Theory of Irreversible Polarographic Waves—Case of Two Consecutive Electrochemical Reactions
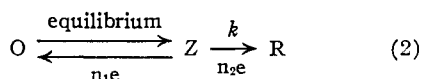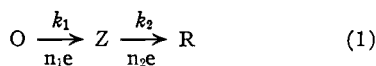
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Rigorous solutions are derived for two boundary value problems corresponding to electrode processes controlled by semi-infinite linear diffusion and by the rates of two consecutive electrochemical reactions. In the first case being treated, the effect of the backward processes is assumed to be negligible; in the second case, electrochemical equilibrium is supposed to be achieved between the substances involved in the first step of the electrode process, and the second step is assumed to be so irreversible that the backward reaction can be neglected. The adaptation of the solutions for linear diffusion to the case of the dropping mercury electrode is briefly discussed, and the commonly accepted interpretation of polarographic waves according to which there is a "potential determining step" in the electrode process is critically examined. It is shown that the usual plot $\log (i_d - i)/i$ vs. potential should not necessarily yield a straight line. The significance of diagrams showing the variations of half-wave potentials with a parameter characterizing a substance in a series of organic substances is also briefly discussed. Application is made to the reduction of chromate ion in 1 molar sodium hydroxide, and it is shown that this reaction proceeds with the intermediate formation of chromium(IV).

Introduction

The theoretical treatment of electrode processes controlled by the rate of an electrochemical reaction and by semi-infinite linear diffusion of the substances involved in the electrode process was developed in this Laboratory[1a-1d] and, independently, by Evans and Hush.[2] This treatment was applied to the interpretation of irreversible polarographic waves corresponding to electrode processes which involve only one rate determining step. Thus, it was assumed that the rate of reduction of a substance O into substance R is controlled by the kinetics of a single step, which may or may not involve the number of electrons required to reduce substance O to R. In the latter case it was assumed that an intermediate substance Z is the first product of the reduction of O and that the rate of reduction of substance Z to R is so large that the characteristics of the irreversible wave are not affected by the reduction of Z to R. We shall now consider the more general case in which the kinetics of the two consecutive steps, namely, the reduction of O to Z and the reduction of Z to R, have to be taken into account. The mathematical analysis does not involve any special difficulty in the case of semi-infinite linear diffusion, but the resulting equations are rather cumbersome to use. Hence, only the following two particular cases will be considered

$$O \xrightarrow[n_1e]{k_1} Z \xrightarrow[n_2e]{k_2} R \qquad (1)$$

$$O \underset{n_1e}{\overset{equilibrium}{\rightleftharpoons}} Z \xrightarrow[n_2e]{k} R \qquad (2)$$

Case 1, in which the effect of the backward reactions is neglected, is studied because it enables one to determine in a relatively simple fashion the effect of the second step on the characteristics of irreversible waves. One example of this type of reaction, namely, the reduction of chromate ion in very alkaline medium, will be presented. Case 2 is discussed here because mechanisms based on the conditions assumed in this case have quite often

(1) (a) P. Delahay, THIS JOURNAL, 73, 4944 (1951); (b) P. Delahay and J. E. Strassner, ibid., 73, 5219 (1951); (c) J. E. Strassner and P. Delahay, ibid., 74, 6232 (1952); (d) P. Delahay, ibid., 75, 1430 (1953).

(2) M. G. Evans and N. S. Hush, J. chim. phys., 49, C 159 (1952).

been advanced in the interpretation of irreversible polarographic waves. It is assumed in such an interpretation that the reduction of substance O to Z is reversible and that the characteristics of this "potential determining step" account for the characteristics of the wave.[3] It will be shown below that such an interpretation cannot be accepted.

Case I. Two Consecutive Irreversible Electrochemical Reactions

Derivation of the Current for Conditions of Semi-infinite Linear Diffusion.—It will be assumed that process (1) occurs on a plane electrode which is such that conditions of semi-infinite linear diffusion are achieved. Substance Z is soluble in the electrolyzed solution. Furthermore a large excess of supporting electrolyte is supposed to be present, and mass transfer under the influence of migration is neglected. Finally it is assumed that the influence of the backward reactions in both steps of process (1) is negligible. This hypothesis is justified provided that the overvoltages for each step of reaction (1) are sufficiently high, say 0.1 volt.

