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

Unified Theory of Polarographic Waves[1]

BY PAUL DELAHAY

RECEIVED JULY 30, 1952

A unified theory of polarographic waves is developed on the basis of a single general equation for polarographic currents. This equation is derived by solving the corresponding boundary value problem for the case of first-order electrode processes. Various features of irreversible waves are deduced from the theoretical treatment. It is shown that polarographic reversibility is observed when the rate constant k_s at the standard potential is larger than 2×10^{-2} cm. sec.$^{-1}$. This condition is also stated in terms of the free energies of activation for the forward and backward electrode processes. It is shown that reversible waves can be observed only in a limited range of potentials. When the rate constant k_s is smaller than 5×10^{-5} cm. sec.$^{-1}$, the effect of the backward process can be neglected. Quasi-reversible waves are observed for k_s comprised between 2.10^{-2} and 5×10^{-5} cm. sec.$^{-1}$. The features of these waves and a method of analyzing experimental quasi-reversible waves are discussed.

Introduction

The foundations of the classical theory of polarography were laid in two papers in which Ilkovic[2] derived his well known equation for the diffusion current, and Heyrovsky and Ilkovic[3] derived an equation for reversible waves. These two papers were of fundamental importance in the development of polarography, and the derivation of Heyrovsky and Ilkovic[3] has been adapted to various types of reversible waves (reduction of complex ions, anodic waves, etc.). However, it was soon recognized that the numerous waves corresponding to irreversible electrode processes could not be analyzed on the basis of the Heyrovsky–Ilkovic treatment, and this inadequacy of the classical theory prompted various authors to develop theoretical treatments of irreversible waves. The first attempt was made by Eyring and co-workers[4] who applied the absolute rate theory to the polarographic problem. These authors solved the diffusion problem by using the concept of the Nernst diffusion layer, and consequently their results are approximate. Tanaka and Tamamushi[5] have also given an approximate solution of the problem of irreversible waves. A treatment in which the boundary value problem corresponding to the diffusion phenomenon at the electrode is solved in a rigorous manner, was developed in this laboratory.[6,7] Finally, two other recent papers also deal with irreversible waves: Tockstein[8] treated the problem by an approximate method which does not seem entirely justified to this author; on the other hand, the views recently expressed by Evans and Hush[9] are not very different from ours, but the mathematical approach used by these authors is somewhat more approximate than ours.

In the treatment of irreversible waves developed in this Laboratory, it is assumed that the effect of the backward reaction can be neglected. This hypothesis is justified provided that the electrode process involves an overvoltage of the order of 0.1 volt. This is not a serious limitation since the great majority of irreversible waves corresponds to reactions involving much larger overvoltages. Nevertheless, the necessity of applying two different theories—the classical theory on one hand, the theory of irreversible waves on the other hand—is somewhat disturbing, and there is a need for a *unified* theory which would account for the characteristics of polarographic waves regardless of the degree of irreversibility of the electrode process. Such a theory is reported in the present paper.

Case of Linear Diffusion

Boundary and Initial Conditions.—Consider the reduction of a substance Ox to another substance Red in an electrode process involving n electrons, and assume that the reduction product Red is soluble either in the solution being reduced or in mercury. The rate of reduction per unit area is

$$-\mathrm{d}N_{\mathrm{ox}}/\mathrm{d}t = k_f C_{\mathrm{ox}}(0,t) - k_b C_{\mathrm{red}}(0,t) \qquad (1)$$

where k_f and k_b are the rate constants for the forward and backward reactions, respectively, and the symbols $C_{\mathrm{ox}}(0,t)$ and $C_{\mathrm{red}}(0,t)$ represent the concentrations of reducible and reduced forms, respectively, at the electrode surface.

The concentrations $C_{\mathrm{ox}}(x,t)$ and $C_{\mathrm{red}}(x,t)$ are functions of x, the distance from the electrode surface, and t, the time elapsed after the beginning of the electrolysis. The functions $C_{\mathrm{ox}}(x,t)$ and $C_{\mathrm{red}}(x,t)$ will be determined by solving the differential equations expressing Fick's second law for substances Ox and Red. Since two functions have to be determined, two boundary conditions are needed. The first boundary condition is obtained by equating the rate given by equation (1) to the flux of substance Ox at the electrode surface. Thus

$$D_0 \frac{\partial C_{\mathrm{ox}}(0,t)}{\partial x} = k_f C_{\mathrm{ox}}(0,t) - k_b C_{\mathrm{red}}(0,t) \qquad (2)$$

where D_0 is the diffusion coefficient of substance Ox. The second boundary condition is obtained by expressing that the sum of the fluxes for substances Ox and Red, at the electrode surface, is equal to zero. Thus

$$D_0 \frac{\partial C_{\mathrm{ox}}(0,t)}{\partial x} + D_r \frac{\partial C_{\mathrm{red}}(0,t)}{\partial x} = 0 \qquad (3)$$

where D_r is the diffusion coefficient of the reduced species.

