stant k_r. The following relationship recently derived[9] will be applied

$$(k_r)_h = (D_{HA}^{1/2}/K^{1/2})k_r^{1/2} \qquad (12)$$

By combining (11) and (12) one obtains

$$\Delta C_{H_3O^+} = -\frac{mK^{1/2}i_{C.D.}}{nFD_{HA}^{1/2}C_A k_r^{1/2}} \qquad (13)$$

Equation (13) can be simplified by introducing the value $k_r = 5.3 \times 10^{13}$ (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ calculated in the previous section, and the approximate value $D_{HA} = 0.6 \times 10^{-5}$ cm.^{2} sec.$^{-1}$.

Thus after numerical transformations

$$\Delta C_{H_3O^+} = -5.8 \times 10^{-10} \frac{mi_{C.D.}K^{1/2}}{nC_A} \qquad (14)$$

From (14) one calculates a relative variation in the concentration of hydronium ions at the surface of the electrode

$$(\Delta C_{H_3O^+})_{\%} = -5.8 \times 10^{-8} \frac{mi_{C.D.}}{nK^{1/2}C_{HA}} \qquad (15)$$

which is expressed in per cent. of concentration $C_{H_3O^+}$.

Values of $(\Delta C_{H_3O^+})_{\%}$ obtained from (15) are by no means negligible when HA is a very weak acid. Consider for example the following case: $m = n$, $K = 10^{-12}$ mole per cm.^{3}, *i.e.*, $K = 10^{-9}$ mole per liter, $C_{HA} = 10^{-4}$ mole per cm.^{3}; under these conditions $(\Delta C_{H_3O^+})_{\%}$ is equal to $-580\ i_{C.D.}$ per cent. of C_{H_3O}. If $i_{C.D.}$ is for example 10^{-2} amp. cm.$^{-2}$—a fairly low current density in electrolysis—$(\Delta C_{H_3O^+})_{\%}$ is 5.80%. Even larger errors would be obtained for lower values of the dissociation constant K. It should be emphasized that the influence of concentration polarization of HA or A^- was not taken into account in the present treatment, and consequently that even larger errors than these calculated from (15) could possibly be observed.

In the case of polarographic electrolyses the current densities are of the order of 10^{-3} to 10^{-5} amp. cm.^{2} and the resulting $(\Delta C_{H_3O^+})_{\%}$ is negligible (see (15)).

From the present treatment it is not possible to decide whether the hydronium ion concentration actually varies at the electrode surface. But, it can be concluded that if the *p*H does not vary at the electrode surface as predicted from (15) it is likely that dissociation of acid HA does not precede the electrode process, and that molecules of HA are directly consumed in the electrode process. Dissociation would then occur in some subsequent step of the electrode process. On the other hand, if undissociated molecules of HA are not directly used in the electrode process, one can predict on the basis of equation (15) that the *p*H at the electrode surface is different from that in solution. The difference in *p*H is appreciable (see above) when HA is very weak ($K = 10^{-9}$ mole per liter) and the current density is not too low (10^{-2} amp. cm.$^{-2}$ or above).

Acknowledgment.—It is a pleasure to acknowledge the support of the Office of Naval Research in the course of this investigation.

BATON ROUGE, LA.

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[9] P. Delahay, THIS JOURNAL, **74**, 3506 (1952).

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

Theory of Catalytic Polarographic Currents

BY PAUL DELAHAY AND GEORGE L. STIEHL

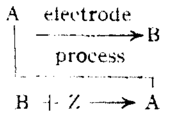
RECEIVED DECEMBER 26, 1951

The theory of polarographic currents controlled by diffusion and by the rate of a catalytic process which regenerates the substance reacting at the dropping mercury electrode is developed. The properties of catalytic currents are derived and a graphic method for the determination of rate constants from experimental currents is reported. The theory is applied to the catalytic currents observed in the reduction of ferric ion in presence of hydrogen peroxide. Calculated and experimental data are in good agreement.

Introduction

In previous publications[1-3] from this Laboratory the theory of polarographic currents controlled by diffusion and by the rate of an heterogeneous reaction was developed and applied to various electrode processes. This theory is applicable to cases in which the chemical process, partially controlling the current, occurs essentially at the surface of the electrode. This condition is fulfilled for many so-called kinetic waves, but there are cases in which the current is controlled by diffusion and by the rate of a reaction occurring at the surface of the electrode and in the vicinity of the electrode. The theory of these so-called catalytic currents is developed in the present paper for cases in which the regeneration process is a second order reaction.