According to a result previously derived,[1a,b,2] the rate of production of substance Z under the above conditions is, per unit area

$$dN_Z/dt = C^0 k_1 \exp(k_1^2 t/D_O) \operatorname{erfc}(k_1 t^{1/2}/D_O) \qquad (3)$$

where N_Z is the number of moles of Z produced t seconds after the beginning of the electrolysis; C^0 the bulk concentration of substance O; D_O the diffusion coefficient of substance O; k_1 the rate constant, at a given potential, for the first step of reaction (1). The notation "erfc" represents the complement of the error function having the quantity between parentheses as argument.

Substance Z is reduced further to substance R and diffuses from the electrode surface into the bulk of the solution. Therefore, the boundary condition for the present problem is obtained by writing the balance for Z at the electrode surface. Thus

$$C^0 k_1 \exp(k_1^2 t/D_O) \operatorname{erfc}(k_1 t^{1/2}/D_O^{1/2})$$
$$- k_2 c_Z(0,t) + D_Z[\partial c_Z(x,t)/\partial x]_{x=0} = 0 \qquad (4)$$

where D_Z is the diffusion coefficient of substance Z; $c_Z(0, t)$ the concentration of substance Z at the elec-

(3) H. A. Laitinen and S. Wawzonek, THIS JOURNAL, 64, 1765 (1942).

trode surface, i.e., for $x = 0$; and k_2 the rate constant, at a given potential, for the second step of reaction (1). The first term in equation 4 is the rate dN_Z/dt defined by equation 3; the second term is the rate of reduction of Z to R, and the third term is the rate of diffusion of substance Z from the electrode surface into the solution.

The initial condition for the present problem is readily written by assuming that the concentration of substance Z is equal to zero before electrolysis. Thus: $C_Z(x, 0) = 0$. Furthermore, one has: $C_Z(x, t) \rightarrow 0$ for $x \rightarrow \infty$.

The current for the above conditions is composed of two terms: the first term corresponds to the reduction of O to Z; the second term, equal to $nFAk_2C_Z(0,t)$ (A, area of the electrode), corresponds to the reduction of Z to R. The first term was previously derived[1-2] and only the concentration $C_Z(0,t)$ has to be calculated. This will be done by solving, for the above conditions, the differential equation expressing Fick's second law. By taking the Laplace transform[4] with respect to the variable t of the partial differential equation for linear diffusion one obtains a second-order ordinary differential equation, whose solution contains only one integration constant different from zero ($\bar{C}_Z(x,s)$ is bounded for $x \rightarrow \infty$). This constant is evaluated by satisfying the transform of the boundary condition (4) and the following transform $\bar{C}_Z(x,s)$ is obtained

$$\bar{C}_Z(x,s) = \frac{C^0 k_1}{D_Z^{1/2}} \frac{\exp(-s^{1/2}x/D_Z^{1/2})}{s^{1/2}(s^{1/2} + k_1/D_O^{1/2})(s^{1/2} + k_2/D_Z^{1/2})} \quad (5)$$

By introducing the value $x = 0$ in equation 5 and taking the inverse transform one obtains the concentration $C_Z(0,t)$ of substance Z at the electrode surface. The contribution of the second step of reaction (1) to the total current is then readily obtained and the total current is accordingly

$$i = n_1 FA C^0 k_1 \exp(k_1^2 t/D_O) \, \mathrm{erfc}(k_1 t^{1/2}/D_O^{1/2})$$

$$+ n_2 FA C^0 \frac{k_2}{\left(\frac{D_Z}{D_O}\right)^{1/2} - \frac{k_2}{k_1}} \left\{ \begin{array}{l} \exp(k_2 t/D_Z) \, \mathrm{erfc}(k_2 t^{1/2}/D_Z^{1/2}) \\ - \exp(k_1^2 t/D_O) \, \mathrm{erfc}(k_1 t^{1/2}/D_O^{1/2}) \end{array} \right\} \quad (6)$$

Two particular cases of equation 6 are of interest. (1) When k_2 is assumed to be infinite, equation 6 reduces itself to the first term on the right-hand in which n_1 is replaced by ($n_1 + n_2$); this can be shown by dividing by k_2 both terms of the fraction in the second term on the right-hand, and by noting that $\exp(k_1^2 t/D) \, \mathrm{erfc}(k_1 t^{1/2}/D_O^{1/2})$ approaches zero when k_2 increases. (2) When k_1 and k_2 are made infinite, equation 6 reduces itself to the equation for a current entirely controlled by semi-infinite linear diffusion; this can be shown by expanding the error integral in the semi-convergent series for large arguments.