---

[1] Paper presented at the Symposium on Electrode Processes held during the 122nd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

[2] D. Ilkovic, *Collection Czechoslov. Chem. Commun.*, **6**, 498 (1934).

[3] J. Heyrovsky and D. Ilkovic, *ibid.*, **7**, 198 (1935).

[4] H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Colloid Chem.*, **53**, 187 (1949).

[5] N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949); **22**, 227 (1949); **23**, 110 (1950).

[6] P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

[7] P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

[8] A. Tockstein, *Collection Czechoslov. Chem. Commun.*, **16**, 101 (1951).

[9] M. G. Evans and N. S. Hush, *J. chim. phys.*, **49**, C 159 (1952).

The initial conditions, on the other hand, are as follows: $C_{ox}(x,0) = C_0$, where C_0 is the bulk concentration of reducible substance, and $C_{red}(x,0) = 0$.

Variations of Concentrations $C_{ox}(x,t)$ and $C_{red}(x,t)$.—The above boundary value problem will be solved by using the Laplace transformation.[10] In order to apply this method it is convenient to introduce the function $u(x,t)$ defined as

$$u(x,t) = C_0 - C_{ox}(x,t) \qquad (4)$$

By taking the Laplace transform of the equation expressing Fick's second law, one obtains a second-order ordinary differential equation, whose solution is

$$\bar{u}(s,x) = \xi \exp\left(-\frac{s^{1/2}}{D_0^{1/2}}x\right) \qquad (5)$$

where $\bar{u}(s, x)$ is the transform of function $u(x, t)$, ξ is an integration constant, and s is the parameter resulting from the transformation.

Similarly for $C_{red}(x,t)$ one obtains the transform

$$\bar{C}_{red}(s,x) = \zeta \exp\left(-\frac{s^{1/2}}{D_r^{1/2}}x\right) \qquad (6)$$

where ζ is another integration constant.

The constant ξ and ζ are determined by introducing the values of $\bar{u}$, $d\bar{u}/dx$, $\bar{C}_{red}$ and $d\bar{C}_{red}/dx$ in the transforms of boundary conditions (2) and (3), and by solving the resulting two linear equations. The complete forms for the transforms $\bar{u}(s,x)$ and $\bar{C}_{red}(s,x)$ are derived by introducing into equations (5) and (6) the values of ξ and ζ thus obtained. The inverse transforms are readily available from tables.[10] After returning to the function $C_{ox}(x,t)$, one finally obtains

$$C_{ox}(x,t) = C_0 \frac{k_f}{D_0^{1/2}Q}\left[\operatorname{erf}\left(\frac{x}{2D_0^{1/2}t^{1/2}}\right) + \exp\left(\frac{Qx}{D_0^{1/2}} + Q^2t\right)\operatorname{erfc}\left(Qt^{1/2} + \frac{x}{2D_0^{1/2}t^{1/2}}\right)\right] \qquad (7)$$

$$C_{red}(x,t) = C_0 - \left(\frac{D_0}{D_r}\right)^{1/2} C_{ox}(x,t) \qquad (8)$$

where

$$Q = \frac{k_f}{D_0^{1/2}} + \frac{k_b}{D_r^{1/2}} \qquad (9)$$

The notation "erf" in equation (7) represents the error function

$$\operatorname{erf}\left(\frac{x}{2D_0^{1/2}t^{1/2}}\right) = \frac{2}{\pi^{1/2}}\int_0^{\frac{x}{2D_0^{1/2}t^{1/2}}} \exp(-z^2)dz \qquad (10)$$

and "erfc" is the complement of this function.

Equations (7) and (8) give the variations—with x and t—of the concentrations of both species involved in the electrode process. For a given value of x, both terms between brackets in equation (7) decrease as t increases. Thus at a given distance from the electrode, the concentration of the substance reacting at the electrode decreases in the course of time. Conversely, the concentration of the substance being produced in the reaction increases in the course of time.

Two particular cases are of interest: 1. When k_f is infinite, equation (7) is identical with that obtained in the theory of simple linear diffusion; 2. When k_b is equal to zero and k_f is finite, the coefficient in front of the brackets of (7) is equal to C_0.

Variations of Current.—The current corresponding to the reduction of substance Ox to Red is obtained by multiplying the charge involved in the reduction of one mole of substance Ox by the flux of this substance at the electrode surface. The flux is calculated by multiplying the derivative $\partial C_{ox}(0,t)/\partial x$ by D_0. Taking into account the area of the electrode, one obtains after transformations

$$i = nFAC_0k_f\exp(Q^2t)\operatorname{erfc}(Qt^{1/2}) \qquad (11)$$

where F is the faraday, A the area of the electrode in cm.^{2}, C_0 the bulk concentration of reducible substance in moles per cm.^{3}, and Q is defined by equation (9).