The nature of catalytic polarographic currents can be explained by considering an electrode process in which a substance A is reduced to another substance B at the dropping mercury electrode (reaction (1)). The solution also contains a substance Z which is not reduced at the dropping mercury electrode at the potential at which the limiting current for A is observed.



$$A \xrightarrow[\text{process}]{\text{electrode}} B \qquad (1)$$

$$B + Z \longrightarrow A \qquad (2)$$

Furthermore, Z reacts with B to regenerate substance A (reaction (2)). Because of this "cat-

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

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

[3] P. Delahay and T. J. Adams, *ibid.*, **74**, 1437 (1952).

alytic" effect of substance Z the limiting current corresponding to reaction (1) is increased when Z is present in solution. The increase in current is determined by the kinetics of reaction (2) and by the diffusion processes of substances A, B and Z.

Various catalytic waves of this type have been reported. Hydrogen peroxide causes a large increase in the limiting currents of ferric ion,[4] and of peroxy-compounds of molybdenum, tungsten and vanadium.[5] Proteins containing a sulfhydryl group yield catalytic waves which have been explained by a mechanism involving reactions of the type represented by equations (1) and (2).[6] Finally, various alkaloids are known to give catalytic waves which can be explained similarly.[7]

In a slightly different type of catalytic wave, substance B produced in the electrode process (equation (1)) reacts with Z to give a substance P which is not reduced at the potential at which the limiting current of A is observed. Under these conditions the limiting current for reaction (1) is not affected by the formation of P, but the latter substance may in some cases yield a wave at more negative potentials. Catalytic waves of this type have been observed in the reduction of oxygen in presence of various substances such as hemoglobin[8] and carbonic acid.[9]

Thus far the only theoretical treatment of catalytic polarographic currents was reported by Brdicka and Wiesner.[10] The theory proposed by these authors does not take into account quantitatively the diffusion phenomena occurring at the dropping mercury electrode. As a result, rate constants for reaction (2) one calculates on the basis of this theory are about 10^4 too high as pointed out by Kolthoff and Parry.[4] Other features of catalytic waves such as the decrease in current resulting from an increase in the head of mercury also cannot be explained on the basis of the theory of Brdicka and Wiesner. A more rigorous treatment accounting quantitatively for the properties of catalytic currents is reported in the present paper. The theory is developed for catalytic currents of the first type described by reactions (1) and (2), but the treatment is also applicable to the case in which a new wave results from the catalytic process (substance P mentioned above).

Case of Linear Diffusion

Equation for Concentration C_A.—Consider a plane electrode at which a substance A is reduced to substance B by a process which is assumed to be instantaneous (reaction (1)). The change of concentration between two planes at the distance x and $x + \mathrm{d}x$ from the electrode is the sum of the following two terms: (1) The difference in the flux of substance A at x and $x + \mathrm{d}x$; (2) The change in concentration caused by regeneration of substance A by reaction (2). The first term is calculated in the theory of linear diffusion,[11] and is equal to the product of $\partial^2 C_A/\partial x^2$ by the diffusion coefficient D_A of substance A. The second term depends on the kinetics of reaction (2) according to the following equation which is written by assuming the activity coefficients of the substances involved to be equal to unity

$$\partial C_A/\partial t = kC_B\,C_Z - k_bC_A \tag{3}$$

In equation (3), t is the time elapsed since the beginning of the electrolysis, the C's are the concentrations in moles per cm.^{3}, k is the rate constant for the forward process in sec.$^{-1}$ (moles per cm.^{3})$^{-1}$ and k_b is the rate constant for the backward reaction in sec.$^{-1}$. In subsequent calculations it will be assumed that k_b is much smaller than k, and consequently the term k_bC_A will be deleted.

The total change in concentration is

$$\frac{\partial C_A}{\partial t} = D_A\,\frac{\partial^2 C_A}{\partial x^2} + kC_BC_Z \tag{4}$$

It will be assumed in the derivation that the concentration of substance Z is sufficiently high and consequently that C_Z is independent of x and t. The relationship between C_A and C_B is obtained by applying Duhamel's theorem.[12] In problems of linear diffusion one obtains

$$C_B = \left(\frac{D_A}{D_B}\right)^{1/2}(C_A^\circ - C_A) \tag{5}$$

in which C_A° is the bulk concentration of A, and the D's are the diffusion coefficients.

The combination of (4) and (5) yields the differential equation for concentration C_A

$$\frac{\partial C_A}{\partial t} = D_A\frac{\partial^2 C_A}{\partial x^2} + k\left(\frac{D_A}{D_B}\right)^{1/2}C_Z(C_A^\circ - C_A) \tag{6}$$

In general the diffusion coefficients D_A and D_B are not very different and consequently the ratio D_A/D_B will be assumed to be equal to unity in further calculations.

