Hg_2Cl_2, $(Cl^-) = 1$. This value at 30° was evaluated by graphical extrapolation of the e.m.f. values for the cell $Hg|Hg_2Cl_2, HCl|H_2$ at 30° derived from the data of Ellis[4] and E_0 was the required potential of the molybdenum system referred to the standard hydrogen electrode.

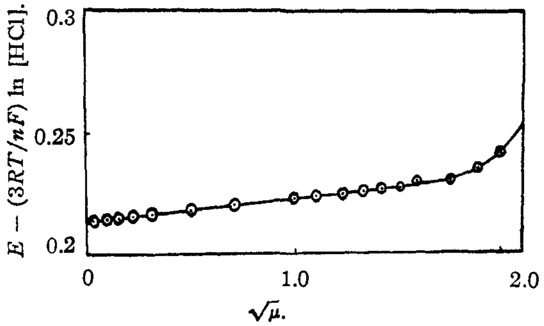

Fig. 4.

The equation for the relationship between E and E_0 can be rearranged as

$$E - \frac{3RT}{nF} \ln [HCl] = E_0' + \frac{RT}{nF} \text{n} f_2 f^3{}_{HCl}/f_1$$

The values for the left-hand side of this equation are plotted against $\sqrt{\mu}$ on the curve shown in Fig. 4. From the plot it becomes clear that graphical extrapolation can lead to a reliable limiting value for E_0' which was found to be 0.2145 v. This gave $E_0 = 0.2145 + 0.2680 = 0.4825$ v. which agrees very well with the value 0.4826 v. obtained against the hydrogen electrode. The fact that the set of oxidation–reduction potentials below 3 N acid, when plotted against $\sqrt{\mu}$, lie on a straight line which can be extrapolated to zero ionic strength, permits the evaluation of E_0 if it is assumed that the profound effect of hydrochloric acid on the molybdenum ions would vanish at infinite dilution. However, in the absence of any other evidence as to the species of molybdenum ions present in solution at zero acid concentration, it is necessary to be very cautious with regard to designation of the extrapolated value as a true standard potential of the Mo(VI)–Mo(V) system.

ALEXANDRIA, EGYPT

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Theory of Irreversible Waves in Oscillographic Polarography

BY PAUL DELAHAY

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A theoretical treatment of irreversible oscillographic waves is developed for the case of a linear variation of the electrode potential. This treatment is based on the following hypotheses: 1. The rate of electron transfer is proportional to the concentration of the substance reacting at the electrode surface. 2. The rate of electron transfer is an exponential function of the electrode potential. The boundary value problem is solved by expressing the concentration of reacting species at the electrode surface in terms of the flux of this substance at the electrode surface, and by solving the resulting integral equation. The current–potential curve exhibits a peak whose height is proportional to various factors among which the most important are: the concentration of reducible substance, the square root of the rate of potential change, the number of electrons involved in the over-all electrochemical process, the square root of the transfer coefficient, and the square root of the number of electrons involved in the rate-determining step. The potential corresponding to the peak of the wave is calculated, and it is shown that this potential is a function of the rate of potential change. The theoretical conclusions are in good agreement with experimental data for the reduction of zinc tetrammine ion. Some features of the oscillographic method in which the anodic wave is recorded immediately after the cathodic wave, are also discussed.

Introduction

In a series of papers,[1-4] it was recently shown that the polarographic method is a powerful tool in the quantitative study of the kinetics of irreversible electrode processes. In conventional polarography it is not possible to study in the same experiment both the cathodic and anodic reactions corresponding to an oxidation-reduction system, but this result can be achieved by applying the oscillographic method originated by Heyrovsky[5] and improved by Sevcik.[6] In this oscillographic method, a substance Ox is reduced at the dropping mercury electrode by varying rapidly the potential of this electrode toward increasingly cathodic values. The substance Red resulting from the reduction of substance Ox is then reoxidized by bringing the potential back to its original value. By comparing the cathodic and anodic patterns thus obtained, one can decide whether the electrode process is virtually reversible or irreversible. These studies of the Czechoslovak school, although interesting, were of a purely qualitative nature, and the value of this very ingenious method would be enhanced if a quantitative treatment of irreversible oscillographic waves were available. Such a treatment is reported here.

The present work constitutes the solution of one of the three fundamental problems of the theory of oscillographic polarography. The other two problems deal with electrode processes for which it can be assumed that equilibrium is achieved either between two soluble species or between a soluble and an insoluble species. The theory of the former type of oscillographic waves was reported independently by Randles[7] and Sevcik,[6] whereas the treatment of the latter type of waves was developed in this Laboratory.[8]

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(1) P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

(2) P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

(3) J. E. Strassner and P. Delahay, *ibid.*, **74**, 6232 (1952).

(4) P. Delahay, *ibid.*, in course of publication.

(5) J. Heyrovsky, *Faraday Soc. Disc.*, **1**, 212 (1947); several references to previous papers dealing with the same topic are quoted in this review.

