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Studies on the Rising Portion of Reversible Polarographic Waves

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An expression for the instantaneous current of a reversible reaction at the dropping mercury electrode at any potential has been derived. Based on this and the Lingane–Loveridge correction term, expressions for the variation of the ratio $\bar{i}/i_{\max}$ and $i_{\max}/\sqrt{h}$ along the rising portion of the wave were derived and experimentally tested.

Introduction

In a previous publication,[1] we discussed the variation of β (the ratio of the mean current at a dropping mercury electrode to the maximum current) in the rising portion of irreversible polarographic waves. A large variation in β was found experimentally in the case of the irreversible reduction of hexaquonickel ion, as had been predicted theoretically. By way of control experiments, determinations of β were also made over the rising portions of certain reversible waves. An unexpected inconstancy of β was observed in some of these cases; interpretation of this effect has given rise to the present paper.

Reversible Processes at a Plane Electrode.—Consider the reversible electroreduction

$$\mathrm{Ox} + N\mathrm{e}^- \rightleftharpoons \mathrm{Rd} \qquad (1)$$

occurring at a plane electrode of area A. We will assume that Rd is either soluble in the solution or in the electrode material and that the concentration of Rd in the bulk of the solution (or in the bulk of the electrode material) is at all times negligible. The concentration of Ox in the bulk of the solution is constant and equal to C^∞. It will also be assumed that mass transfer of Ox and Rd to or from the electrode surface is governed by diffusive processes only (this will be true *e.g.* if the solution contains a large excess of indifferent electrolyte).

If it is assumed that equation 1 represents an electron transfer reaction that is both reversible and rapid (compared with rates of diffusion), the Nernst relationship

$$\frac{f_{\mathrm{ox}}C^0_{\mathrm{ox}}}{f_{\mathrm{rd}}C^0_{\mathrm{rd}}} = \exp\frac{NF}{RT}(E - E_0) \qquad (2)$$

must apply at the electrode surface at all instants in time. E_0 is the reversible thermodynamic potential of the Ox/Rd system, E is the potential applied to the cell (in volts), F, R and T have their usual significance, f_{ox}, f_{rd}, C^0_{ox} and C^0_{rd} are activity coefficients and surface concentrations of Ox and Rd. If the experimental conditions are such that the activity coefficients may be assumed to be invariant, the Nernst equation may be written in the form

$$\frac{C^0_{\mathrm{ox}}}{C^0_{\mathrm{rd}}} = \exp\frac{NF}{RT}(E - E_0') \qquad (3)$$

where E_0' is a constant. Fick's second law must govern the diffusion of Ox to the interface and the diffusion of Rd away from it. Let it be supposed that at time $t = 0$, the electrode is at such a potential that no reaction occurs, but that an effective potential, E, is applied thereafter. Fick's second law can then be solved for Ox under the following appropriate conditions

$$\begin{aligned} C_{\mathrm{ox}} &= C^\infty,\ x = \infty,\ t \geqslant 0 \\ C_{\mathrm{ox}} &= C^\infty,\ x = 0,\ t = 0 \\ C_{\mathrm{ox}} &= C^0_{\mathrm{ox}},\ x = 0,\ t > 0 \end{aligned} \qquad (4)$$

where x represents the distance coördinate measured from the electrode surface. The solution is

$$(C_{\mathrm{ox}})_{x,t} = C^\infty \operatorname{erf}\frac{x}{2\sqrt{D_{\mathrm{ox}}t}} + C^0_{\mathrm{ox}} \operatorname{erfc}\frac{x}{2\sqrt{D_{\mathrm{ox}}t}} \qquad (5)$$

where D_{ox} is the diffusion coefficient of Ox and

$$1 - \operatorname{erfc} y = \operatorname{erf} y = \frac{2}{\sqrt{\pi}}\int_0^y \exp(-y^2)\,\mathrm{d}y \qquad (6)$$