The product of the last two terms of the right-hand side of (11) decreases as t increases, and consequently the current decreases in the course of the electrolysis. By making t infinite in (11) it can be seen, by expanding the error function,[11] that the current approaches zero as t increases. The initial current, equal to $nFAC_0k_f$, is independent of the rate of the backward process.

Two particular cases of equation (11) are of interest: 1. When k_f is infinite, equation (11) is identical with that obtained for the current in the theory of simple linear diffusion; 2. When k_f is finite and k_b is made equal to zero, equation (11) is identical with the equation previously derived for such a case.[6,7]

As an example, currents were calculated from (11) for various values of k_b and for the following data: $n = 1$, $A = 1$ cm.^{2}, $C_0 = 10^{-3}$ mole per cm.^{3}, $k_f = 5 \times 10^{-3}$ cm. sec.$^{-1}$, $D_0 = D_r = 10^{-5}$ cm.^{2} sec.$^{-1}$. The results are shown in Fig. 1, where the ratio i/i_0 of the current at time t to the current for $t = 0$ is plotted against time. Note that, in the present case, the effect of the backward reaction is negligible when k_b is smaller than 5×10^{-4} cm. sec.$^{-1}$, *i.e.*, k_b smaller than 0.1 k_f. Conversely, when k_b is larger than 5×10^{-2} cm. sec.$^{-1}$, *i.e.*, k_b larger than 10 k_f, the current is virtually equal to zero shortly after the beginning of the electrolysis.

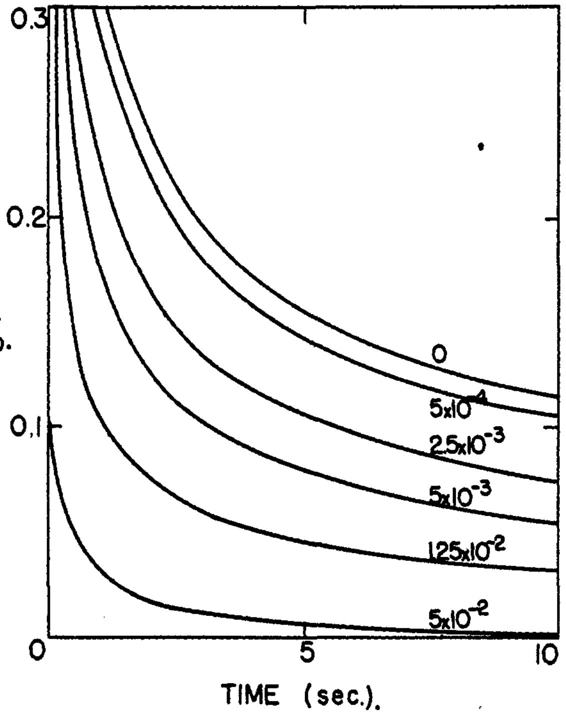

Fig. 1.—Influence of the backward process on the current as calculated from equation (11). The current at time zero is i_0. The number on each curve is the value of k_b in cm. sec.$^{-1}$. See text for other data.

General Equation for the Case of the Dropping Mercury Electrode

The above treatment could be transposed to the case of the dropping mercury electrode by applying the corresponding equations for spherical diffusion. The calculations, however, would be elaborate[12]

---

[10] See for example, R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1944. The notations of this author are used in the present paper.

[11] See for example, B. C. Peirce, "A Short Table of Integrals," Ginn and Company, Boston, Mass., 1929, p. 120.

[12] Even in the much simpler case of a current entirely diffusion controlled, the writing is rather heavy. See D. MacGillavry and E. K. Rideal, *Rec. trav. chim.*, **56**, 1013 (1937).

and the case of the dropping mercury electrode can be treated in a less arduous manner by the following method.

The value of the area of the dropping mercury electrode is calculated in terms of the characteristics m and t of the capillary and the resulting value of A is introduced in equation (11). Furthermore, the rate constants k_f and k_b are made equal to infinity and zero, respectively, and the resulting equation is compared with the Ilkovic equation. In this manner, it is concluded that equation (11) can be applied to the case of the dropping mercury electrode provided that the current be multiplied by the factor $(7/3)^{1/2}$. A similar conclusion was reached by Ilkovic,[2] for the case of a simple diffusion process. It should, however, be emphasized that such a derivation is not rigorous. After numerical transformations, one obtains the following equation for the *instantaneous* current during the drop life for any point along the wave[13]

$$i = 1255nm^{2/3}t^{2/3}C_0k_f \exp(Q^2t) \operatorname{erfc}(Qt)^{1/2} \qquad (12)$$

where i is in microamp., m in mg. sec.$^{-1}$, t in sec., C_0 in millimoles per liter, k_f and k_b in cm. sec.$^{-1}$, D_0 and D_r in cm.^{2} sec.$^{-1}$.