(6) A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 349 (1948).

(7) J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948).

(8) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 555 (1953).

Initial and Boundary Conditions

Consider the irreversible electrolytic reduction of a substance Ox to another substance Red. Furthermore, assume that the potentials at which substance Ox is reduced, are such that the influence of the anodic process, *i.e.*, the oxidation of substance Red, is negligible. This assumption is entirely justified for the majority of the irreversible waves which are encountered in oscillographic polarography. If the electrolytic reduction of substance Ox is a first-order process, its rate $q(t)$ is given by an equation of the type

$$q(t) = k_f C(o,t) \tag{1}$$

where $q(t)$ represents the number of moles of substance Ox being reduced per unit of time and per unit area t sec. after the beginning of the electrolysis; k_f is the rate constant for the electrode process at the potential at which the rate is measured; and $C(o, t)$ is the value—at the electrode surface—of the function $C(x, t)$ representing the concentration of substance Ox as a function of the distance x from the electrode and the time t.

In order to calculate the current corresponding to the above reaction, it is necessary to determine the function $C(x, t)$. Such a problem is solved by applying Fick's second law, *i.e.*, by solving the partial differential equation for the corresponding diffusion problem. For the sake of simplicity it will be assumed here that the electrode is plane. In the case of the dropping mercury electrode, this simplifying hypothesis is entirely justified because the influence of the curvature of the electrode can be neglected[9] on account of the short duration of the recording of a wave (less than 1 sec.).

The boundary condition for the present problem is obtained by equating the rate $q(t)$ to the flux of substance Ox at the electrode surface. Thus

$$q(t) = k_f C(o,t) = D\,(\partial C(o,t)/\partial x) \tag{2}$$

where D is the diffusion coefficient of substance Ox, and t is the time elapsed since the beginning of the electrolysis.

The boundary condition (2) is also encountered in the theory of irreversible waves in conventional polarography,[1,2] but there, k_f can be assumed to be independent of time since the potential of the dropping mercury electrode is virtually constant during the drop life. In oscillographic polarography, such an hypothesis cannot be made, and it is necessary to introduce, at this stage of the deviation, a relationship between the rate constant k_f and the potential of the dropping mercury electrode. As it has been shown in various experimental studies and also in a development of the absolute rate theory, the rate constant k_f is in many cases an exponential function of the electrode potential. Therefore, if one assumes that the potential during the electrolysis varies linearly with time, as it is the case in the Sevcik method,[6] the rate constant k_f is determined by the equation

$$k_f = k_0 \exp{(\beta t)} \tag{3}$$

where k_0 and β are constants depending on the relationship between the electrode potential and time. The values of k_0 and β will be explicitated below.

The combination of equations (2) and (3) yields the boundary condition for the present problem. The initial condition, on the other hand, is simply $C(x, 0) = C_0$, where C_0 is the original concentration of substance Ox.

Derivation of the Current

The solution of the diffusion problem for the boundary condition derived in the previous section involved serious difficulties because of the presence of the function of time $\exp(\beta t)$ in the boundary condition. Such an elegant method as the Laplace transformation cannot be applied, and it is necessary to use a less direct approach. The problem, however, can be solved if one considers that, from the point of view of oscillographic polarography, it is not necessary to know $C(x, t)$, but that it is sufficient to calculate the flux of reducible substance at the electrode surface. Once the flux is known as a function of time, the derivation of the current is a trivial matter.

The concentration $C(o, t)$ can be expressed in terms of the flux $q(t)$ by applying Duhamel's theorem.[10] Thus

$$C(x,t) = C_0 - \frac{1}{(\pi D)^{1/2}} \int_0^t q(t - \tau) \exp\left(-\frac{x^2}{4D\tau}\right) \frac{d\tau}{\tau^{1/2}} \tag{4}$$

where τ is an auxiliary variable of time. By introducing into equation (4) the following value of the function $q(t)$, as obtained from (2) and (3)

$$q(t) = k_0 \exp{(\beta t)}\; C(o,t) \tag{5}$$

and by transforming the resulting equation after the introduction of the function $\varphi(t)$ and the variable θ defined below, one obtains a Volterra integral equation of the second kind.[11] Thus

$$\varphi(t) = C(o,t)/C_0 \tag{6}$$

$$\theta = t - \tau \tag{7}$$

and

$$\varphi(t) = 1 - \frac{k_0}{(\pi D)^{1/2}} \int_0^t \varphi(\theta) \exp{(\beta\theta)} \frac{d\theta}{(t - \theta)^{1/2}} \tag{8}$$

Further transformation of equation (8) is desirable because of the numerical values of k_0 and β involved in the present problem (see below). By making the substitutions

$$y = \beta t \tag{9}$$

$$z = \beta\theta \tag{10}$$

$$\frac{k_0}{(\pi\beta D)^{1/2}} = \exp{(-a)} \tag{11}$$

$$\psi(y) = \varphi(t) \tag{12}$$

equation (8) becomes

$$\psi(y) = 1 - \int_0^y \psi(z) \exp{(z - a)} \frac{dz}{(y - z)^{1/2}} \tag{13}$$

This equation will be used below in the course of the discussion, but it is convenient to make one further substitution and to introduce the function $\chi(y)$ defined by

$$\chi(y) = \psi(y) \exp{(y - a)} \tag{14}$$

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(9) The validity of this assertion can be verified by comparing equations for linear and spherical diffusion which are given, for example, by I. M. Kolthoff and J. J. Lingane in "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, Chapter II.

