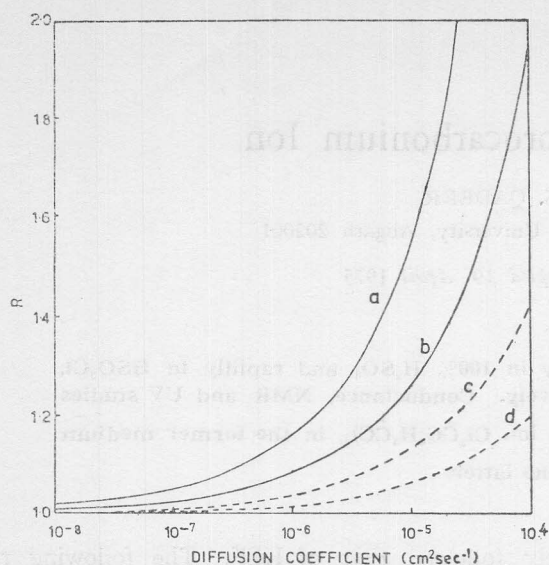


Fig. 3 — Change in spherical correction factor (R) with Diffusivity [—, radius=0.25 mm; ---, radius=1.0 mm] a, $\tau=20$ sec ($r=0.25$ mm); b, $\tau=5$ sec ($r=0.25$ mm); c, $\tau=20$ sec ($r=1.0$ mm); d, $\tau=5$ sec ($r=1.0$ mm)

range 10 millisecc to 20 sec, and diffusion coefficients from 10^{-8} to 10^{-4} $\text{cm}^2 \text{sec}^{-1}$ (refs. 13, 14).

For a given set of conditions (i.e. r_0 and τ), the correct value of R that should be applied can only be obtained by a series of approximations. For the first approximation the value of D should be estimated on the assumption that Sand's equation holds. This then enables estimation of the ratio $D^{1/2}/r_0$ so that an approximate value of R can be read from Tables 1 and 2. Employing that correction factor the diffusion coefficient can be recalculated with a greater precision leading to a more precise value of $D^{1/2}/r_0$ and R .

By a judicious choice of r_0 and i_0 (hence τ) the effect of sphericity can be kept below 1% as is seen from the tabulated values of R and one could still use Sand's equation. On the other hand major errors in diffusion coefficients could result if the effect of sphericity were neglected.

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