Equation 6 can be adapted to the case of the dropping mercury electrode by expressing the area A in terms of the rate of flow of mercury and the time elapsed since the beginning of the drop time. Furthermore, a correction should be made for the expansion of the drop. One can use as correction factor the quantity $(7/3)^{1/2}$,[5] but this is only correct for the diffusion current. As was recently pointed out by Kern,[6] the correction factor varies along the wave from unity at the bottom of the wave to $(7/3)^{1/2}$ in the upper plateau. A more nearly correct equation for the dropping mercury electrode would in principle be obtained by solving the above boundary value problem for diffusion at an expanding sphere, but the derivation is hopelessly complicated. The present treatment will therefore be limited to equation 6, which, at any rate, is sufficient as a basis for the interpretation of the effect of the second step of reaction (1) on the characteristics of irreversible polarographic waves.

Discussion of Equation 6 and Interpretation of Polarographic Waves.—It is useful to visualize the

(4) See for example, R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Company, Inc., New York, N. Y., 1944. The notations of this author are used in this paper.

(5) D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, 6, 498 (1934); *J. chim. phys.*, 35, 129 (1938).

(6) D. M. H. Kern, THIS JOURNAL, 75, 2473 (1953).

relative effects of the two consecutive steps of reaction (1) by considering polarographic waves corresponding to various values of the ratio k_1/k_2. In order to do so it is necessary to correlate the rate constants k_1 and k_2 to the electrode potential. The following equation will be applied

$$k = k^0 \exp(-\alpha n_a FE/RT) \quad (7)$$

where E is the electrode potential with respect to the normal hydrogen electrode; α the transfer coefficient; n_a the number of electrons involved in the activation step of the step of reaction (1) being considered; the other notations are conventional. The values of k^0, α, n_a for the two consecutive steps in reaction (1) are generally not the same, but in the following discussion it will be assumed, in order to simplify the presentation of results, that the products αn_a for the consecutive steps of reaction (1) are equal. The general validity of the conclusion deduced below is not infirmed when the αn_a's are not equal. When the product αn_a is the same for the two steps of reaction (1), the ratio k_1/k_2 is independent of the electrode potential (see equation 7), i.e., the ratio k_1/k_2 is the same for any point along the wave. It is then easy to construct polarographic waves for various values of k_1/k_2 by application of equation 6, the graphic method previously reported[1a,b] being used in the determination of average currents. Such waves are represented in Fig. 1 for a drop time of 3 seconds and for the following data: $m = 10^{-3}$ g. sec.$^{-1}$, $C^0 = 10^{-6}$ mole cm.$^{-3}$, $n_1 = n_2 = n_{a,1} = n_{a,2} = 1$, $D_O = D_Z = 10^{-5}$ cm.^{2} sec.$^{-1}$, $k_1^0 = 10^{-6}$ cm. sec.$^{-1}$. Values of the ratio k_1/k_2 are indicated for each curve. The following conclusions can be drawn from Fig. 1. (1) Waves become flatter as the rate of the second step decreases. When the ratio k_1/k_2 is larger than 100 a split in two waves becomes noticeable. (2) When k_2 is appreciably larger than $k_1(k_1/k_2 \leq 0.1)$, the wave has essentially the same shape as in the case of a process controlled by one step. The effect of the second step is barely noticeable in the upper half of the wave, and this segment of the wave can thus be used in the determination of the characteristics of the *first* step. (3) When k_2 is appreciably smaller than $k_1(k_1/k_2 \geq 10)$, the lower half of the wave (compare curves 4 and 5) is essentially determined by the kinetics of the first step.
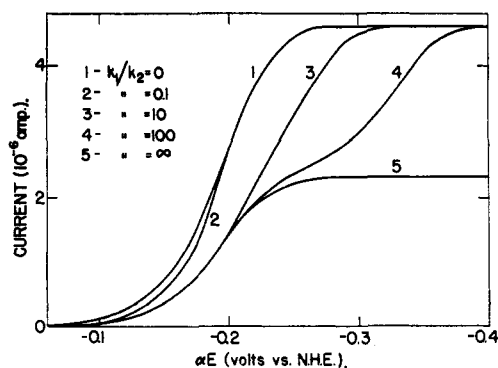

Fig. 1.—Variations of average current with the product αE for various values of the ratio k_1/k_2. See data in text.