(10) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, Oxford, 1947, p. 57, eq. (9).

(11) For a general discussion of integral equations see for example H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, Chapt. XIV. Reference to classics in the field are given in this book.

where $\chi(y)$ is proportional to the flux as follows from equations (5), (6) and (12).

The combination of (13) and (14) yields

$$\chi(y) = \exp(y - a) - \exp(y - a)\int_0^y \chi(z)\frac{\mathrm{d}z}{(y - z)^{1/2}} \qquad (15)$$

Using intervals of width h and letting $y = ph$ and $z = \mu h$, one may approximate the integral in equation (15) by the sum

$$\int_0^{pk} \chi(z)\frac{\mathrm{d}z}{(y - z)^{1/2}} = \sum_{\mu=0}^{\mu=p} B_\mu \chi(ph - \mu h) \qquad (16)$$

To determine the values of B_μ, Huber[12] approximated the unknown function by linear expressions in the individual intervals, but a greater accuracy is obtained by using a quadratic expression for each two consecutive intervals as was recently suggested by Wagner.[13] In the following calculations Wagner's procedure has been used.

By substituting the value of the integral (16) in equation (15), one obtains the recurrence formula

$$\chi(ph) = \frac{1 - \sum_{\mu=1}^{\mu=p} B_\mu \chi(ph - \mu h)}{\exp(a - ph) + B_0} \qquad (17)$$

From (17), the stepwise calculation of the current is immediate if one recalls that the current is the product of the flux of reducible substance at the electrode surface by the charge involved in the reduction in one mole of reducible substance. Combining (5), (6), (11), (12) and (14), one obtains

$$i = nFA\pi^{1/2}\beta^{1/2}D^{1/2}C_0\chi(\beta t) \qquad (18)$$

where n is the number of electrons involved in the electrode process; F the faraday; A the electrode area, and the other symbols have already been defined.

From (18) it is seen that the current i is known provided that the function $\chi(\beta t)$ is known. In principle, it is necessary to determine $\chi(\beta t)$ for a wide range of values of the parameter a defined by (11), *i.e.*, for various values of the rate constant k_0 at time $t = 0$ (see equation (3)). In oscillographic polarography k_0 is always much smaller than $(\pi\beta D)^{1/2}$ and thus, according to equation (11), $\exp(-a) << 1$. If $\exp(-a)$ is smaller than 10^{-3}, it is sufficient to compute the solution of equation (15) for only one particular value of a, *e.g.*, $a = 7$, whereupon values of $\chi(y)$ for $a > 7$ may be obtained with the aid of the transformation in equation (23). This can be shown in the following manner.

Letting $s = y - z$, equation (13) can be rewritten in the form

$$\psi(y) = 1 - \int_0^y \psi(y - s)\exp(y - s - a)\frac{\mathrm{d}s}{s^{1/2}} \qquad (19)$$

The solution $\psi(y)$ depends upon the value of a in (19), *i.e.*, on the initial rate constant k_0 (see eq. (11)). If a in (19) is replaced by a larger value $a = a + \Delta a$, another solution $\psi^*(y)$ defined by (20) is to be expected. Thus

$$\psi^*(y) = 1 - \int_0^y \psi^*(y - s)\exp(y - s - a - \Delta a)\frac{\mathrm{d}s}{s^{1/2}} \qquad (20)$$

For the argument $y + \Delta a$ one has from (20) after subdividing the integral

$$\psi^*(y + \Delta a) = 1 - \int_0^y \psi^*(y + \Delta a - s)\exp(y - s - a)\frac{\mathrm{d}s}{s^{1/2}} - \int_y^{y+\Delta a} \psi^*(y + \Delta a - s)\exp(y - s - a)\frac{\mathrm{d}s}{s^{1/2}} \qquad (21)$$

Since $\psi^*(y + \Delta a)$ is smaller than unity in view of (6) and (12), the second integral in (21) practically vanishes if the exponential $\exp(-a)$ is much smaller than unity. This will be so for sufficiently large values of a. By comparing equations (19) and (21), it follows that

$$\psi^*(y + \Delta a) = \psi(y) \qquad (22)$$

In view of equations (14) and (22) the function $\chi^*(y)$ for a parameter $a + \Delta a$ is obtained from $\chi(y)$ for parameter a by the following transformation

$$\chi^*(y) = \chi(y - \Delta a) \qquad (23)$$

Consequently, once a solution has been found for (19), *i.e.*, for (17), for a sufficiently high value of a, the solution for any greater value $a + \Delta a$ of the parameter a is readily obtained from (23). *In other words, in a plot of $\chi(y)$ vs. y, curves for $\chi^*(y)$ are displaced by Δa in the direction of the abscissa.*

