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Nernst-controlled Currents in Hanging-drop Polarography

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An equation for the current at a concentration-polarized spherical electrode is derived for the case in which the ratio of concentrations of oxidized and reduced forms at the electrode surface is governed by the Nernst equation, the diffusion coefficients are equal, and the potential changes linearly with time. The result can be expressed as the sum of two terms, the current at a plane electrode under the same conditions, and a second term involving only easily calculable functions. Evaluation of the first term is discussed.

Nernst-controlled currents at stationary microelectrodes with linearly changing potential have recently received considerable attention. Randles,[1] Ševčik,[2] and Berzins and Delahay[3] treated the case in which the equations of linear diffusion could be assumed to apply. Nicholson[4] extended the investigation to cylindrical electrodes and Frankenthal and Shain[5] to spherical electrodes.

Because these cases are of considerable potential importance for analytical and physico-chemical techniques, the present work was undertaken with the hope of simplifying some of the results of these previous workers. The case treated by Frankenthal and Shain is approached in a somewhat different manner by means of the Laplace transformation. A modification of Ševčik's equation is proposed for the calculation of current at a plane electrode.

Theory.—Consider the reaction $O + ne^- \rightarrow R$ at a spherical electrode with diffusion the only factor affecting the movement of these species in the solution. The concentration of the oxidized form, C_O, as a function of time, t, and radial distance from the center of the electrode, r, is governed by Fick's second law of spherical diffusion

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

where D_O is the diffusion coefficient of the oxidized form. A corresponding equation for the reduced form can be written in which the subscript O is replaced by subscript R.

The initial conditions are $C_O = C^*_O$ and $C_R = C^*_R$ when $t = 0$ where C^* denotes concentration at the beginning of the experiment. The boundary conditions are, first, $C_O \rightarrow C^*_O$ and $C_R \rightarrow C^*_R$ when $r \rightarrow \infty$. The sum of the fluxes of the oxidized and reduced forms at the electrode surface is zero

$$D_O\frac{\partial C_O}{\partial r} + D_R\frac{\partial C_R}{\partial r} = 0 \text{ at } r = r_0 \qquad (2)$$

where r_0 is the radius of the electrode. The ratio of the concentrations at the surface is given by the Nernst equation

$$\frac{C_O}{C_R} = \theta \exp(-at) \text{ at } r = r_0 \qquad (3)$$

where

$$\theta = \frac{f_O}{f_R}\exp\left[\frac{RT}{nF}(E_i - E^0)\right]$$

E_i is the potential at the start of the experiment; $a = nFw/RT$, w is the rate of change of potential with time; and the other symbols have their usual thermodynamic significance.

These conditions are for the case in which both species are soluble in the solution. The case in which the reduced form is soluble in the electrode material is much more difficult because of the finite volume of the electrode phase. The solution for the present case is, however, an excellent approximation. This is so because the region in which diffusion of the reduced species is the limiting factor is at the foot of the wave where the spherical contribution is small and further where small deviations are not noticeable. In the experimentally important region of the wave, from approximately E^0 on, it is the diffusion process of the oxidized form which is most important in determining the shape of the wave. The same condition was implicitly imposed by Frankenthal and Shain[5] in their calculations. They assumed that the sum of the concentrations of the oxidized and reduced forms is constant at the electrode surface. This is true for a spherical electrode with changing potential only when both species are soluble in the solution and their diffusion coefficients are equal.

In the present approach also it has been assumed that the diffusion coefficients are equal. The same assumption was made by Nicholson[4] in the case of the cylindrical diffusion. The experimental results indicate that the error introduced by the assumption in that case is negligible. By analogy, the same result would be expected here.

The solution to the above-stated problem is given in Appendix I. It can be seen that the current at a spherical electrode can be represented as

$$i_s = i_p + nFAC^*_O\frac{D}{r_0}\left[\frac{1 - \exp(-at)}{1 + \theta\exp(-at)}\right] \qquad (4)$$

where i_p is the current which would be observed at the corresponding plane electrode.