In the analysis of actual irreversible waves it is not known *a priori* whether the electrode process

involves one or several consecutive steps. Therefore, the wave will be first analyzed by *assuming* that only one step is involved. The results obtained in this manner can be interpreted by considering the diagram of Fig. 2, which was constructed by analyzing the waves of Fig. 1 on the basis of this assumption. It is seen from this diagram that the occurrence of two consecutive reactions can be easily detected when the ratio k_1/k_2 is larger than 10. In that case it is possible to obtain some information on each step provided that the value of n_1 and n_2 can be reasonably postulated. The method of analysis is as follows. The lower segment of the wave is analyzed by the method previously developed[1a,b] and on the basis of a diffusion current equal to the actual diffusion current multiplied by the ratio $n_1/(n_1 + n_2)$. The resulting log k versus E diagram gives the characteristics of the kinetics of the first step of the electrode process. Conversely, the upper segment of the wave is analyzed on the basis of a diffusion current equal to $n_2/(n_1 + n_2)$ times the total diffusion current. The resulting log k vs. E diagram can be used in the determination of αn_a and k^0 for the second step of the electrode process. Great caution is in order and any quantitative result deduced from the above analysis should be considered with some scepticism. The above analysis may, however, be useful in detecting the occurrence of a stepwise reduction.
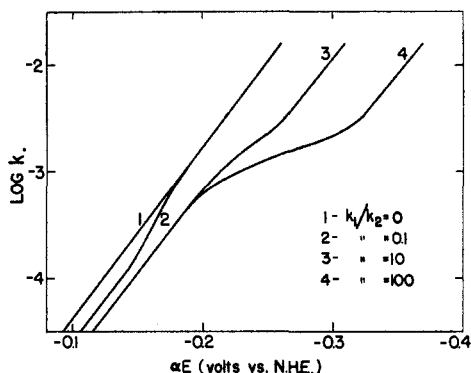

Fig. 2.—Variations of the logarithm of the rate constant k with the product αE, as deduced from Fig. 1.

An example which probably corresponds to the conditions assumed in the above treatment was found in the course of a study of the reduction of chromate ion in 1 M sodium hydroxide. It is well known that this cathodic process yields a single wave which results from the reduction of chromium(VI)[7] to the trivalent state. Diagrams showing the variations of log k with potential for the chromate wave are shown in Fig. 3 for various temperatures and for the following concentrations: $1mM$ in chromate ion, 1 M sodium hydroxide, and 0.005% gelatine. The general shape of the resulting log k vs. E curves indicates that at least two steps are involved in the reduction of chromium(VI) to chromium(III). The effect is more pronounced as the temperature is lowered, and at $0°$ the slope of the upper segment of the log k vs. E is *very approximately* one-half of the slope of the lower segment of

the log k vs. E curve. On the basis of the relative slopes of the lower and upper segments of the log k vs. E curve it can be assumed that chromium(IV) is the intermediate substance formed in the reduction of chromium(IV) under the conditions indicated above. The existence of such an intermediate is not unreasonable since several derivatives of chromium(IV) have been prepared.[8] It is true that such substances are not stable in aqueous solution, but there is nevertheless strong evidence that chromium(IV) is formed as an intermediate in various oxidations by chromic acid as Westheimer[9] pointed out. Additional evidence for the stepwise reduction of chromate ion was obtained recently in this Laboratory in the course of a study of this process by electrolysis at constant current.[10]
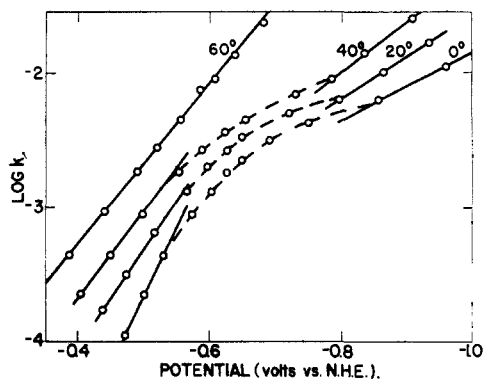

Fig. 3.—Variations of log k with potential for the reduction of chromate ion in sodium hydroxide. The curves for 20, 40 and 60° are shifted toward less cathodic potentials by 0.04, 0.08, and 0.12 volt, respectively.