On the basis of the above reasoning, the function $\chi(\beta t)$ was calculated for a single value of the parameter a, and the value $a = 7$, which approximately corresponds to $k_0 = 10^{-3}(\pi\beta D)^{1/2}$, was selected. Values of the function $\chi(\beta t)$ were calculated from (17) by using an interval $h = 0.2$. The resulting curve is plotted in Fig. 1. Forty points of this curve were determined from $\beta t = 0$ to $\beta t = 7.8$. Values of $\chi(\beta t)$ for values of βt larger than 7.8 were not calculated because the numerical calculations become somewhat uncertain. In view of practical applications, however, the descending branch is not of great interest.

Notice that $\chi(\beta t)$ exhibits a maximum equal to 0.282. The value of the maximum can, conservatively, be estimated to be correct within 1%. For $a = 7$, the maximum corresponds to a value of $y = \beta t = 7.20$. In view of equation (23) the general relation is $y_{\max} = a + 0.20$.

Properties of Irreversible Oscillographic Waves

Up to this point the equation for oscillographic waves has been discussed in terms of the rate constant defined by equation (3). In order to derive the characteristic features of oscillographic waves it is necessary to explicitate the coefficients k_0 and β in equation (3).

Recalling that the electrode potential varies linearly with time, one can write

$$E = E_i - vt \qquad (24)$$

where E_i is the initial potential and v is the rate of potential change. By introducing this value of the electrode potential in the equation for k_f which has been derived by application of the absolute rate theory,[14] one obtains

$$k_0 = \frac{kT}{h}\,\delta\exp[(-\Delta G^{\ddagger} - \alpha n_a FE_i)/RT] \qquad (25)$$

$$\beta = \alpha n_a F/RT \qquad (26)$$

where k is the Boltzmann constant; h the Planck constant; δ is of the order of the average distance in solution, between two molecules or ions of the

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(12) A. Huber, *Monatshefte f. Mathematik, u. Physik*, **47**, 240 (1939).

(13) C. Wagner, to be published elsewhere.

(14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., pp. 584–587.

reducible substance; $\Delta G^{\ddagger}$ the free energy of activation for the reduction of substance Ox; n_a the number of electrons involved in the rate-determining reaction; α the transfer coefficient; and the other notations are conventional or have already been defined.

Peak Current.—By combining equation (18) and (26) and introducing the value $\chi(\beta t) = 0.282$ corresponding to the peak of the function $\chi(\beta t)$, one obtains the following fundamental equation for the peak current of irreversible oscillographic waves

$$i_p = \frac{0.282\pi^{1/2}F^{3/2}}{R^{1/2}T^{1/2}}\, n(\alpha n_a)^{1/2}AD^{1/2}C_0v^{1/2} \qquad (27)$$

or at 25°

$$i_p = 3.01 \times 10^5 n(\alpha n_a)^{1/2}AD^{1/2}C_0v^{1/2} \qquad (28)$$

The units in (27) and (28) are as follows: i in amp.; A in cm.^{2}; D in cm.^{2} sec.$^{-1}$; C_0 in moles·cm.$^{-3}$; v in volts·sec.$^{-1}$.

If a dropping mercury electrode is used, one generally expresses the area A in terms of the rate of flow of mercury (m) and the time of the drop life at which the peak current is measured (t). By doing so, one obtains after numerical transformations and for 25°

$$i_p = 2.56 \times 10^5 n(\alpha n_a)^{1/2}m^{2/3}t^{2/3}D^{1/2}C_0v^{1/2} \qquad (29)$$

where the units are the same as in (28), and m and t are in g. sec.$^{-1}$ and sec., respectively.

From equations (27)–(29), it is readily seen that the peak current is proportional to the concentration of reducible substance, to the area of the electrode, and to the square root of the diffusion coefficient of the reducible substance. These features of irreversible peak currents are the same as those for peak currents corresponding to reversible electrode processes.[15] Furthermore, equations (27)–(29) show that the peak current is proportional to the square root of the product (αn_a) of the transfer coefficient α by the number n_a of electrons involved in the rate-determining reaction. This rather unique feature of irreversible oscillographic waves makes it possible to calculate the product αn_a from experimental peak currents. Since n_a is an integer, and an assumption can be made about the value of α,[2,3] it is possible to determine n_a from experimental peak currents. It should be emphasized that the present treatment and consequently the calculation of n_a is valid only when equation (1) is obeyed, *i.e.*, when there are no kinetic complications such as those resulting from a control by the rates of consecutive electrode processes. Furthermore in the calculation of n_a from the peak current, it should be ascertained that the experimental data have been corrected for the various causes of experimental errors that might possibly affect the peak current. Because of these errors it is useful to compare the value of n_a thus obtained by the above procedure with the value of n_a which can be deduced from the shape of the wave as described below.