Equation (12) embodies the features of all types of polarographic waves at the exclusion of kinetic and catalytic waves (and waves resulting from some special adsorption effects or the deposition of an insoluble substance). In the following sections, more familiar forms of the various equations for polarographic waves are deduced by introducing in equations (12) the value of the quantity Q (see equation (9)) calculated in terms of the electrode potential.

Irreversible Waves

Consider the case in which the effect of the backward reaction can be neglected, *i.e.*, $k_b \ll k_f$. The quantity Q defined by equation (9) can then be written in the simplified form $Q = k_f/D_0^{1/2}$ and the resulting expression for the current has the same form as equation (12) except that Q is replaced by $k_f/D_0^{1/2}$. Such an equation was previously derived in this Laboratory.[7,8]

The condition $k_b \ll k_f$ can be stated quantitatively by substituting for k_b and k_f the values derived in the absolute rate theory.[14] From the resulting equation one concludes that the effect of the backward process can be neglected for any point of the wave for which the overvoltage is at least of the order of 0.1 volt. Essentially two methods can be applied in order to ascertain that this condition is fulfilled. First, one can compare the experimental wave with the calculated wave which one would observe if the electrode process were reversible. In order to apply this method, it is necessary to know the standard free energy change for the electrode process, and since very often this datum is not known, the usefulness of such a procedure is rather limited. In another approach one can compare the positions—in the scale of potentials—of the cathodic and anodic waves corresponding to a given electrode process. This can be done very conveniently by applying the oscillographic technique in which the anodic wave is recorded immediately after the cathodic wave.[15,16] The same result can also be achieved by recording the anodic wave corresponding to the reaction Red + $ne^- \rightarrow$ Ox, and by comparing the position of this anodic wave with the cathodic wave for the reduction of substance Ox. It should be kept in mind that the comparison of cathodic and anodic waves is misleading in the case in which the electrode process is followed by a chemical transformation. In that case the electrode process appears as irreversible whereas it could possibly be reversible.[17]

Consecutive Electrochemical Processes.—The equation for irreversible waves (equation (12) in which Q is made equal to $k_f/D_0^{1/2}$) is also applicable to cases in which the reduction Ox → Red is followed by another electrochemical process, provided that the rate of the latter process is much larger than the rate of reduction of substance Ox to Red. The current, however, is increased accordingly. Let n_a be the number of electrons involved in the rate-determining step, *i.e.*, the reduction of substance Ox to Red, and n be the total number of electrons in the over-all electrode reaction, *i.e.*, the reduction Ox to a substance Z. Since the rate of the reduction Red → Z is much larger than that of the process Ox → Red, substance Red is consumed at the electrode surface as soon as it is produced. Therefore, the current through the cell is the sum of two terms: 1, the current for the first step Ox → Red as calculated on the basis of a n_a electron transfer; 2, the current for the second step Red → Z which is equal to the first component of the current multiplied by the ratio $(n - n_a)/n_a$. The current along the wave is simply proportional to the *total* number of electrons involved in the over-all electrode reaction, but the shape of the wave is determined by the kinetics of the rate-determining step. When the rate of the two consecutive steps are of the same order of magnitude the previous mathematical analysis of the wave is not valid. This problem is being investigated at the present.

Calculation of $\Delta G_f^{\ddagger}$ and αn_a.—The characteristic features of irreversible polarographic waves have already been discussed in previous publications from this Laboratory,[7,8,18] and only a few additional remarks will be made here. The analysis of experimental irreversible waves by the method previously described[7,8] yields the value of the rate constant k_f as a function of the electrode potential E.[19] The variations of k_f are interpreted on the basis of the equation

$$k_f = k_f^0 \exp\left[-\frac{\alpha n_a FE}{RT}\right] \qquad (13)$$

where k_f^0 is the vaue of k_f for $E = 0$, the potential being measured with respect to the normal hydrogen electrode. The factor α in equation (13) is the transfer coefficient for the forward electrode process, and n_a is the number of electrons involved in the rate determining step. It is readily seen from equation (13) that a plot of log k_f *versus* E yields the value of αn_a and k_f^0.

The heat of activation for the forward electrode process can be determined by measuring the rate constant k_f^0 at various temperatures and by plotting log k_f^0 *versus* $1/T$; the heat of activation is directly obtained from the slope of

---

[13] Note that the current given by (12) could be corrected to take into account a secondary diffusion effect resulting from the curvature of the electrode. See H. von Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950); J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

[14] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 584–587.

[15] A. Sevcik, *Collection Czechoslov. Chem. Commun.*, **13**, 340 (1948).

[16] See also, J. Heyrovsky, *Faraday Soc. Disc.*, **1**, 212 (1947).

[17] For a discussion of this type of waves, see L. I. Smith, I. M. Kolthoff, S. Wawzonek and P. M. Ruoff, THIS JOURNAL, **63**, 1018 (1941).

[18] P. Delahay and J. E. Strassner, *ibid.*, **74**, 893 (1952).