The evaluation of current at a plane electrode has been undertaken by several authors. Ševčik[2] evaluated expression 18 by approximating the integral with a series. Randles,[1] Nicholson,[4] and Frankenthal and Shain[5] have also calculated this current by numerical integration of Fick's second law. An inherently more accurate approach is as follows. The above expression is unsatisfactory for graphical integration because of the factor $\sqrt{t - \tau}$ in the denominator. However, integrating

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(1) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).
(2) A. Ševčik, *Coll. Czech. Chem. Comms.*, **13**, 349 (1948).
(3) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 555 (1953).
(4) M. M. Nicholson, *ibid.*, **76**, 2539 (1954).
(5) R. P. Frankenthal and I. Shain, *ibid.*, **78**, 2969 (1956).

by parts, the expression can be transformed into

$$i = nFAC^*_O\sqrt{\frac{D}{\pi}}\left[\frac{2a\sqrt{t}}{\theta + 1} + \frac{a^2}{2}\int_0^t \sqrt{t - \tau}\,\frac{\tanh\,(\ln\theta - a\tau)/2}{\cosh^2\,(\ln\theta - a\tau)/2}\,d\tau\right] \quad (5)$$

Assuming $\theta >> 1$ and substituting $\mu = \ln\,\theta$, $z = at - a\tau$, and $y = at$ gives

$$i = nFAC^*_O\sqrt{\frac{Da}{\pi}}\left[2\sqrt{y}\exp(-\mu) + \frac{1}{2}\int_0^y \sqrt{z}\,\frac{\tanh\,(\mu - y + z)/2}{\cosh^2\,(\mu - y + z)/2}\,dz\right] \quad (6)$$

This expression can be evaluated readily by graphical integration and the results for the representative value $\mu = 6$ are given in Table I.

TABLE I

CURRENT AT A PLANE ELECTRODE WITH LINEARLY CHANGING POTENTIAL[a]

$E - E^{0'}$ (mv.)	$i/nFAC^*_O\sqrt{aD}$	$E - E^{0'}$ (mv.)	$i/nFAC^*_O\sqrt{aD}$
149.7	0.003	0	0.378
136.1	.006	−13.6	.425
122.5	.010	−27.2	.445
108.9	.017	−32.6	.446
95.3	.028	−40.8	.440
81.7	.045	−54.4	.419
68.0	.072	−68.0	.390
54.4	.111	−81.7	.361
40.8	.165	−95.3	.334
27.2	.231	−108.9	.310
13.6	.311		

[a] Initial potential assumed in these calculations was 163.3 mv. Accuracy of the calculations is approximately 1%.

If an initial potential is chosen corresponding to $\theta >> 1$, the form of the current–time curve can be shown to be nearly independent of θ and the curve is merely shifted laterally along the time axis for different initial potentials. The proof of this is analogous to the one given by Delahay[6] for the case of irreversible reduction under the same conditions. Substituting into equation 18, the expression for current at a given time corresponding to y and a given initial potential corresponding to μ is

$$i(y,\mu) = K\int_0^y \frac{dz}{\sqrt{z}\,\cosh^2\,(\mu + z - y)/2} \quad (7)$$

where

$$K = nFAC^*_O\sqrt{aD/\pi}$$

The current at the same time but with a more reducing initial potential corresponding to $\mu + \Delta y$ is

$$i(y,\mu + \Delta y) = K\int_0^y \frac{dz}{\sqrt{z}\cosh^2\,(\mu + z - y + \Delta y)/2} \quad (8)$$

With an initial potential μ but at a time corresponding to $y - \Delta y$, the potential applied to the electrode is the same as that in the case represented by Equation 21 but the current is

$$i(y - \Delta y,\mu) = K\int_0^y \frac{dz}{\sqrt{z}\cosh^2\,(\mu + z - y + \Delta y)/2} \quad (9)$$

The difference in current between the two cases is

$$\Delta i = K\int_{y\text{-}\Delta y}^y \frac{dz}{\sqrt{z}\cosh^2\,(\mu + z - y + \Delta y/2} \quad (10)$$

Since we have assumed θ and hence μ to be large, this term is small compared to i except at the foot of the current-time curve and can be ignored. That is

$$i(y,\mu + \Delta y) \cong i(y - \Delta y,\mu) \quad (11)$$

Discussion

Plane Electrode.—The currents at a plane electrode calculated from equation 6 should be comparable with the values obtained by Randles,[1] Sevcik,[2] Nicholson,[4] and Frankenthal and Shain[5] for this case. The normalized values of these authors for peak current are, respectively, 0.454, 0.361, 0.451 and 0.456 as compared with 0.446 here. It will be noted that Ševčik's value is lower than the rest by approximately 20%. It seems extremely likely that his value was miscalculated by a factor of $\sqrt{\pi/2}$. With this correction his value for peak current (as well as for other values of y as nearly as can be estimated from his graphed data) is in good conformity with the others.