Variations of Concentration C_A.—By introducing the variable u defined by

$$u = C_A^\circ - C_A \tag{7}$$

equation (6) is transformed into

$$\frac{\partial u}{\partial t} = D_A\,\frac{\partial^2 u}{\partial t^2} - kC_Zu \tag{8}$$

Equations (6) and (8) should be solved for the following initial and boundary conditions: for $t = 0$, $C_A = C_A^\circ$ and $u = 0$; for $t > 0$ and $x = 0$, $C_A = 0$ and $u = C_A^\circ$. Equation (8) can be solved by different methods[13] among which is the Laplace transformation. The latter method will be applied here. From tables,[14] one obtains the following Laplace transform of equation (8)

$$\frac{\mathrm{d}^2\bar{u}}{\mathrm{d}x^2} - \frac{s + kC_Z}{D_A}\,\bar{u} = 0 \tag{9}$$

which is to be solved for $\bar{u} = C_A^\circ/s$ at $x = 0$. Thus

$$\bar{u} = \frac{C_A^\circ}{s}\exp\left[-x\left(\frac{s + kC_Z}{D_A}\right)^{1/2}\right] \tag{10}$$

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(4) I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 3728 (1951).

(5) I. M. Kolthoff and E. P. Parry, *ibid.*, **73**, 5315 (1951).

(6) For the very abundant literature on this subject, see I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 405-420.

(7) See for example, H. F. W. Kirkpatrick, *Quart. J. Pharm. Pharmacol.*, **18**, 245, 338 (1946); **19**, 8, 127, 526 (1946); **20**, 87 (1947).

(8) R. Brdicka and C. Tropp, *Biochem. Z.*, **289**, 301 (1936). See also ref. 6.

(9) P. Van Rysselberghe, *et al.*, *J. Phys. Chem.*, **54**, 754 (1950).

(10) R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 39 (1947).

(11) See ref. 6, p. 18.

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

(13) See ref. 12, p. 60.

(14) R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1944, pp. 295-302. See also ref. 12, p. 269.

The corresponding function u can be obtained from table of transforms,[14] and after returning to the variable C_A one obtains the concentration C_A as a function of x and t

$$C_A = C_A^\circ \left\{ \begin{array}{l} 1 - \frac{1}{2} \exp\left[-x\left(\frac{kC_Z}{D_A}\right)^{1/2}\right] \operatorname{erfc}\left[\frac{x}{2(D_A t)^{1/2}} - (kC_Z t)^{1/2}\right] \\ -\frac{1}{2} \exp\left[x\left(\frac{kC_Z}{D_A}\right)^{1/2}\right] \operatorname{erfc}\left[\frac{x}{2(D_A t)^{1/2}} + (kC_Z t)^{1/2}\right] \end{array} \right\} \quad (11)$$

in which the notation erfc (ξ) represents the complement of the error function as defined by

$$\operatorname{erfc}(\xi) = 1 - \frac{2}{\pi^{1/2}} \int_0^\xi \exp(-z^2) dz \qquad (12)$$

The value of C_A from equation (11) was plotted against x in Fig. 1 for the following data: $C_A^\circ = 10^{-5}$ mole per cm.^{3}, $D_A = 10^{-5}$ cm.^{2} sec.$^{-1}$, $C_Z = 10^{-3}$ mole per cm.^{3}, $t = 10$ sec. The various curves correspond to values of the rate constant k from 0 to 1000 sec.$^{-1}$ (moles per cm.^{3})$^{-1}$. This diagram shows that the decrease of concentration C_A is less pronounced when there is regeneration by reaction (2). When k is smaller than 10 sec.$^{-1}$ (moles per cm.^{3})$^{-1}$, the catalytic effect is negligible after 10 seconds.

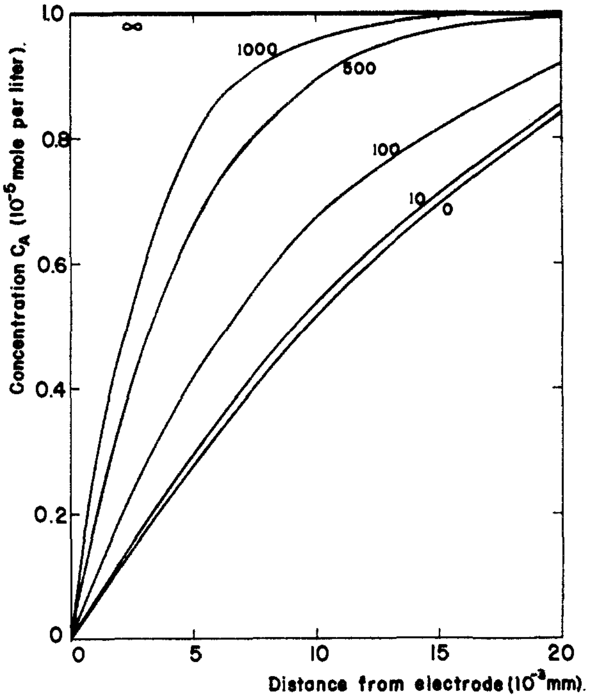

Fig. 1.—Variations of concentration C_A with the distance from the electrode. Number on each curve is the value of rate constant k in sec.$^{-1}$ (moles per cm.^{3})$^{-1}$. Concentrations after 10 sec. are in 10^{-5} mole per cm.^{3} (instead of 10^{-5} mole per liter as indicated on diagram).