Similarly, solution of Fick's second law for Rd under the boundary conditions

$$\begin{aligned} C_{\mathrm{rd}} &= 0,\ x = \infty,\ t \geqslant 0 \\ C_{\mathrm{rd}} &= 0,\ x = 0,\ t = 0 \\ C_{\mathrm{rd}} &= C^0_{\mathrm{rd}},\ x = 0,\ t > 0 \end{aligned} \qquad (7)$$

gives

$$(C_{\mathrm{rd}})_{x,t} = C^0_{\mathrm{rd}} \operatorname{erfc}\frac{x}{2\sqrt{D_{\mathrm{rd}}t}} \qquad (8)$$

By Fick's first law, the current, i_t, at any instant will be given by

$$i_t = NAFD_{\mathrm{ox}}\left(\frac{\partial C_{\mathrm{ox}}}{\partial x}\right)_{0,t} = NAFD_{\mathrm{rd}}\left(\frac{\partial C_{\mathrm{rd}}}{\partial x}\right)_{0,t} \qquad (9)$$

From equations 5, 8 and 9, two separate equations for i_t may be derived, thus

$$i_t = NAF(C^\infty - C^0_{\mathrm{ox}})\sqrt{\frac{D_{\mathrm{ox}}}{\pi t}} = NAFC^0_{\mathrm{rd}}\sqrt{\frac{D_{\mathrm{rd}}}{\pi t}} \qquad (10)$$

Solution of equations 3 and 10 gives

$$i_t = \frac{NAFC^\infty\sqrt{D_{\mathrm{ox}}D_{\mathrm{rd}}}}{\sqrt{D_{\mathrm{rd}}\,\pi t} + \sqrt{D_{\mathrm{ox}}\,\pi t}\,\exp\frac{NF}{RT}(E - E_0')} \qquad (11)$$

The limiting form of equation 11 as E becomes very negative corresponds to complete concentration polarization of the electrode with respect to Ox. In this case it reduces to a form which is identical with the previously derived[2] equation for a diffusion current at a plane electrode.

Application to the Dropping Mercury Electrode

It has been shown[3] that, to a good approximation, the diffusion limited current at an expanding spherical electrode is related to that at a plane electrode by the inclusion of the factor $(7/3)^{1/2}$. Solution of the expanding spherical electrode problem for an electrode process involving Nernst-equilibrium limitations in addition to diffusion limita-

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(1) P. Kivalo, K. B. Oldham and H. A. Laitinen, THIS JOURNAL, **75**, 4148 (1953).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 24.

(3) D. Ilkovic, *J. chim. phys.*, **35**, 129 (1938); see also ref. 2, p. 35 *et seq.*

tions, differs from the solution of the similar problem involving diffusion control alone, only by involving different (potential dependent) boundary conditions. The imposition of these different boundary conditions does not affect the solution as regards its relation to the corresponding plane electrode problem. Hence simple multiplication of the right-hand side of equation 11 by $(7/3)^{1/2}$ gives an expression for the instantaneous current at any potential on a reversible polarographic wave. In the case of a dropping mercury electrode, the instantaneous area may be expressed in terms of d, the density of mercury, m, the rate of flow of mercury through the capillary and t, the age of the drop. Thus the following expression for the current of a reversible reaction at a dropping mercury electrode, at any potential and at any instant, t, in the drop life, may be derived

$$i_t = \sqrt{\frac{7}{3}}\left(\frac{36\pi}{d^2}\right)^{1/3} NFC^{\infty}\,\frac{m^{2/3}t^{1/6}}{\sqrt{\pi}} \times \left[\frac{\sqrt{D_{ox}D_{rd}}}{\sqrt{D_{rd}} + \sqrt{D_{ox}}\exp\frac{NF}{RT}(E - E_0')}\right] \quad (12)$$

at all points in a reversible polarographic reduction wave. Experimentally this is not the case and it follows that equation 12 does not therefore adequately represent the true conditions pertaining at the dropping mercury electrode.