In Fig. 1 the current-voltage curve from the values in Table I is compared with the calculated values of Nicholson[4] and Frankenthal and Shain.[5] It will be observed that the agreement is excellent with small deviations at the foot of the wave. In this region, the initial potential assumed in the calculations makes an important contribution. Consequently, variation among values calculated by various authors is to be expected. This factor also accounts in part for the small discrepancies in the

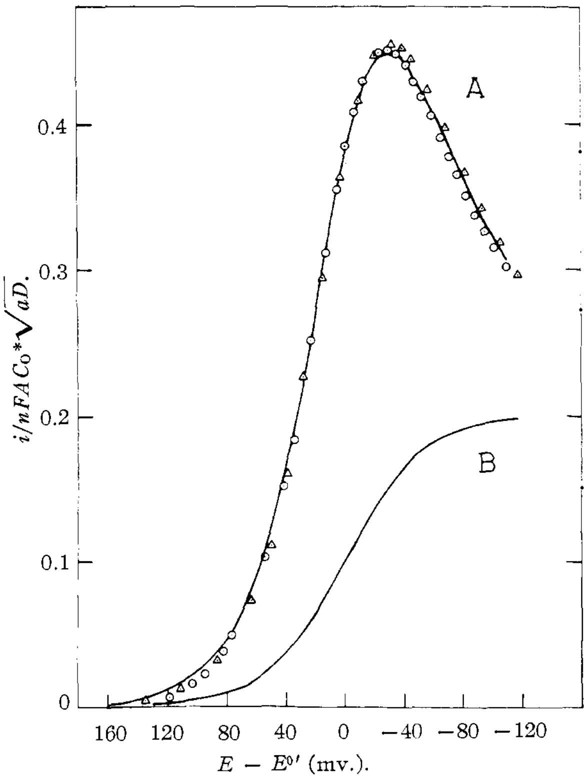

Fig. 1.—Theoretical current-voltage curves at plane and spherical electrodes: A, plane electrode—solid line, this work; triangles, Frankenthal and Shain[5]; circles, Nicholson[4]; B, spherical contribution for $(1/r_0)(D_O/nw)^{1/2} = 0.20$.

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(6) P. Delahay, THIS JOURNAL, **75**, 1190 (1953).

values of peak current. These latter deviations are, however, within computational error. If, for very exact work, it is desired to have values of greater accuracy, the currents for any value of the initial potential can be calculated from those in Table I by applying the correction given by equation 10. The graphical integration is readily performed in this case because, within the limits of integration, the argument remains bounded.

Spherical Electrodes.—From equations 4 and 15 the term representing the spherical contribution can be written as

$$nFAD(C^*_{\mathrm{O}} - C^s{}_{\mathrm{O}})/r_0$$

where $C^s{}_{\mathrm{O}}$ is the instantaneous concentration of the reduced form at the surface. The value of this term is plotted for a representative value of the parameters in Fig. 1. It will be observed that the curve of this term *versus* potential takes the same sigmoid form associated with the conventional polarographic wave. In fact, this spherical contribution can be written approximately in the form

$$E = E^{0\prime} + \frac{RT}{nF}\ln\frac{i_{\mathrm{sc}\infty} - i_{\mathrm{sc}}}{i_{\mathrm{sc}}} \qquad (12)$$

where $E^{0\prime}$ is the formal electrode potential of the reaction; i_{sc} is the spherical contribution at any point, and $i_{\mathrm{sc}\infty}$ is the limiting value. This last term is, of course, the same as the steady-state current which would be obtained at a sufficiently large value of t at a stationary sphere with a constant applied potential such that $\theta << 1$.

While the current at a plane electrode is proportional to the square root of the rate of change of potential, the corresponding spherical contribution carries no such dependence. Consequently, as has been suggested by Delahay,[6] the latter term becomes negligible at very fast rates of potential scan and in particular in oscillographic work.