By introducing $k = 0$ in equation (11) it can be seen that the resulting value of C_A is identical with that obtained in the theory of simple linear diffusion.[11] This is to be expected since there is no catalytic effect. On the other hand when k is infinite one obtains $C_A = C_A^\circ$ after expanding[15] the error integrals in (11). This is to be expected since for $k = \infty$, substance A is regenerated as soon as it is consumed.

Variations of Current.—The current is obtained by multiplying the flux at the electrode surface by the charge involved in the reduction of one mole of substance A. The flux is the product of the diffusion coefficient D_A by the gradient of concentration $(\partial C_A/\partial x)_{x=0}$ which is obtained by differentiating (11) with regard to x and introducing $x = 0$ in the resulting equation. Noticing that erf $(-\xi) = -\operatorname{erf}(\xi)$ one obtains after transformations

$$i = nFAD_A^{1/2}C_A^\circ \left\{(kC_Z)^{1/2} \operatorname{erf}\left[(kC_Z t)^{1/2}\right] + \frac{\exp(-kC_Z t)}{(\pi t)^{1/2}}\right\} \quad (13)$$

in which n is the number of electrons involved in the electrode process, F the faraday, A the area of the electrode in cm.^{2}, and the notation erf (ξ) represents the error integral

$$\operatorname{erf}(\xi) = \frac{2}{\pi^{1/2}} \int_0^\xi \exp(-z^2) dz \qquad (14)$$

When $k = 0$, equation (13) is identical with the equation for a current controlled by simple linear diffusion.[11] When $k = \infty$ equation (13) yields an infinite current. This is to be expected since it was assumed that concentration C_Z at the surface of the electrode is the same as in the bulk of the solution. Actually for $k = \infty$, one should take into account the decrease in C_Z at the surface of the electrode, but this decrease was neglected in the present treatment.

As an example, the current i given by (13) is plotted against time in Fig. 2 for the following data: $n = 1$, $A = 1$ cm.^{2}, $D_A = 10^{-5}$ cm.^{2} sec.$^{-1}$, $C_A^\circ = 10^{-5}$ mole per cm.^{3}, $C_Z = 10^{-3}$ mole per cm.^{3}; and for values of k from 0 to 1000 sec.$^{-1}$ (moles per cm.^{3})$^{-1}$. Figure 2 shows that because of the catalytic effect the current decreases less rapidly than in the case of simple diffusion. In the present case, the catalytic effect is noticeable when k is larger than 10 sec.$^{-1}$ (moles per cm.^{3})$^{-1}$.

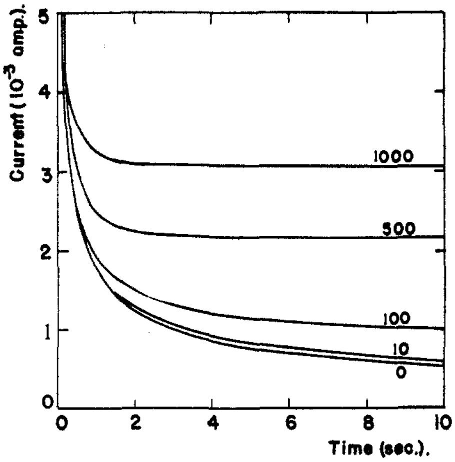

Fig. 2.—Variations of current (equation (13)) with time. Number on each curve is the value of rate constant k in sec.$^{-1}$ (moles per cm.^{3})$^{-1}$.

Case of the Dropping Mercury Electrode

Instantaneous Total Current.—In principle, catalytic polarographic currents could be calculated by following the method applied in the previous section and by using the corresponding equations of spherical diffusion. However, the mathematical treatment would be arduous, and it is much simpler to apply the following method. When the rate constant is equal to zero, equation (13) is identical to the Ilkovic equation provided that the right-

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[15] B. O. Pierce, "A Short Table of Integrals," Ginn and Company, New York, N. Y., 1929, p. 120.

hand side of (13) be multiplied by $(7/3)^{1/2}$. This is the factor which was used by Ilkovic to adjust the results of linear diffusion to the case of the dropping mercury electrode.[16] By using the same factor in the case of a rate constant different from zero, and replacing the area A by its value calculated in terms of the characteristics of the capillary, one obtains after numerical transformations

$$i_t = 1.255 \times 10^6 n m^{2/3} t^{2/3} D_A{}^{1/2} C_A^0 \times \left\{ (kC_Z)^{1/2} \operatorname{erf} [(kC_Z t)^{1/2}] + \frac{\exp(-kC_Z t)}{(\pi t)^{1/2}} \right\} \quad (15)$$

in which i_t is in microamperes, m is the rate of flow of mercury in mg. sec.$^{-1}$, t the time in sec. of the drop life at which the current is measured, D_A the diffusion coefficient in cm.^{2} sec.$^{-1}$, k the rate constant in sec.$^{-1}$ (moles per liter)$^{-1}$ for the forward reaction (2), and C_A^0 and C_Z the concentrations of A and Z in moles per liter.