The above derivation neglects the curvature of the expanding spherical electrode. This factor was similarly neglected in the derivation of the Ilkovic equation. Recent revisions of the Ilkovic equation[6-8] have taken the curvature into account; an additional term is thereby introduced into the expression for the surface flux

$$D\left(\frac{\partial C}{\partial x}\right)_{0,t} = C^{\infty}\left[\sqrt{\frac{7D}{3\pi t}} \pm \left(\frac{4\pi d}{3mt}\right)^{1/3} D\right] \quad (15)$$

The plus sign applies to the flux in the solution while the minus sign is applicable if diffusion occurs in the mercury. Though it is only approximate, this correction has proved useful in giving much better experimental agreement than the unmodified Ilkovic equation.[9] If similar correction terms are included in the present derivation, equation 12 becomes modified to

$$i_t = \frac{Pm^{2/3}t^{1/6}\sqrt{D_{ox}D_{rd}}\,(1 + QD_{ox}^{1/2}t^{1/6}m^{-1/3})\,(1 \pm QD_{rd}^{1/2}t^{1/6}m^{-1/3})}{\sqrt{D_{rd}}\,(1 \pm QD_{rd}^{1/2}t^{1/6}m^{-1/3}) + \sqrt{D_{ox}}\left[\exp\frac{NF}{RT}(E - E_0')\right](1 + QD_{ox}^{1/2}t^{1/6}m^{-1/3})} \quad (16)$$

This equation has the same inherent accuracy as the Ilkovic equation, to which it reduces when $-E$ assumes large values.

Effect of Variation of Mercury Head.—It has been shown[4] that for a given dropping mercury capillary in a given solution, m is directly proportional to h, the effective mercury head (the actual reservoir height less a small correction term); whereas t_m, the drop time, is inversely proportional to h. If the values of m and t_m, m_0 and $(t_m)_0$ are known at a certain value, h_0, of h, it follows that

$$m^{2/3}t_m^{1/6} = \frac{m_0^{2/3}(t_m)_0^{1/6}}{h_0^{1/2}}\sqrt{h} \quad (13)$$

If i_m represents the maximum current at any potential (*i.e.*, the value of i_t when $t = t_m$) and $(i_m)_0$ is the value of i_m when $h = h_0$, it is readily demonstrated from equations 12 and 13 that the ratio $i_m/(i_m)_0$ is equal to the square root of the ratio h/h_0 at all points on the wave.

The β-Function.—The function β will be defined (as in previous papers[1,5]) as the ratio, at any point of the wave, of the mean current, $\bar{i}$, to the maximum current, i_m, at the instant $t = t_m$. Hence

$$\beta = \frac{\int_0^{t_m} i_t \mathrm{d}t}{t_m i_m} \quad (14)$$

From equation 12, it follows directly that $\beta = 6/7$, throughout the entire wave.

Modification of Equation 12

The results of the two preceding sections show that equation 12 predicts that a plot of $i_m/(i_m)_0$ *vs.* $\sqrt{h/h_0}$ should give a straight line of gradient unity and that β should have the constant value 0.857

where P and Q are constants for a given solution

$$P = \sqrt{\frac{7}{3\pi}}\left(\frac{36\pi}{d^2}\right)^{1/3} NFC^{\infty} = 709NC^{\infty} \quad (17)$$

$$Q = \sqrt{\frac{3\pi}{7}}\left(\frac{4\pi d}{3}\right)^{1/3} = 44.6 \quad (18)$$

The numerical constants apply at 25° when the variables are expressed in their usual polarographic units. Algebraic manipulation of equation 16 gives

$$\log\frac{(i_d)_m - i_m}{i_m} = \log\frac{\sqrt{D_{ox}}\,(1 + QD_{ox}^{1/2}t_m^{1/6}m^{-1/3})}{\sqrt{D_{rd}}\,(1 \pm QD_{rd}^{1/2}t_m^{1/6}m^{-1/3})} + \frac{NF\log e}{RT}(E - E_0') \quad (19)$$