From the point of view of analytical chemistry, the dependence of the peak current on the transfer coefficient α is a drawback, because variations of α, *i.e.*, variations of i_p, may result from the presence of traces of adsorbable substances in solution.[3]

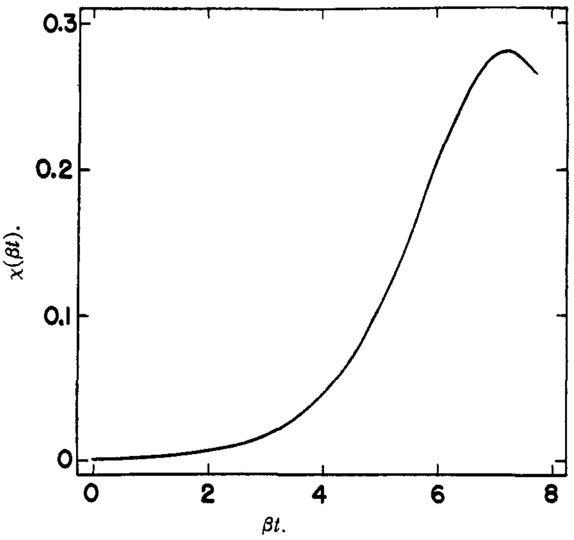

Fig. 1.—Variations of function $\chi(\beta t)$ (eq. (17)) with βt (eq.(6) and (26)). The present curve corresponds to a = 7 (eq. (11)).

From equations (27)–(29), it can be concluded that the peak current is proportional to the square root of the rate of potential change. Experimentally it was observed, by using the multisweep method,[15a] that the curve showing the variations of the peak current with the square root of the rate of potential change exhibits a curvature which becomes more pronounced as the rate of potential change is increased. This effect was attributed to the irreversibility of the electrode process,[15a] and to the combined effect of the resistance of the cell[16] and the progressive depletion of reducible substance from one sweep of potential to another.[17] On the basis of equations (27)–(29) it can be concluded that the curvature in the i_p–$v^{1/2}$ diagrams cannot be attributed to the irreversibility of the electrode process in the case of an electrode reaction whose kinetics obeys equation (1). It should be added, however, that if there are kinetic complications a curvature in the i–$v^{1/2}$ diagram could possibly be expected.

Peak Potential.—From Fig. 1, it is seen that the value of βt corresponding to the peak current is equal to $a + 0.20$. By recalling the definition of a (see eq. (11)), and by introducing the value of β from (26), one obtains the following value of the product vt at the peak potential

$$(vt)_p = \frac{RT}{\alpha n_a F}\left[Q + 1.151 \log \frac{\alpha n_a F}{RT}\, v\right] \qquad (30)$$

where

$$Q = 0.77 + 1.151 \log \beta D - 2.303 \log k_0 \qquad (31)$$

By introducing the product $(vt)_p$ from (30) in equation (24), one obtains the peak potential E_p

$$E_p = E_l - \frac{RT}{\alpha n_a F}\left[Q + 1.151 \log \frac{\alpha n_a F}{RT}\, v\right] \qquad (32)$$

or at 25°

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[15] Compare with the results reported in references 6 and 7.

[15a] P. Delahay, *J. Phys. Colloid Chem.*, **54**, 630 (1950).

[16] P. Delahay and G. L. Stiehl, *ibid.*, **55**, 570 (1951).

[17] P. Delahay and G. Perkins, *ibid.*, **55**, 586 (1951); **55**, 1146 (1951); P. Delahay, *Anal. Chim. Acta*, **5**, 129 (1951).

$$E_p = E_i - \frac{0.02569}{\alpha n_a}\left[Q + 1.151 \log (38.9\ \alpha n_a) + 1.151 \log v\right] \qquad (33)$$

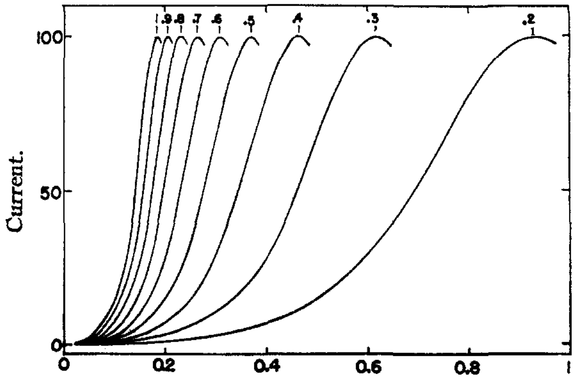
Equation (32) is important because it enables one to calculate the rate constant k_0, and consequently the free energy of activation $\Delta G^{\ddagger}$ (see eq. (25)). In this calculation it is necessary to know the value of the product αn_a, but this datum can be obtained either from the peak current (see above) or by comparing the shapes of experimental and theoretical waves (see below).