Separation of Diffusion and Catalytic Currents.—It is interesting for further discussion to separate the current given by equation (15) into the catalytic current due to reaction (2) and the limiting current which is observed when substance Z is not present. By subtracting the latter current—as given by the Ilkovic equation—from equation (15) one obtains the instantaneous *catalytic current* i_c. Thus

$$i_c = 1.255 \times 10^6 n m^{2/3} t^{2/3} D_A{}^{1/2} C_A^0 \left\{ (kC_Z)^{1/2} \operatorname{erf} [(kC_Z t)^{1/2}] - \frac{1 - \exp(-kC_Z t)}{(\pi t)^{1/2}} \right\} \quad (16)$$

in which the units are the same as in equation (15).

Average Catalytic Current and Determination of *k* from Experimental Currents.—The average catalytic current during the drop life τ can be written in the abridged form

$$(i_c)_{av} = 1.255 \times 10^6 \sigma n m^{2/3} D_A{}^{1/2} C_A^0 \quad (17)$$

in which the function σ is defined by

$$\sigma = (kC_Z)^{1/2} \frac{1}{\tau} \int_0^\tau t^{2/3} \operatorname{erf} [(kC_Z t)^{1/2}] \mathrm{d}t - \frac{1}{\tau \pi^{1/2}} \int_0^\tau t^{1/6} [1 - \exp(-kC_Z t)] \mathrm{d}t \quad (18)$$

Values of function σ were calculated for drop times from 1 to 5 sec., and for values of kC_Z from 0.01 to 100 sec.$^{-1}$. The results are plotted in the diagram of Fig. 3. The principle of the calculation of σ is as follows. The functions under the integral sign in (18) were plotted against t, and the values of the integrals of (18) were obtained by graphic integration for different values of τ and kC_Z.

The rate constant k is calculated from an experimental current in the following manner. First, the value of σ is obtained from the experimental current by application of (17); and the point having the corresponding coördinates σ and τ is located on the diagram of Fig. 3. The value of kC_Z for the curve passing through this point is determined by interpolation, and the rate constant is calculated from the value of kC_Z thus obtained.

When kC_Z is larger than 100 sec.$^{-1}$, $\operatorname{erf}[(kC_Z t)^{1/2}]$ is practically equal to unity even for values of t as small as 0.15 sec. Furthermore, the term exp $(-kC_Z t)$ in (18) is practically equal to zero when kC_Z is larger than 100. As a result, equation (18) is greatly simplified and the integration can be performed. Thus for $kC_Z > 100$ sec.$^{-1}$

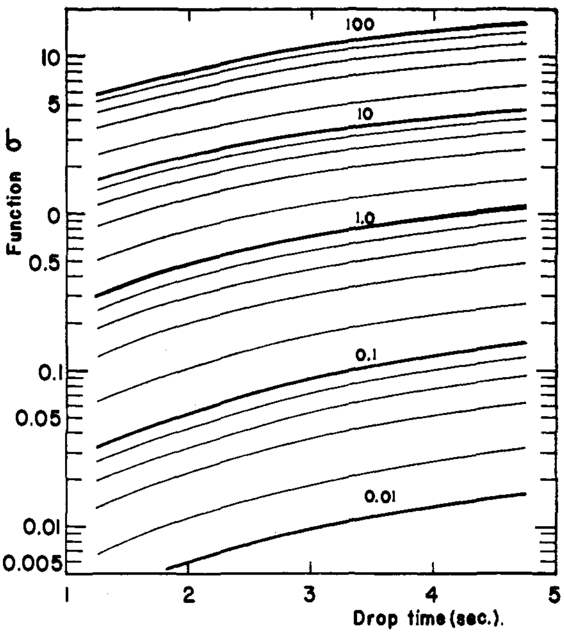

Fig. 3.—Variations of σ (equation (18)) with drop time τ. Number on each curve is the value of kC_Z in sec.$^{-1}$. Intermediate curves correspond to values of kC_Z which are multiple or submultiple of 2, 4, 6, 8.