It is apparent that "the log plot slope" remains unaltered by the introduction of the correction terms. However, apart from the exceptional cases where $D_{ox} = D_{rd}$ and Rd is soluble in the solution, it follows that the position of the wave along the potential axis is dependent on the capillary constants. Consider a typical example of the reduction of a monovalent cation to a metal soluble in mercury. Taking $D_{ox} = D_{rd} = 10^{-5}$ cm.^{2} sec.$^{-1}$ and $t_m = 4$ sec., equation 19 predicts that for a change of m from 0.5 to 3 mg. sec.$^{-1}$ the whole wave will be shifted by some 5 millivolts toward positive potentials. This is not a large effect but does illustrate the impossibility of reproducing half-wave potentials to better than a few millivolts when using different capillaries. It is equally apparent from equation 19 that, in general, the ratio

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[4] Reference 2, pages 78 *et seq.*

[5] N. S. Hush and K. B. Oldham, *Nature*, in press (1953).

[6] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

[7] T. Kambara and I. Tachi, *Proc. I Pol. Cong. I, Prague, Czech.*, 126 (1951).

[8] H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[9] L. Meites and T. Meites, THIS JOURNAL, **72**, 4843 (1950).

γ_m, defined as $i_m/(i_d)_m$, will not be constant at a given potential with varying values of h.

Equation 16 is the fundamental equation relating the variables t, E and i; it may be written in the more convenient form

$$i_t = Pm^{2/3}t^{1/6} \bigg/ \left(\frac{1}{\sqrt{D_{ox}}\,(1 + QD_{ox}^{1/2}t^{1/6}m^{-1/3})} + \frac{\exp \dfrac{NF}{RT}(E - E_0')}{\sqrt{D_{rd}}\,(1 \pm QD_{rd}^{1/2}t^{1/6}m^{-1/3})} \right) \quad (20)$$

In the upper reaches of the wave (and on the diffusion plateau itself) the first term in the denominator of equation 20 becomes predominant and therefore the correction factor in the second denominator term may be neglected. Hence, for the head of the wave

$$i_t = \frac{Pm^{2/3}t^{1/6}\sqrt{D_{ox}D_{rd}}\,(1 + QD_{ox}^{1/2}t^{1/6}m^{-1/3})}{\sqrt{D_{rd}} + \sqrt{D_{ox}} \exp \dfrac{NF}{RT}(E - E_0') + QD_{ox}t^{1/6}m^{-1/3} \exp \dfrac{NF}{RT}(E - E_0')} \quad (21)$$

The third term in the denominator of equation 21 is very small compared with the first and can therefore be neglected; equation 21 reduces to

$$i_t = \frac{Pm^{2/3}t^{1/6}\sqrt{D_{ox}D_{rd}}\,(1 + QD_{ox}^{1/2}t^{1/6}m^{-1/3})}{\sqrt{D_{rd}} + \sqrt{D_{ox}} \exp \dfrac{NF}{RT}(E - E_0')} \quad (22)$$

which is of the form

$$i_t = Bm^{2/3}t^{1/6} + BQD_{ox}^{1/2}m^{1/3}t^{1/3} \quad (23)$$

where B is a constant at a given potential.

A similar approximation can be made for the lower reaches of the curve, giving

$$i_t = Bm^{2/3}t^{1/6} \pm BQD_{rd}^{1/2}m^{1/3}t^{1/3} \quad (24)$$

Equations 23 and 24 should apply to a reasonable degree of accuracy for, say, $i_t > 0.8(i_d)_t$ and $i_t < 0.2(i_d)_t$, respectively.

Effect of Variation of Mercury Head.—From equations 13 and 23, it is readily demonstrated that

$$(i_m)_{\gamma_m > 0.8} = Bm_0^{2/3}(t_m)_0^{1/6}\sqrt{\frac{h}{h_0}} + BQD_{ox}^{1/2}m_0^{1/3}(t_m)_0^{1/3} \quad (25)$$

Also, clearly

$$((i_m)_0)_{\gamma_m > 0.8} = Bm_0^{2/3}(t_m)_0^{1/6} + BQD_{ox}^{1/2}m_0^{1/3}(t_m)_0^{1/3} \quad (26)$$