[19] In a previous paper (ref. 7), the variations of k_f with the overvoltage were determined, but it is more logical to calculate k_f in terms of the electrode potential. This matter was previously discussed. See J. E. Strassner and P. Delahay, *ibid.*, **74**, 6232 (1952).

the resulting line. The free energy of activation for the forward electrode process $\Delta G_f \ddagger$ can be calculated by explicitating the value of k_f^0 on the basis of general principles of the absolute rate theory. Thus

$$k_f^0 = \frac{kT}{h} \rho \exp\left[-\frac{\Delta G_f \ddagger}{RT}\right] \tag{14}$$

where k is the Boltzmann constant, and h the Planck constant. The factor ρ is the "thickness of the reaction layer" which is introduced because the electrochemical reaction is an heterogeneous process. The introduction of the factor ρ is somewhat artificial, and the value of ρ has not been derived as far as we know. It is probably of the same order of magnitude as the average distance in solution between two molecules or ions of reducible substance. This distance is of the order of 10^{-6} cm. for dilute solutions (10^{-3} molar) and this value can be adopted. The corresponding value of the free energy of activation is approximate, but the error is undoubtedly minor since $\Delta G_f \ddagger$ appears as exponent in equation (14).

Significance of the Half-wave Potential.—In the case of a reversible wave, the half-wave potential has an important theoretical significance,[3,20,21] but it should be emphasized that this is not so for irreversible waves. In the latter case, the half-wave potential is no more significant than any other point along the wave. However, it is convenient to characterize the position of an irreversible wave by reporting its half-wave potential. In following this procedure it should be kept in mind that the half-wave potential for an irreversible wave depends on the concentration of reducible substance and on the drop time. This can be shown in the following manner.

The rate constant k_f at the half-wave potential has a value which was previously calculated for various drop times.[6] For example, it was shown that the value of log $(k_f D_0^{-1/2})$ at the half-wave potential varies from -0.19 for a drop time of 1 sec. to a value of -0.47 for a drop time of 4 sec. By calling λ the value of $k_f D_0^{-1/2}$ at $E_{1/2}$, the following value of the half-wave potential is obtained from equation (13)

$$E_{1/2} = 2.3 \frac{RT}{\alpha n_a F} \log \frac{k_f^0}{\lambda D_0^{1/2}} \tag{15}$$

The half-wave potential varies with the drop time since the quantity λ in equation (15) varies with drop time.[6] This shift in $E_{1/2}$, however, is very small. For example, for $\tau = 2$ sec. log $\lambda = -0.33$, whereas for $\tau = 4$ sec. log $\lambda = -0.47$.[6] The corresponding shift in half-wave potential is $+0.0083$ volt ($\alpha n_a = 1$, $T = 298.1°$) as the drop time varies from 2 to 4 sec. A shift of the half-wave potential of this order of magnitude was reported by Orlemann and Kolthoff.[22] These authors observed that the half-wave potential for the wave corresponding to reduction of iodate ion in 0.05 *M* potassium chloride was shifted from -1.256 to -1.250 volts (*vs.* S.C.E.) as the drop time was changed from 2.05 to 4.10 sec. For drop times larger than 3 sec. the quantity λ remains almost constant,[6] and consequently the half-wave potential is virtually independent of the drop time under those conditions. In discussing the dependence of $E_{1/2}$ on drop time it should be kept in mind that according to von Strehlov and von Stackelberg[13] the secondary diffusion effect due to the curvature of the electrode causes a variation of $E_{1/2}$ with the drop time. The resulting shift in $E_{1/2}$ is generally of the order of a few millivolts.

Criterion of Polarographic Reversibility

The conditions under which polarographic reversibility is observed can be stated rigorously on the basis of equation (12). By expanding the error integral[11] in equation (12) one obtains the instantaneous current for any point along the wave

$$i = 708nm^{2/3}t^{1/6}C_0D_0^{1/2}\, 1\Big/\left(1 + \frac{k_b}{k_f}\left(\frac{D_0}{D_r}\right)\right)^{1/2}\left[1 - \frac{1}{2Q^2t} + \frac{1.3}{(2Q^2t)^2}\cdots\right] \tag{16}$$

or by introducing the value k_b/k_f derived from the absolute rate theory[14]

$$i = 708nm^{2/3}t^{1/6}C_0D_0^{1/2} \times \frac{[1 - 1/2Q^2t + 1.3/(2Q^2t)^2\cdots]}{1 + (D_0/D_r)^{1/2}\exp(\Delta G^0/RT)\exp(nFE/RT)} \tag{17}$$

In equation (17) the right-hand term—with the exception of the series—is simply the current corresponding to a reversible electrode process. Therefore equation (17) can be written under the abridged form

$$i = i_{\text{rev}}\left[1 - \frac{1}{2Q^2t} + \frac{1.3}{(2Q^2t)^2}\cdots\right] \tag{18}$$

where i_{rev} is the current which would be observed if the electrode process were reversible. By integrating equation (18) over the drop life one obtains the average current

$$i_{\text{av}} = (i_{\text{rev.}})_{\text{max}}\left[\frac{6}{7} - \frac{3}{Q^2\tau}\cdots\right] \tag{19}$$

where $(i_{\text{rev}})_{\text{max}}$ is the maximum current—corresponding to the drop life τ—which would be observed if the electrode process were reversible.