From equation (32), it is seen that the peak potential, for a given electrode process, is shifted toward more cathodic values as the rate of potential change is increased. It should be noted, however, that the shift of the peak potential is relatively small. Taking $\alpha n_a = 1$, for example, the shift of E_p at 25° for a tenfold increase in the rate of potential change, is 0.030 volt toward more cathodic values.

Finally, on the basis of equation (23) and the reasoning which led to this equation, it follows that the peak potential is independent of the initial potential provided that the current at this potential is negligible in comparison with the peak current.

Equation of the Wave.—On the basis of equations (11), (18) and (26), one could write the equation for the complete wave in terms of the function $\chi(\beta t)$. The writing is rather heavy and it is much simpler to calculate the current along the wave for predetermined values of αn_a. This is readily done by using the diagram of Fig. 1 and by applying equation (26). Results for 25° are shown in Fig. 2 for values of αn_a from 0.2 to 1. Approximate values of αn_a can be determined by superposing experimental curves on the diagram of Fig. 2.

From Fig. 2 it is seen that oscillographic waves are more drawn out as the product αn_a decreases.



Potential (volt).

Fig. 2.—Oscillographic irreversible waves for various values of αn_a (eq. 26)). Currents are in per cent. of the peak current. The potential $E = 0$ corresponds to $a = 7$ (eq. (11)) for all the waves. Peak potentials are indicated by vertical lines, and the number above each line is the value of αn_a.

Case of an Anodic Wave.—The previous treatment is readily transposed to anodic waves. The following changes should be made: 1. In equation (24), the term $-vt$ should be replaced by $+vt$; 2. In (25) the term $-\alpha n_a F E_i$ should be replaced by $+\alpha n_a F E_i$, α being the transfer coefficient for the anodic process. The second term on the right-hand of (32) and (33) should be preceded by a positive sign.

Experimental

The cathodic–anodic waves were recorded by applying the Sevcik modification of the Heyrovsky method. In this method, a voltage wave exhibiting the shape of an isosceles triangle is applied to the polarographic cell. In the ascending branch of the voltage wave, reduction occurs at the dropping mercury electrode; in the descending branch of the voltage wave, the product resulting from the cathodic process is reoxidized. In the instrument used in this investigation, the voltage wave was generated by integrating the output voltage of a square-wave generator.[18] The output of the integrating circuit was connected to another amplifier having a low output impedance. The polarographic cell was connected to this amplifier. A cathode-ray oscillograph was used for the determination of the current–potential curves. The horizontal deflection was proportional to the voltage applied to the cell, whereas the vertical deflection was proportional to the current flowing through the cell. The instrument which was used in the present investigation is fairly similar to the one described by Loveland and Elving[19] and the reader is referred to the work of these investigators for a description of the circuits.

An H-cell with a saturated calomel electrode was used throughout this work. Long capillaries (20 cm.) were used in order to increase the drop time up to 5–10 seconds. Waves were recorded during the life of a single drop, and the drop life was timed. The temperature was 30 ± 0.1°.

Great care was taken in the calibration of the horizontal scale of the cathode ray tube, *i.e.*, the potential scale. This calibration was obtained by applying a known voltage—measured with a Leeds and Northrup student potentiometer—to the polarographic cell and by tracing on the screen a vertical line corresponding to this voltage. By repeating the operation for a few voltages, the horizontal scale was calibrated and the linearity of the horizontal deflection amplifier could be ascertained.

Description and Discussion of Results

Cathodic and Anodic Current–Potential Curves.—The waves obtained by the Sevcik method for 1 millimolar zinc tetrammine ion in 2 molar ammonium hydroxide +2 molar ammonium chloride +0.01% gelatin are shown in Fig. 3. These waves were recorded with rates of potential change of 14.8 volt sec.$^{-1}$ and 19.9 volt sec.$^{-1}$ for the cathodic and anodic branches, respectively. Waves were recorded during the life of a single drop, but for the sake of clarity, only the pattern corresponding to the maximum size of the mercury drop is shown in Fig. 3.

Since diagrams of the type shown in Fig. 3 were not discussed by Sevcik,[6] the shape of such current–potential curves will be briefly explained. Along curve ABCDEFG, reduction occurs at the electrode. In the initial segment of the wave AB, the rate constant for the electrode process is very small and only the capacity current is virtually observed. As the potential of the dropping mercury electrode becomes more negative, the wave BCD is observed. At point D, the voltage applied to the cell is maximum. As soon as this voltage decreases the capacity current is reversed.[20] Thus, the distance DE represents the double of the

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[18] For a discussion of integrating circuits see for example, I. A. Greenwood, Jr., J. V. Holdam, Jr., and D. Macrae, Jr., "Electronic Instruments," McGraw-Hill Book Co., Inc., New York, N. Y., 1948, Chapter IV.