From equations 25 and 26

$$\left[\frac{i_m}{(i_m)_0}\right]_{\gamma_m > 0.8} = \frac{\sqrt{\dfrac{h}{h_0}} + QD_{ox}^{1/2}m_0^{-1/3}(t_m)_0^{1/6}}{1 + QD_{ox}^{1/2}m_0^{-1/3}(t_m)_0^{1/6}} \quad (27)$$

The analogous expression for the lower reaches of the curve is

$$\left[\frac{i_m}{(i_m)_0}\right]_{\gamma_m < 0.2} = \frac{\sqrt{\dfrac{h}{h_0}} \pm QD^{1/2}m_0^{-1/3}(t_m)_0^{1/6}}{1 \pm QD_{rd}^{1/2}m_0^{-1/3}(t_m)_0^{1/6}} \quad (28)$$

The above theory predicts that plots of $i_m/(i_m)_0$ vs. $\sqrt{h/h_0}$ will give straight lines. but that the gradients will not, in general, be unity. At the head of the wave, the gradients of these plots should be always less than unity by an amount dependent on D_{ox}. At the foot of the wave, the gradient of this graph will be less than or greater than one, depending whether Rd is soluble in the solution or in mercury. From the gradients it is theoretically possible to calculate D_{ox} and D_{rd}.

The β-Function.—From the definition of β (equation 14) and equation 23 we have, for the head of the wave

$$\beta_{(\gamma_m > 0.8)} = \frac{\int_0^{t_m} (m^{2/3}t^{1/6} + QD_{ox}^{1/2}m^{1/3}t^{1/3})\mathrm{d}t}{t_m(m^{2/3}t_m^{1/6} + QD_{ox}^{1/2}m^{1/3}t_m^{1/3})} \quad (29)$$

Performing the integration, we have

$$\beta_{(\gamma_m > 0.8)} = \frac{6}{7}\left(\frac{m^{1/3} + \frac{7}{8}QD_{ox}^{1/2}t_m^{1/6}}{m^{1/3} + QD_{ox}^{1/2}t_m^{1/6}}\right) \quad (30)$$

The second terms in both the numerator and the denominator of equation 30 are small compared with $m^{1/3}$. Hence, to a good approximation, we can write

$$\beta_{(\gamma_m > 0.8)} = \frac{6}{7}\left(1 - \frac{QD_{ox}^{1/2}t_m^{1/6}}{8m^{1/3}}\right) \quad (31)$$

The analogous expression for the foot of the wave is

$$\beta_{(\gamma_m < 0.2)} = \frac{6}{7}\left(1 \mp \frac{QD_{rd}^{1/2}t_m^{1/6}}{8m^{1/3}}\right) \quad (32)$$

The above theory predicts that for large values of γ_m, β will always be less than 6/7; this effect has previously been observed on the diffusion plateau, where γ_m becomes unity.[10] For reversible reductions where the product is soluble in the solution, β will never exceed 6/7 but may vary slightly over the wave if D_{ox} and D_{rd} are sufficiently dissimilar. In cases where the reduction product is soluble in mercury, a marked variation in β is to be expected, β being greater than 6/7 in the initial parts of the wave but decreasing over the wave to give a constant value less than 6/7 as the limiting plateau is approached.

Experimental.—The experimental technique has been described previously.[1]

Results and Discussion

Effect of Variation of Mercury Head.—Equations 27 and 28 were tested using a 4 millimolar cadmium solution, containing 0.2 M potassium nitrate and a 2 millimolar trisethylenediamine-cobalt(III)[11] solution containing 0.1 M potassium chloride and 0.01 M ethylenediamine. As a maximum suppressor, 0.005% gelatin was added to both solutions. In Table I the results are listed. In order to calculate the theoretical gradients, the following data were used: $(t_m)_0$ = 7.85 sec., m_0 = 1.108 mg. sec.$^{-1}$, h_0 = 35.5 cm. Additionally, the following diffusion coefficients were used: $D_{Cd^{++}} = 0.72 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[12] $D_{Cd,Hg} = 1.52 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[13] $D_{Co\ en_3^{+++}} = 0.65 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.[11]

[10] Reference 2, p. 77.