Since equation 4 gives, within the accuracy of computation of the methods employed, the same theoretical predictions as the calculations of Frankenthal and Shain,[5] their comparisons with experiment can be referred to for a test of its validity. The agreement with experiment is excellent. For example, using the data of Ross, Demars, and Shain[7] theoretical peak currents calculated by both methods for 10^{-4} *M* thallous ion agree with experiment to better than 1%.[8]

Conclusion.—A simplified equation for Nernst-controlled currents in hanging-drop polarography is presented. This equation has been found to be in agreement with experiment.[4,7,8] Its use in the determination of diffusion constants and other parameters of interest in electrochemical systems seems particularly inviting because of the inherently greater accuracy of the theory as opposed to that of the corresponding polarographic approach.

Appendix.—The problem outlined in the theoretical section can be approached most easily by means of the Laplace transformation.[9] The calculations are simplified if the following substitutions are made

$$u(r,t) = rC^*_{\mathrm{O}} - rC_{\mathrm{O}}(r,t),\ v(r,t) = rC_{\mathrm{R}}(r,t) - rC^*_{\mathrm{R}}$$

The transforms of the Fick's law differential equations are

$$s\bar{u} = D(\partial^2 u/\partial r^2),\ s\bar{v} = D(\partial^2 v/\partial r^2)$$

where s is the transform variable and $\bar{f}(s)$ represents the transform of the function $f(t)$. The solutions to these equations are of the form

$$\bar{u} = \alpha \exp(r_0 - r)\sqrt{\frac{s}{D}} + \gamma \exp(r - r_0)\sqrt{\frac{s}{D}} \qquad (13)$$

$$\bar{v} = \beta \exp(r_0 - r)\sqrt{\frac{s}{D}} + \delta \exp(r - r_0)\sqrt{\frac{s}{D}} \qquad (14)$$

where α,β,γ and δ are integration constants which must be determined from the transforms of the boundary conditions. They are functions of s but not of r.

From the condition that u and v remain finite as $r \rightarrow \infty$, it follows that $\gamma = \delta = 0$. Transforming the boundary condition of equation 2 gives $\alpha = \beta$. From equations 12 and 13 it is apparent that α and β are simply the transformed values of the functions u and v, respectively, at the electrode surface. Inverse transformation gives $u = v$ at $r = r_0$. Combining this relation with the boundary condition of equation 3 gives an explicit expression for u and v at the electrode surface as a function of time.

$$u_s = v_s = r_0 C_{\mathrm{O}}\left[\frac{1 - \exp(-at)}{1 + \theta\exp(-at)}\right] \qquad (15)$$

If the expression in brackets is represented as ψ, the transformed expression for the concentration of the oxidized form becomes

$$\bar{u} = r_0 C^*_{\mathrm{O}}\bar{\psi}\exp(r_0 - r)\sqrt{s/D} \qquad (16)$$

The current at the electrode is

$$i = nFAD(\partial C_{\mathrm{O}}/\partial r)_{r=r_0} = nFADu_s/r^2{}_0 - nFAD\frac{1}{r_0}(\partial u/\partial r)_{r=r0} \qquad (17)$$

The first term on the right-hand side can be evaluated from equation 15. By substituting equation 16 into equation 17 it can be shown that the second term in the latter equation is the inverse-transform of the expression

$$nFAC^*_{\mathrm{O}}\bar{\psi}\sqrt{sD}$$

Since $\psi = 0$ at $t = 0$, s is the transform of $(\partial\psi/\partial t)$. From this fact, by means of the convolution integral[9] the above expression becomes

$$-nFAC\sqrt{\frac{aD}{\pi}}\int_0^t \frac{1}{\sqrt{t - \tau}}\operatorname{sech}^2\left[\frac{\ln\theta - a\tau}{2}\right]d\tau \qquad (18)$$

This is the same expression as that obtained by Ševčik[2] for the current at a plane electrode under these conditions.

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(7) J. W. Ross, R. D. Demars and I. Shain, *Anal. Chem.*, **28**, 1768 (1956).

(8) I. Shain, private communication.

(9) For a detailed discussion see, for example, R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., New York, N. Y., 1954.