It should be added that the curvature in the log k vs. E diagrams of Fig. 3 could possibly be caused by the formation of a film of insoluble chromic hydroxide. This explanation, however, must be ruled out on account of the solubility of chromic hydroxide in the supporting electrolyte used in this work (1 M sodium hydroxide). According to Latimer,[11] who quotes Fricke and Windhausen,[12] the equilibrium constant for the reaction

$$Cr(OH)_3 = CrO_2^- + H^+ + H_2O$$
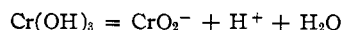
is 9×10^{-17}. Hence, in 1 M sodium hydroxide the solubility of chromic hydroxide is approximately 10^{-2} M, *i.e.*, ten times the concentration of chromium in the solution used in the recording of the waves which were used in the construction of Fig. 3.

Case II. Electrode Reactions Involving a So-called "Potential Determining Step"

Derivation of the Current for Conditions of Semi-infinite Linear Diffusion.—Consider the electrode process (2), and assume that the electrode is such that the mass transfer process is solely controlled by semi-infinite diffusion. Substance Z is assumed to be soluble in solution. Under such conditions, the current for reaction (2) is

$$i = n_1 F A D_0 [\partial C_0(x,t)/\partial x]_{x=0} + n_2 F A k C_Z(0,t) \quad (8)$$

(7) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Vol. II, Interscience Publishers, New York, N. Y., p. 455.

(8) H. Wartenberg, Z. anorg. Chem., 247, 139 (1941); 250, 122 (1942).

(9) F. H. Westheimer, Chem. Revs., 45, 419 (1949).

(10) P. Delahay and C. C. Mattax, unpublished investigation.

(11) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Edition, Prentice-Hall, Inc., New York, N. Y., 1952, p. 248.

(12) R. Fricke and O. Windhausen, Z. anorg. allgem. Chem., 132, 273 (1924).

The application of equation 8 requires the knowledge of the terms $(\partial C_O(x, t)/\partial x)_{x=0}$ and $C_Z(0, t)$; these will be derived by solving the system of two partial differential equations expressing Fick's second law for substances O and Z. In order to do so, boundary and initial conditions have first to be prescribed.

Since electrochemical equilibrium between substances O and Z is achieved at the electrode, one has

$$C_O(0,t)/C_Z(0,t) = \theta \qquad (9)$$

with

$$\theta = \frac{f_Z}{f_O} \exp[n_1 F(E - E^0)/RT] \qquad (10)$$

Equation 9 is the first boundary condition for the present problem. The second condition is obtained by expressing that the sum of the fluxes of substances O, Z and R on the electrode surface is equal to zero. By writing this condition one introduces a term in $(\partial C_R(x, t)/\partial x)_{x=0}$ in the derivation, but this can be avoided by noting that the flux of substance R at the electrode surface is equal to $-kC_Z \cdot (0, t)$. The second boundary condition is then

$$D_O[\partial C_O(x,t)/\partial x]_{x=0} + D_Z[\partial C_Z(x,t)/\partial x]_{x=0} - kC_Z(0,t) = 0 \qquad (11)$$

Initial conditions are immediate. Thus: $C_O(x, 0) = C^0$; $C_Z(x, 0) = C_R(x, 0) = 0$. Furthermore, one has $C_O(x, t) \rightarrow C^0$ for $x \rightarrow \infty$, and $C_Z(x, t) \rightarrow 0$ for $x \rightarrow \infty$.

The above boundary value problem was solved by applying the Laplace transformation method,[4] and the following transform $\bar{i}$ of the current was obtained by standard procedures

$$\frac{\bar{i}}{nFA} = \frac{C^0 D_O^{1/2}[(D_Z s)^{1/2} + k]}{s^{1/2}[(\theta D_O^{1/2} + D_Z^{1/2})s^{1/2} + k]}$$
$$+ \frac{C^0 k}{\theta s}\left[1 - \frac{(D_Z s)^{1/2} + k}{(\theta D_O^{1/2} + D_Z^{1/2})s^{1/2} + k}\right] \qquad (12)$$

Equation 12 is written for the sake of simplicity on the assumption that $n_1 = n_2 = n$; the modification for $n_1 \neq n_2$ is trivial.