[19] J. W. Loveland and P. J. Elving, *J. Phys. Chem.*, **56**, 250 (1952).

[20] See for example ref. (16) and (19).

capacity current at the potential corresponding to point D or E. In the region EF the current decreases because of the progressive exhaustion of reducible substance in the vicinity of the electrode. As the potential becomes less cathodic the rate constant for the electrode process decreases and the current decreases accordingly (FG). Afterwards, in the segment GH, the current is essentially determined by the differential capacity of the double layer in this potential range. Neither oxidation nor reduction virtually occurs along the segment GH. At more anodic potentials, the substance, which has been formed at the electrode in the course of the cathodic process, is reoxidized (HIJ). At point J the voltage applied to the cell increases again, and consequently the direction of the capacity current is reversed. Thus the distance JK represents the double of the capacity current at the potential corresponding to point J or K. Along KL the anodic current decreases progressively because of the disappearance of the oxidizable substance. In general the oxidizable form will not be reoxidized completely because of losses by diffusion either in solution or in mercury (in the case of a metal forming an amalgam). The incompleteness of the anodic process is indicated by the variations of current along LA. Such a decrease in the anodic current is caused by a decrease in the rate constant for the anodic process (the potential becomes less anodic). Had the reoxidation process been completed at the potential corresponding to point L, the current would not have virtually changed between L and A, except for a possible variation of the differential capacity of the double layer.

In general it is observed that the cathodic peak potential is shifted toward more negative values as the drop grows. This shift is caused by an increase in the ohmic drop in the cell and the measuring circuit. Likewise, the anodic peak potential is shifted toward more positive or less negative potentials as the drop grows. The shifts in the peak potentials are indicated in Fig. 3 by dotted lines. In order to obtain correct peak potentials it suffices to extrapolate the potential to zero current as indicated in Fig. 3 (points $E_{\text{p,c}}$ and $E_{\text{p,a}}$).

The relative positions of the cathodic and anodic branches depend on the magnitude of the overvoltages involved in the electrode process. For certain electrode reactions the anodic branch is shifted in the potential range where mercury is oxidized, and it is impossible to observe the anodic current–potential curve with a mercury electrode.

From the present discussion, it is seen that the theoretical treatment reported in this paper is applicable to the cathodic branch of the wave. This is not rigorously so, however, for the anodic branch, because the initial distribution of oxidizable substance in the solution or in mercury does not correspond to the semi-infinite diffusion problem which is treated in the present paper, *i.e.*, the initial concentration of oxidizable substance $C(x,o)$ is not independent of x. The mathematical treatment of the problem corresponding to the experimental conditions achieved in the present experiment would be exceedingly intricate, and it is far more convenient, but also less rigorous, to apply the present theory to the anodic segment of the current–potential curve.

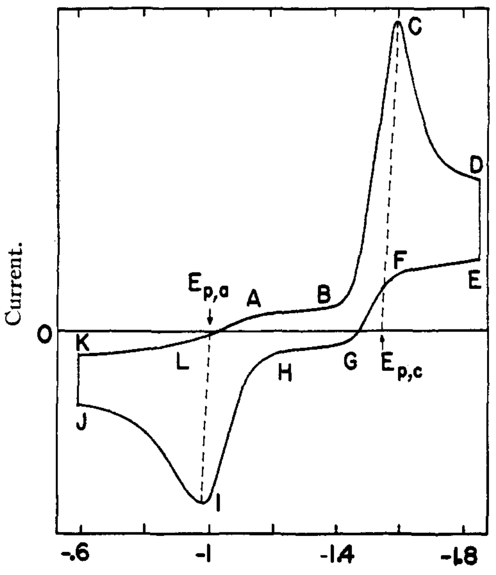

Fig. 3.—Cathodic and anodic waves for zinc tetrammine ion (see text). Potentials are values *versus* the saturated calomel electrode.

The heights of the cathodic and anodic waves are generally not the same since these heights are proportional to the quantity $(\alpha n_a)^{1/2}D^{1/2}$. It is only when this quantity is the same for both the cathodic and anodic processes that one could expect waves of equal heights but, even then, losses of the oxidizable substance by diffusion during the cathodic cycle would cause the anodic peak current to be somewhat smaller than the cathodic peak current. Likewise, the shape of the cathodic and anodic waves will generally not be the same. For example, if αn_a for the anodic process is smaller than for the cathodic process, the anodic wave is more drawn out than the cathodic wave (see Fig. 2).