From equation (19) it is seen that the reversible current is virtually observed when the quantity $3/Q^2\tau$ is negligible in comparison with 6/7. This is the case when Q is larger than 10 sec.$^{-1/2}$, the drop time τ having a normal value of the order of 3 sec. This criterion for polarographic reversibility will now be stated in a quantitative manner.

The quantity Q defined by equation (9) varies with the potential of the electrode, and passes through a minimum at the potential at which the following condition is satisfied

$$k_b/k_f = \alpha/(1 - \alpha) \tag{20}$$

Condition (20) was derived by equating d $Q(E)$/dE to zero, assuming that $D_0 = D_r$. The right-hand member of (20) is of the order of unity, and consequently $Q(E)$ is minimum when the rate constants k_f and k_b are approximately equal. This is the case at the standard potential. By calling k_s the rate constant at the equilibrium potential, the condition for polarographic reversibility $Q \geqslant 10$ sec.$^{-1/2}$, derived from equation (19), can be stated ($D_0 = D_r = 10^{-5}$ cm^2. sec.$^{-1}$) as (see equation (9)).

$$k_s \quad 2 \times 10^{-2} \tag{21}$$

Thus, when condition (21) is fulfilled, the rate of the forward and/or backward processes are much larger than the rates of mass transfer toward and from the electrode under the influence of natural diffusion. Electrochemical equilibrium is virtually achieved at the electrode and the resulting wave is reversible.

Condition (21) can be written in terms of the free energy of activation $\Delta G_f \ddagger$ in the case in which n_a and n are equal. Since the rate constant at the standard potential (assuming $n = n_a$) is

$$k_s = (kT/h)\,\rho \exp[(\alpha\Delta G^0 - \Delta G_f \ddagger)/RT] \tag{22}$$

condition (21) becomes ($\rho = 10^{-6}$ cm., $T = 298.1°$)

$$\Delta G_f \ddagger \leqslant 11.5 + \alpha\Delta G^0 \tag{23}$$

---

[20] M. von Stackelberg, *Z. Elektrochem.*, **45**, 466 (1939).

[21] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[22] E. F. Orlemann and I. M. Kolthoff, *ibid.*, **64**, 1970 (1942).

where $\Delta G_f^{\ddagger}$ and ΔG^0 are in kcal. In terms of the free energy of activation for the backward process condition (23) is

$$\Delta G_b^{\ddagger} \leqslant 11.5 - (1 - \alpha)\Delta G^0 \qquad (24)$$

An interesting implication of conditions (23) and (24) is that polarographic reversibility can be observed only in a certain range of standard potentials. By introducing the condition that $\Delta G_f^{\ddagger}$ and $\Delta G_b^{\ddagger}$ are positive, one obtains the following limits within which polarographic reversibility can possibly be observed

$$0.5/\alpha n > E^0 > -0.5/(1 - \alpha)n \qquad (25)$$

where E^0 is in volts *vs.* the normal hydrogen electrode (European convention). The standard potential E^0 in (25) is almost equal to the half-wave potential for a reversible wave since the ratio $(D_0/D_r)^{1/2}$ is not very different from unity (see equation (16)). *Therefore, one concludes from (25) that cathodic waves can possibly exhibit the characteristics of polarographic reversibility only when their half-wave potentials are less negative than $-0.5/(1-\alpha)n$ volts versus the normal hydrogen electrode.* Experimentally, it is indeed observed that the great majority of reversible waves exhibits half-wave potentials in the 0–1 volt range.[23] It should be emphasized, however, that condition (25) should be satisfied in the case of polarographic reversibility, but that even when this condition is fulfilled the corresponding wave is not necessarily reversible.

Quasi-reversible Waves

When the rate constant k_s, for a given electrode process, is smaller than 2×10^{-2} cm. sec.$^{-1}$ the resulting wave is not reversible (see condition (21)) and is shifted toward more negative potentials with regard to the corresponding reversible wave. This shift of the wave is more pronounced as k_s decreases. This is shown in Fig. 2. The waves in this diagram were constructed by applying equation (12) for the following data: $D_0 = D_r = 10^{-5}$ cm.^{2} sec.$^{-1}$, $\alpha = 0.5$, $T = 298.1°$. Instantaneous currents corresponding to $t = 3$ sec. rather than average currents were calculated in order to reduce the labor involved in the preparation of Fig. 2. From this diagram it is seen that the overvoltage corresponding to appreciable currents is larger than $2 \times 2.3\ (RT/nF)$ volts when k_s is equal or smaller than 3×10^{-5} cm. sec.$^{-1}$. In such cases the effect of the backward reaction can be neglected and the wave is said to be *irreversible.* For values of k_s comprised between 2×10^{-2} and 3×10^{-5} cm. sec.$^{-1}$, the effect of the backward reaction should be taken into account. It is proposed that such waves be called *quasi-reversible* in order to distinguish them from reversible and irreversible waves. It should be emphasized that such a classification, although convenient, is rather artificial.