[11] Shown by M. W. Grieb to be reversible; Ph.D. Thesis, University of Illinois, 1953.

[12] Reference 2, p. 52.

[13] Reference 2, p. 201.

Since data are not available, it was assumed that $D_{\text{Co en}_2^{++}} = D_{\text{Co en}_3^{+++}}$.

TABLE I

VARIATION OF CURRENT WITH HEIGHT OF MERCURY COLUMN ALONG RISING PORTION OF WAVE

	γ_m		$d\frac{i_m}{(i_m)_0}/d\sqrt{\frac{h}{h_0}}$	
E vs. S.C.E.	*h* 77.5 cm.	*h* 33.5 cm.	Exptl.	Theor.
		Cadmium(II)		
−0.800	1.00	1.00	0.88	0.86
− .610	0.72	0.71	0.92	..
− .582	.37	.33	1.16	..
− .564	.20	.17	1.47	1.31
		Trisethylenediaminecobalt(III)		
−0.750	1.00	1.00	0.93	0.87
− .650	0.73	0.73	.93	.87
− .450	.37	.37	.93	.87
− .400	.13	.13	.94	.87

As expected for a metal soluble in mercury, the cadmium case shows an increased value of $d(i_m/(i_m)_0)/d\sqrt{h/h_0}$ going along the wave toward more positive potentials. Moreover, this gradient is less than unity at the head of the wave, but greater than one for small values of γ_m. As can be seen, the values of γ_m, quoted for two representative values of *h* in Table I, are not constant at a constant potential. This effect had been predicted to occur in all cases except where D_{ox} and D_{rd} are identical and the reduced form is soluble in the solution phase. The trisethylenediaminecobalt case approximates to this exceptional condition and hence γ_m would here be expected to be constant as is observed experimentally. For the same reason, we should expect $d(i_m/(i_m)_0)/d\sqrt{h/h_0}$ to be nearly constant at a value less than unity for the cobalt complex and this is the experimental result, though the quantitative agreement in this case is not too great.

The β-Function.—The testing of equations 31 and 32 was performed using the same solutions as mentioned above. In calculating the theoretical expressions, the following values were used: t = 4.50 sec. (h = 58.5 cm.), m = 1.935 mg. sec.$^{-1}$. The results are shown in Table II.

Again, the agreement with theory is seen to be good, especially in the qualitative sense. As predicted for reduction to a metal soluble in mercury, the β-value for the cadmium case is less than 0.857 at the head of the wave, but increases with decreasing γ_m ratio to acquire a value considerably in excess of 6/7 at the foot of the wave. The cobalt complex shows a nearly constant β-value, which is less than 0.857 in accordance with equations 31 and 32.

TABLE II

BEHAVIOR OF β-FUNCTION ALONG RISING PORTION OF WAVE

		β	
E vs. S.C.E.	γ_m	Exptl.	Theor.
	Cadmium(II)		
−0.800	1.0	0.83	0.845
− .700	1.0	.83	.845
− .650	0.97	.83	.845
− .625	.87	.85	.845
− .600	.62	.88	...
− .576	.30	.89	...
− .550	.10	.91	.880
− .540	.07	.90	.880
	Trisethylenediaminecobalt(III)		
−0.850	1.0	0.83	0.845
− .750	1.0	.83	.845
− .650	0.73	.84	...
− .500	.51	.84	...
− .450	.37	.85	...
− .400	.13	.85	.845

Thallous ion and quinone were found to show similar behaviors to cadmium and the cobalt complex, respectively.

Conclusion

It has theoretically been shown and experimentally verified that the current in a reversible polarographic reduction at the foot of the wave is governed by the diffusion of the reduced form, whereas in the upper reaches of the wave, the diffusion of the oxidized form is the limiting factor.

A derivation which does not take into account the curvature of the electrode does not permit the effect to be readily observed. The Lingane–Loveridge correction term has therefore been used in this treatment.

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