Verification of Equations (18) and (32).—The present treatment was verified for the case of Fig. 3. The theoretical cathodic and anodic waves corresponding to values of αn_a equal to 1 and 0.6, respectively, are shown in Fig. 4. Dots in the same diagram are experimental currents obtained by correcting the experimental data for the ohmic drop and the capacity current. In the comparison of the experimental and theoretical results, the peak current and peak potential of both the experimental and theoretical waves were assumed to be identical. From Fig. 4 it is seen that the agreement between experimental and calculated values is very good. It should be added, however, that the position of the corrected experimental points is somewhat uncertain mainly on account of the correction for the capacity current. Therefore, the agreement between experiment and theory is possibly not as good as one would infer from Fig. 4. Note that the above value of $\alpha n_a = 1$ is in fairly good agreement with the value $\alpha n_a = 0.93$ which was calculated from data obtained for 35° by the conventional polarographic method.[3]

The free energy of activation $\Delta G^{\ddagger}$ was calculated by application of equation (32) and on the basis of the following data: $\alpha n_a = 1$ (see above), $\delta = 2.55 \times 10^{-7}$ cm., $D = 0.6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$,[21] $v = 14.8$ volts sec.$^{-1}$, $E_p = -1.29$ volts (*versus* N.H.E.). The corresponding activation free energy of 33 kcal. is in good agreement with the value of 37 kcal. obtained by the conventional polarographic method for a temperature of 35°.

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(21) This is an estimated value.

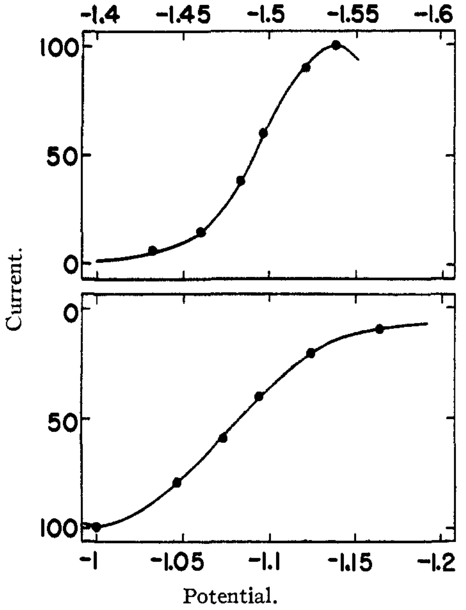

Fig. 4.—Comparison of theoretical and experimental cathodic (top) and anodic waves for zinc tetrammine ion (see text). Curves are theoretical waves and dots are corrected experimental currents. Potentials are referred to the saturated calomel electrode, and currents are in per cent. of the peak current.

As a final comment it is of interest to note that the sum of the products αn_a for the cathodic and anodic processes should be an integer if the anodic and cathodic processes involved the same rate-determining step. This is readily accounted for if one considers that the sum of the transfer coefficient for the cathodic and anodic processes is equal to 1.[14] In the case of the reduction of zinc tetrammine ion (Fig. 3 and 4), the above sum is equal to 1.6. The difference between this value of 1.6 and the next integer, 2, is too large to be accountable by experimental errors. Two explanations can be advanced for this abnormal value of 1.6. First, it can be argued that the theoretical treatment is not rigorous in the case of anodic waves obtained by the present experimental method. This is unquestionably so, but it is doubtful that the change in the shape of the wave would be so drastic as to cause a variation of αn_a (for the anodic wave) from 1 to 0.6 (see Fig. 2). The abnormal value of 1.6 can also be explained by assuming that the electrode process involves two simultaneous rate-determining steps consuming one and two electrons, respectively.[22] If the latter explanation is considered, it should be kept in mind that equation (1) is still valid in the case of a process involving two simultaneous rate-determining steps, but that the parameter k_f represents then the sum of two rate constants. As a result, the present treatment is not rigorously applicable since equation (3) is not obeyed when k_f is the sum of two exponential functions of the electrode potential. However, the sum of two exponential functions can be approximated by an exponential function in a reasonable interval of variation of the variable. Hence, equation (3) can be used as a first approximation, and this accounts for the agreement between experimental and theoretical data as indicated in Fig. 4. Likewise, this explains why the log k_f *vs.* E diagram obtained by the conventional polarographic method is linear.

The above considerations show that kinetic complications can sometimes be detected by calculating the sum of the products αn_a for the cathodic and anodic waves.

Conclusion

The properties of irreversible oscillographic waves are quantitatively accounted for by the theory developed in this paper. In applying the present treatment, it should be kept in mind that the above derivation is valid only for electrode processes whose kinetics obeys equations (1) and (3). Discrepancies resulting from kinetic complications can be detected by comparing the shape of experimental and theoretical waves or by calculating the sum of the products αn_a for the cathodic and anodic waves.

Summarizing, the oscillographic method is to be regarded, from the point of view of electrochemistry, as a useful complement of conventional polarography.

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[22] The latter hypothesis is substantiated by a recent investigation of the reduction of zinc tetrammine ion by the conventional polarographic method. It was observed in this Laboratory by Mr. C. F. Pillon that the product αn_a for the above reduction varies markedly with temperature.