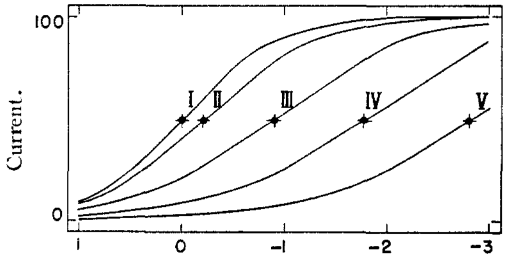

Fig. 2.—Waves for various values of the rate consant k_s. Currents are in per cent. of the diffusion current: I, reversible process; II, $k_s = 10^{-3}$ cm. sec.$^{-1}$; III, $k_s = 3 \times 10^{-4}$; IV, $k_s = 10^{-4}$; V, $k_s = 3 \times 10^{-5}$.

Quasi-reversible waves are more drawn out than the corresponding reversible waves, and consequently the slope of the log $(i_d - i)/i$ *versus* E diagram is smaller than the theoretical value $n/0.059$ for the reversible case. Actually, plots of log $(i_d - i)/i$ *versus* E are not even linear, although the departure from linearity is minor. It is therefore possible to characterize quasi-reversible waves by a coefficient θ which is the ratio of $n/0.059$ to the slope of the log $(i_d - i)/i$ *versus* E diagram for a given quasi-reversible wave. Of course, this coefficient θ has no theoretical significance, but is merely a number enabling one to express the characteristics of a wave in a convenient manner. The coefficient θ was determined for the waves of Fig. 2 and for other similar waves, and the resulting values of θ are plotted in Fig. 3 (curve II) against the value of $\Delta G_f^{\ddagger} - \alpha\Delta G^0$ (see equation (22)). Values of the overvoltage at the half-wave potential are plotted in the same diagram, which can thus be used in the determination of ΔG^0 and $\Delta G_f^{\ddagger}$ from experimental data. It should be added, however, that it is necessary to know α for a given electrode process in order to construct diagrams similar to Fig. 3 for actual cases. This condition limits somewhat the usefulness of the procedure, although useful information could possibly be obtained in a given process simply by imposing to α an *a priori* selected value.

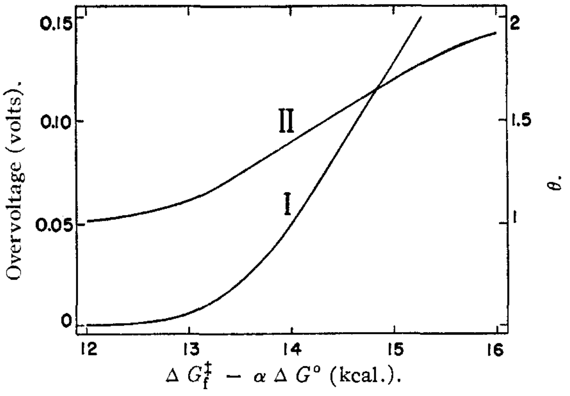

Fig. 3.—Variations of the overvoltage at $E_{1/2}$ (curve I) and coefficient θ (see text) with the quantity $\Delta G_f^{\ddagger} - \alpha\Delta G^0$. Data taken from Fig. 2.

Conclusion

A unified theory of polarographic currents can be developed on the basis of a single general equation, and the theoretical treatment of irreversible, quasi-reversible and reversible waves can be deduced from

---

[23] Note that the sodium and potassium waves are reversible, although their half-wave potentials are in the neighborhood of −2 volts (*vs.* S.C.E.). This indicates that the transfer coefficient for the reduction of these ions is relatively large (0.7 at least).

this general equation. The theory of irreversible polarographic waves previously developed[6,7] is applicable when the rate constant at the standard potential is smaller than approximately 5×10^{-5} cm. sec.$^{-1}$. Experimental quasi-reversible waves which correspond to values of k_s from 5×10^{-5} to 2×10^{-2} cm. sec.$^{-1}$ can still be interpreted although the method is somewhat awkward. Processes for which k_s is larger than 2×10^{-2} cm. sec.$^{-1}$ yield reversible waves, and no information on the kinetics of these electrode processes can be obtained from polarographic data. Other methods such as electrolysis with superposed alternating voltage have to be used.[24] The latter method can be applied[25] for values of k_s up to 1 cm. sec.$^{-1}$, but markedly irreversible processes cannot be studied by this method. Thus, the polarographic method and electrolysis with superposed alternating voltage are the complement of each other in the study of the kinetics of electrode processes.