By making the necessary inverse transforms in equation 12 one obtains the current

$$\frac{i}{nFA} = \frac{C^0}{\theta + (D_Z/D_O)^{1/2}}\left[\left(\frac{D_Z}{\pi t}\right)^{1/2} + \right.$$
$$\left. \frac{k[2\theta + (D_Z/D_O)^{1/2}]}{\theta + (D_Z/D_O)^{1/2}} \exp(a^2 t)\, \mathrm{erfc}(at^{1/2})\right] \qquad (13)$$

with

$$a = k/(\theta D_O^{1/2} + D_Z^{1/2}) \qquad (14)$$

It is of interest to note that equation 12 reduces to the form

$$\frac{i}{nFA} = \frac{C^0}{\theta + (D_Z/D_O)^{1/2}}\left(\frac{D_Z}{\pi t}\right)^{1/2} \qquad (15)$$

when k is made equal to zero. This is precisely the equation one would derive for an electrode process in which electrochemical equilibrium is achieved between the substance being reduced and its reduction product. It can be shown by a few simple transformations that equation 15 can be written under the form

$$E = E^0 + \frac{RT}{nF}\ln\frac{f_O}{f_R}\left(\frac{D_R}{D_O}\right)^{1/2} + \frac{RT}{nF}\ln\frac{i_d - i}{i} \qquad (16)$$

where i_d is the current for E approaching $-\infty$ (the limiting current). It is to be noted that equation 16 has the form of the usual equation for a "reversible" polarographic wave and that the current i_d and i in equation 16 are functions of the time t elapsed since the beginning of electrolysis.

Equation 13 can be written for the case of the dropping mercury electrode as was suggested in the discussion of Case I.

Discussion of Equation 13.—Equation 13, although condensed in form, is rather involved because both k and θ are functions of the electrode potential E as shown by equations 7 and 10. Therefore, it is fruitful to consider an example of application of equation 13, and to this end, equation 7 will be written under the form

$$k = k^0_{E-E^0} \exp[-\alpha n_a F(E - E^0)/RT] \qquad (17)$$

which related k to the quantity $\alpha n_a F(E - E^0)/RT$. Values of the current calculated from 13 on the basis of the data given below are plotted against the quantity $F(E - E^0)/RT$ in Fig. 4. The data adopted in the construction of this diagram were as follows: $m = 1$ mg. sec.$^{-1}$, $t = 3$ sec., $C^0 = 1$ millimole per liter, $n_1 = n_2 = 1$, $D_O = D_Z = 10^{-5}$ cm.^{2} sec.$^{-1}$, $\alpha = 0.5$. The number on each curve is the value of $k^0_{E-E^0}$ in cm. sec.$^{-1}$. The curve corresponding to the reversible reduction of O to R in a two-electron step is also shown in Fig. 4 (dashed line). It is seen from Fig. 4 that the shape of the
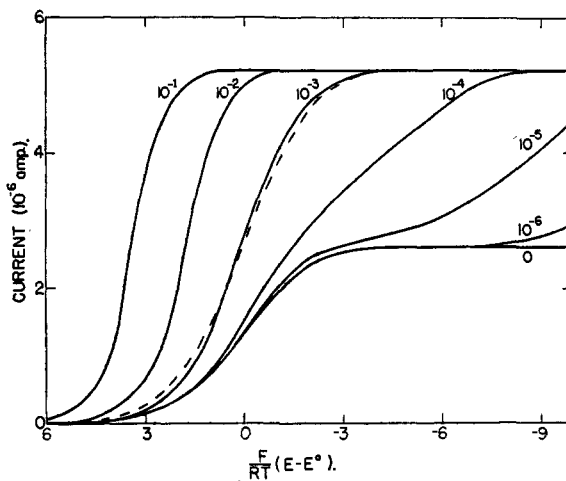

Fig. 4.—Current–potential curves for an electrode process involving a so-called "potential determining step."