$$\sigma \simeq \frac{3}{5} (kC_Z)^{1/2} \tau^{2/3} - \frac{6}{7\pi^{1/2}} \tau^{1/6} \quad (19)$$

and kC_Z is directly calculable from (17) and (19). Note that the second term on the right-hand side is much smaller than the first term. Therefore, the catalytic current is almost equal to the total current. Thus when kC_Z is larger than 100 sec.$^{-1}$, an approximate value of k can be obtained from the total current given by (15). The latter equation takes then the simplified form

$$(i_c)_{av} \simeq (i_t)_{av} \simeq \frac{3}{5} 1.255 \times 10^6 n m^{2/3} \tau^{2/3} D_A{}^{1/2} C_A^0 C_Z{}^{1/2} k^{1/2} \quad (20)$$

which yields directly the rate constant k.

Properties of Catalytic Currents

Dependence of i_c on Concentration C_A^0.—From equations (16) and (17) one concludes that the catalytic current is proportional to the concentration C_A^0 of the substance which is regenerated by the catalytic process.

Dependence of i_c on Concentration C_Z and Rate Constant *k*.—Since the catalytic current is a function of the product kC_Z (see (16)) the influence of these two factors is discussed in the same section. Equations (16), (17) and (18) show that the catalytic current increases with kC_Z. However, there is no direct proportionality between i_c and kC_Z. For values of kC_Z larger than 100 sec.$^{-1}$ the current is practically proportional to the square root of kC_Z (see equation (20)). An example is described in the experimental part (Fig. 5).

Dependence of i_c on the Head of Mercury.—The dependence of the average catalytic current

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[16] D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **6**, 498 (1934).

on the head of mercury is obtained by replacing m and τ in equations (17) and (18) by their values in terms of the head of mercury. The rate of flow of mercury is proportional to the head of mercury H as corrected for the back pressure; τ is inversely proportional to H.[17] Since the equation showing the dependence of i_c on H is rather intricate, it is easier to discuss a specific case. Average catalytic currents are plotted against H in Fig. 4 for various values of kC_Z. The average total current obtained by adding to $(i_c)_{\text{average}}$ the average diffusion current is also plotted *versus* H in Fig. 4. It is seen from Fig. 4 that the catalytic current decreases when the head of mercury is increased. The larger the value of kC_Z, the less pronounced is the relative decrease in current. The total current increases with the head of mercury, and the relative increase is more pronounced when kC_Z decreases. For $kC_Z > 100$ sec.$^{-1}$ it is found that the current is independent of the head of mercury as one would expect from equation (20) (factor $m^{2/3}\tau^{2/3}$). When $k = 0$ the total current is simply the diffusion current which is proportional to $H^{1/2}$. When $kC_Z = 0$ the first integral in (18) takes the form 0×0 and the second integral is equal to zero. By calculating the limit of the first integral for $kC_Z = 0$, one reaches the conclusion that the average catalytic current becomes inversely proportional to the head of mercury when kC_Z approaches zero.

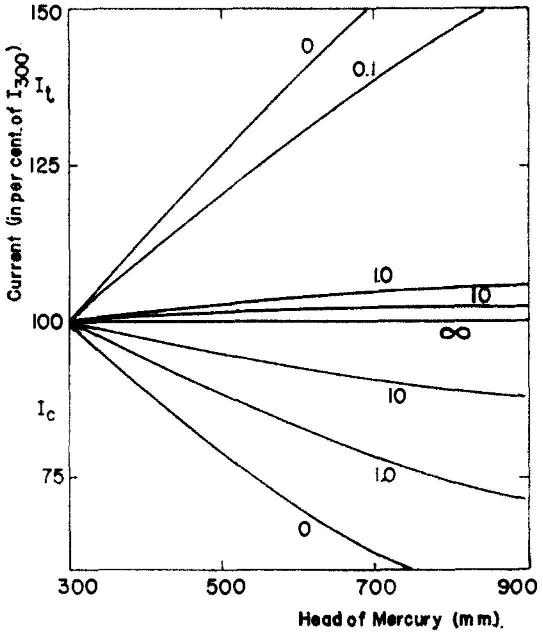

Fig. 4.—Variations of catalytic current with the head of mercury: $m = 1.5$ mg. sec.$^{-1}$ and $\tau = 4$ sec. for $H = 300$ mm. Number on each curve is the value of kC_Z in sec.$^{-1}$. Curves whose ordinates are higher than 100 represent the total current; curves whose ordinates are smaller than 100 represent the catalytic current.

Influence of Temperature.—The influence of temperature is obtained by differentiating (17) and (18) with regard to temperature. Various terms in the equation thus obtained can be combined as in the case of the Ilkovic equation.[18] Nevertheless, the writing is rather heavy and it is much easier to calculate k at various temperatures from the experimental current (see above). The energy of activation for the catalytic process is obtained from a conventional log k *vs.* $(1/T)$ plot.