Note on a Review by Tanford and Wawzonek (Added after the completion of this manuscript)

There appeared recently a review[26] of polarography in which it is stated that we claimed "entirely without foundation" that our treatment of irreversible waves is more general than previous theories.[4,5] Since an authoritative character is conferred to this statement by its publication in a well-known series on physical chemistry, the author feels compelled to challenge this remark.

Tanford and Wawzonek failed to recognize one fundamental point, namely, that *the mass transfer problem is solved rigorously in our treatment* (at least for the linear case), whereas the *Nernst diffusion layer theory is applied in the previous papers on this question.* It is generally possible to apply the Nernst diffusion layer theory to any problem of mass transfer, but results derived in this manner are approximate since the concept of diffusion layer is somewhat artificial.[27] In the case of irreversible waves, for example, the diffusion layer thickness is an unknown function of the rate of the electrode process, and this unknown function is contained implicitly under the form of the diffusion layer thickness in the equations for the irreversible waves derived by previous investigators.

This remark is not made to deny any value to previous work on irreversible waves, but merely to point out the significance of our contribution.

Acknowledgment.—This investigation is part of the project NR-051-258 which is sponsored by the Office of Naval Research. The author gladly acknowledges the support of this organization. Mr. Berzins carried out the numerical calculations involved in the construction of Fig. 1.

BATON ROUGE, LOUISIANA

---

(24) J. E. B. Randles, *Discussion Faraday Soc.*, **1**, 11 (1947); B. Ershler, *ibid.*, **1**, 269 (1947), *J. Phys. Chem., U.S.S.R.*, **22**, 683 (1948); H. Gerischer and K. Vetter, *Z. physik. Chem.*, **197**, 92 (1951); D. C. Grahame, "Mathematical Theory of the Faradaic Admittance," Technical Report to the Office of Naval Research, No. 8 (1952).

(25) J. E. B. Randles, *Trans. Faraday Soc.*, **48**, 828 (1952).

(26) Article by C. Tanford and S. Wawzonek in "Annual Review of Physical Chemistry," G. K. Rollefson and R. E. Powell, Editors, Annual Reviews, Stanford, Calif., 1952. See p. 255.

(27) L. L. Bircumshaw and A. C. Riddiford, *Quart. Rev. Chem. Soc.*, **6**, 157 (1952).

[CONTRIBUTION FROM THE PLASTICS RESEARCH LABORATORY OF THE MONSANTO CHEMICAL COMPANY]

Effects of Chemical Heterogeneity in Copolymers on Some Physical Properties

BY LAWRENCE E. NIELSEN

RECEIVED SEPTEMBER 3, 1952

Homogeneous copolymers in which all the molecules have the same chemical structure and heterogeneous copolymers in which the chemical composition varies from molecule to molecule have been prepared. Several such vinyl type copolymer systems were investigated. Proof of chemical hetereogeneity was obtained by fractionations and chemical analysis. The dynamic shear modulus and mechanical damping were measured over a temperature range. The damping goes through a maximum at the transition temperature while the modulus changes greatly in the transition region. The heterogeneous copolymers have a much broader transition (softening) region than the homogeneous ones. Mixtures of two polymers were investigated. Dynamic mechanical tests are sensitive to changes in chemical heterogeneity, molecular aggregation, and freedom of molecular motion in high polymeric materials.

Introduction

The literature contains many references[1] on the preparation of copolymers and on the determination of monomer reactivity ratios. However, very little has been published on the chemical heterogeneity of copolymers and its effects on various physical properties. Skeist[2] has developed a method of computing the chemical heterogeneity of a copolymer, and deButts[3] has given a method of integrating the rate equations while Wall[4] has shown experimentally that chemical heterogeneity can exist in rubber-like copolymers.

In general the chemical composition of copolymer molecules is not uniform but varies during the course of the polymerization reaction. The first molecules formed are rich in the more reactive component while the molecules formed at the end of the reaction are rich in the less reactive component. Thus, there results a heterogeneity in the chemical composition of the copolymer. In many respects it is expected that changes in physical properties are more dependent upon the degree of heterogeneity than upon such factors as variations in molecular weight where each polymer segment is the same and finds itself in essentially the same type of neighborhood or force fields as every other segment.

Several copolymers have been prepared which

---

(1) F. R. Mayo and C. Walling, *Chem. Revs.*, **46**, 191 (1950).

(2) I. Skeist, THIS JOURNAL, **68**, 1781 (1946).

(3) E. H. deButts, *ibid.*, **72**, 411 (1950).

(4) F. T. Wall, R. W. Powers, G. D. Sands and G. S. Stent, *ibid.*, **70**, 1031 (1948).