current–potential curve depends on the kinetics of the second step of reaction (2). A single wave is observed in the present case when the rate $k^0_{E-E^0}$ is larger than 10^{-4} cm. sec.$^{-1}$, and as the rate $k^0_{E-E^0}$ increases, the wave is shifted toward less cathodic potentials. This is understandable since the concentration of Z at the electrode, for a given potential, becomes smaller as the rate constants $k^0_{E-E^0}$ increase. Further appreciation of the effect of the second step of reaction (2) can be gained by plotting (Fig. 5) the conventional diagram log $(i_d - i)/i$ vs. E for the current–potential curves of Fig. 4. The resulting diagram shows that such logarithmic plots are by no means linear. Even if one traces an average straight line through the curves marked 10^{-1} and 10^{-2} one obtains a value of the reciprocal slope which is very different from the value $2.3RT/nF$ (with $n = 1$ in this case) which such line is supposed to have according to views commonly accepted.[8]
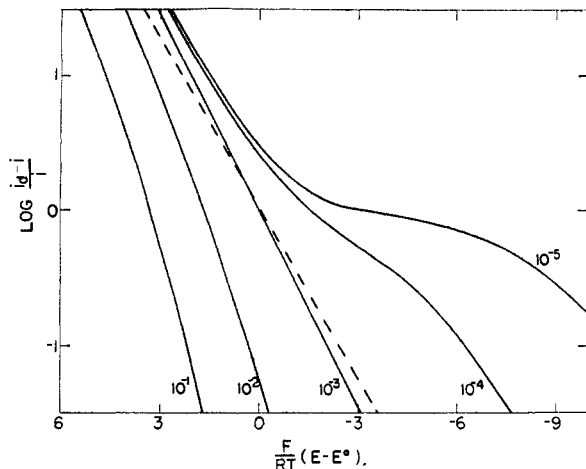
Fig. 5.—Logarithmic diagram as deduced from Fig. 4.

Summarizing, the conclusion that the reciprocal slope of the diagram log $(i_d - i)/i$ *vs.* E *should be* $2.3RT/nF$, n *being the number of electrons in the so-called "potential-determining step," cannot be accepted.*

Significance of Half-wave Potential Plots in Organic Polarography

It has become the current practice in studying groups of substances in organic polarography to plot half-wave potentials against a quantity which characterizes in some way the molecules being studied. Quite obviously this procedure may lead to significant results when electrochemical equilibrium is achieved at the electrode ("reversible" waves) since the half-wave potential is then related in a simple manner to the change of free energy involved in the electrode process. In contrast a cautious approach is in order in the case of irreversible electrode reactions, because the half-wave potential is not related in a direct manner to the change of free energy for the electrode process, or even to the activation energy for this reaction. In the case of an irreversible wave corresponding to an electrode process which involves one rate determining step and for which the backward process can be neglected, the half-wave potential depends both on the rate constant k^0 and the transfer coefficient α (see equation 7). Thus, in the comparison of a series of substances it is the values of k^0 for these substances which are generally significant. How-

ever, the corresponding variations in the half-wave potential one would expect on the basis of a constant transfer coefficient may be altered if α varies from one substance to another. In fact this will generally be so unless the substances have very "similar" structures. Such variations of α are probably reflected as anomalies or irregularities in the half-wave potential plot. When there are kinetic complications such as those discussed in the present paper, the half-wave potential is correlated in such a complicated manner to the kinetic characteristics of the reactions involved in the electrode processes that any deductions based on values of half-wave potentials are likely to be purely empirical. This remark might be kept in mind in the evaluation of the significance of plots showing the variations of half-wave potentials with some parameter characterizing a series of organic derivatives. Some of these diagrams have their merits, but even in cases in which the comparison of half-wave potentials is in good agreement with other facts of organic chemistry the utmost caution should be the rule.

Experimental

Waves were recorded by following well known methods of polarography. A Sargent polarograph model XXI was used in this work. The voltage span on this instrument was selected in such a manner as to spread the wave and improve the accuracy of the measurements of potential (span of 0.5 volt for the chromate wave). The potential scale of the polarograms was carefully calibrated by means of a student potentiometer. Corrections for the ohmic drop were made, the resistance of the cell being measured with an a.c. bridge. Electrolyses were carried out with an H cell which was completely immersed in a constant temperature water-bath in such a manner that the tube connected to the mercury reservoir was partially immersed in water; in this fashion the temperature of the solution and mercury were exactly at the same temperature. One of the arms of the cell was connected to an external electrode by means of a salt bridge whose ends were closed by fritted glass disks of coarse porosity. This bridge was filled with a saturated solution of potassium chloride. Both compartments of the H cell were filled with the solution being studied. Any diffusion of chloride ion in the compartment of the dropping mercury electrode was prevented by this method. This precaution was taken because chloride ion might affect the kinetics of the reduction of chromate ion. The calomel electrode was not immersed in the water, and its temperature was that of the room. The solutions of chromate were prepared from a 10^{-2} molar solution of potassium chromate which was obtained by direct weighing of the salt.