Verification for the Reduction of Ferric Ion in Presence of Hydrogen Peroxide

The theory developed in the previous sections was applied to the catalytic wave obtained in the reduction of ferric ion in presence of hydrogen peroxide. This case of catalytic wave was thoroughly studied by Kolthoff and Parry,[4] and only the results pertaining to the present theory will be discussed. In this case, the catalytic process is the oxidation of ferrous ion by hydrogen peroxide. This reaction involves two ferrous ions for each molecule of hydrogen peroxide, but the rate of the oxidation process is proportional to the product of the activities of ferrous ion and hydrogen peroxide.[4] Consequently, the present theory is applicable without any change (see reaction (2)).

Experimental

The experimental methods described by Kolthoff and Parry were followed without change. Waves were recorded with a Sargent Polarograph model XXI, and potentials were measured with a Leeds and Northrup student potentiometer. An H cell was used for all recordings; the calomel electrode arm of this cell was filled with 0.25 molar sulfuric acid, and the cell was connected to a saturated calomel electrode by a bridge filled with a 1 molar potassium nitrate solution containing 4% of agar-agar. Unless otherwise indicated the temperature was 31.40 ± 0.03°.

Description and Discussion of Experimental Results

Determination of Rate Constant k.—Values of the catalytic current for concentrations of hydrogen peroxide[19] ranging from 0.0145 to 0.362 mole per liter are listed in Table I together with the corresponding rate constants determined from equation (17) and Fig. 3. The supporting electrolyte was 0.25 molar H_2SO_4, and the following data were used in the calculations: $m = 1.52$ mg. sec.$^{-1}$, $\tau = 4.02$ sec., $C_{Fe^{+++}} = 2.5 \times 10^{-4}$ mole per liter. The diffusion coefficient of ferric ion was determined from the diffusion current for ferric ion in the absence of hydrogen peroxide, and the value $D_{Fe^{+++}} = 0.73 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ was obtained from the Ilkovic equation.

TABLE I

DATA FOR CATALYTIC CURRENTS OF FERRIC ION IN PRESENCE OF HYDROGEN PEROXIDE AT 31.4°

$C_{H_2O_2}$ mole per l.	Experimental $(i_c)_{av}$ microamp.	Calcd. k, sec.$^{-1}$ (moles per l.)$^{-1}$
0.0145	1.13	69
.0355	2.02	78
.0724	2.91	72
.181	5.18	72
.362	9.03	93
	Average	77

The rather large deviations from the average rate constant are caused mainly by experimental difficulties. Firstly, the waves are poorly defined[4]; secondly, hydrogen peroxide undergoes catalytic decomposition during the measurements.[4] Nevertheless, it can be concluded from the data of Table I that essentially the same value of k is obtained regardless of the hydrogen peroxide concentration.

Dependence of i_c on the Concentration of Hydrogen Peroxide.—Variations of the catalytic current with the concentration of hydrogen peroxide are shown in Fig. 5. The curves were calculated on the basis of the lowest and highest values of k listed in Table I, *i.e.*, for $k = 69$ and $k = 93$

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(17) See ref. 6, p. 67.

(18) See ref. 6, pp. 74-76.

(19) Titrations of hydrogen peroxide were carried out by Mr. J. E. Strassner, whose help is gladly acknowledged.

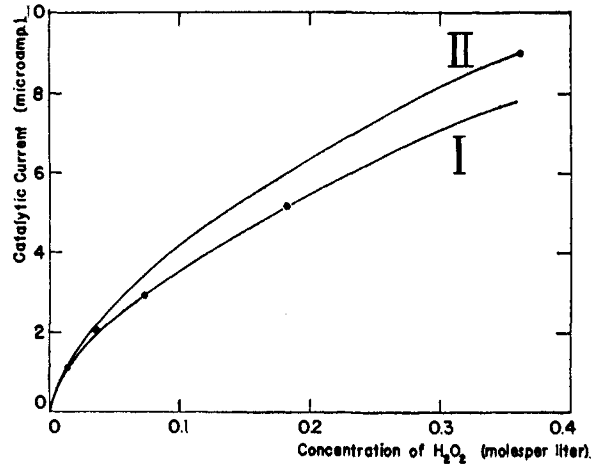

Fig. 5.—Variations of the catalytic current of ferric ion with the concentration of hydrogen peroxide: I, calculated curve for $k = 69$ sec.$^{-1}$ (moles per liter^{-1}); II, calculated curve for $k = 93$ sec.$^{-1}$ (moles per liter^{-1}). Dots are experimental values.

sec.$^{-1}$ (moles per liter)$^{-1}$, respectively. Points are experimental currents. Taking into account the relative inaccuracy of the experimental data, it can be concluded that the agreement between experimental and calculated data is excellent. The concentration of hydrogen peroxide was not lowered below 1.45×10^{-2} mole per liter since it was assumed in the previous theory that $C_{H_2O_2}$ is much larger than $C_{Fe^{+++}}$. In the present case $C_{Fe^{+++}}$ is 2.5×10^{-4} molar and the above condition would not have been fulfilled for values of $C_{H_2O_2}$ appreciably smaller than 1.45×10^{-2} mole per liter.

The relationship between catalytic current and concentration of ferric ion was not investigated, since the proportionality between these two quantities was verified by Kolthoff and Parry.[4]

Dependence of i_c on the Head of Mercury.—Data for three values of the head of mercury are listed in Table II.

TABLE II

VARIATIONS OF i_c WITH THE HEAD OF MERCURY

H,[a] mm.	Experimental $(i_c)_{av}$ microamp.	Calcd. $(i_c)_{av}$ microamp.
611	2.02	2.01
727	1.96	1.95
886	1.65	1.74

[a] Not corrected for the back pressure.

The following data were used in the calculations: $C_{H_2O_2} = 3.55 \times 10^{-2}$ mole per liter, $C_{Fe^{+++}} = 2.5 \times 10^{-4}$ mole per liter, $D_{Fe^{+++}} = 0.73$ cm.^{2} sec.$^{-1}$; τ: 4.02, 3.40 and 2.71 sec., respectively; m, 1.52, 1.82 and 2.25 mg. sec.$^{-2}$, respectively. The average value $k = 77$ sec.$^{-1}$ (mole per liter)$^{-1}$ of Table I was used in calculations. Table II shows that the agreement between experimental and calculated data is good. The total current remained practically unchanged in agreement with previous observations of Kolthoff and Parry.[4]

Dependence of $(i_c)_{av}$ on Temperature.—The catalytic current was measured at 0.6° and rate constant k was calculated on the basis of the following data: $C_{Fe^{+++}} = 2.5 \times 10^{-4}$ mole per l., $D_{Fe^{+++}} = 0.25 \times 10^{-5}$ cm.^{2} sec.$^{-1}$, $\tau = 4.23$ sec.; $C_{H_2O_2}$: 0.0344, 0.0687 and 0.172 mole per l., respectively; i_c: 0.317, 0.581 and 1.195 microamp., respectively. The corresponding values of k were as follows: 14, 18, and 29 sec.$^{-1}$ (moles per l.)$^{-1}$. Logarithms of extreme values of k obtained at 31.4 and 0.6° are plotted against the reciprocal of absolute temperature in Fig. 6, which shows that the polarographic values of k are in good agreement with the data obtained by a chemical method by Baxendale, *et al.*[20]

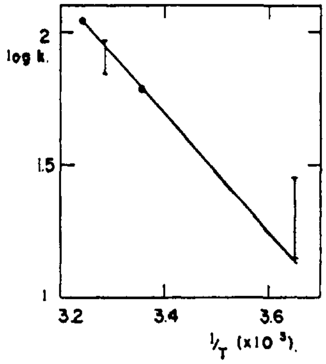

Fig. 6.—log k *vs.* $(1/T)$ plot for the oxidation of ferrous ion by hydrogen peroxide. Dots are values obtained by a chemical method by Baxendale, *et al.* Vertical lines represent extreme polarographic values.

The polarographic values of k at 0.6° are slightly too high as indicated by Fig. 6. This can be explained as follows. The polarographic cell was immersed in the waterbath at 0.6°, but the tube connecting the capillary of the dropping mercury electrode to the mercury reservoir was not. As a result, the mercury dropping in the cell, and the solution surrounding the mercury drop, were at a temperature above 0.6°. Therefore, the rate constants thus obtained are too high. A completely immersed cell was not used because the manipulations of such a cell would have prolonged the operations involved in the recording of a wave to a point where the catalytic decomposition of hydrogen peroxide would have interfered.

Conclusion

The theory developed in the present paper accounts quantitatively for the properties of catalytic waves. Since rate constants can be determined accurately from polarographic data,[21] catalytic currents can be used in the study of kinetic processes which are too rapid to be followed by conventional methods. Likewise, reactions involving unstable substances can also be studied. However, it should be pointed out that the occurrence of a catalytic wave requires the fulfillment of certain conditions which are discussed in the Introduction, and that these conditions limit somewhat the scope of the method. Application of the present theory to various catalytic waves will be reported in subsequent papers.

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(20) J. H. Baxendale, M. G. Evans and G. S. Park, *Trans. Faraday Soc.*, **42**, 155 (1946).

(21) The fluctuations observed for the catalytic current of ferric ion in presence of hydrogen peroxide result from experimental difficulties rather than from approximations in the theoretical treatment.