represented by equation 10. In this equation, $K$ and $K_0$ are equilibrium or rate constants for the substituted and unsubstituted materials, $\sigma$ is the

$$\log K = \log K_0 + \rho\sigma \qquad (10)$$

substituent function for which Hammett has tabulated[42] empirical values, and $\rho$ is the reaction constant. For the ionization of substituted benzoic acids, the reaction constant in water, $\rho^w$, is equal to unity, and $\rho$ varies greatly with solvent (see Table III).

TABLE III

REACTION CONSTANTS FOR THE IONIZATION OF SUBSTITUTED BENZOIC ACIDS IN VARIOUS SOLVENTS, 22 ± 4°

| Solvent | $\rho$ | $Y_-$ | Reference[d] |
|---|---|---|---|
| Water | 1.000 | 0.000 | 41 |
| 50 Vol. % ethanol | 1.464 | $0.737^a$ | 18 |
| Ethanol | 1.626 | 1.000 | 17 |
| 50 Vol. % methanol | 1.241 | $0.384^b$ | 42 |
| Methanol | 1.374 | $0.595^b$ | 17 |
| Butanol-1, 0.05 $M$ LiCl | 1.476 | $0.758^{b,c}$ | 15 |

[a] By interpolation from Table II. [b] Calculated from equation 11. [c] Using the data of Wooten and Hammett[15] for aliphatic acids and benzoic acid in butanol-1, and of Table II for the same acids in 50.1% ethanol, the ratio of $\mathbf{Y}_-$ values for the two solvents has been computed from equation 8. On this basis, $\mathbf{Y}_- = 0.727$ for butanol-1. [d] In some cases, $\rho$ values were computed by the present authors from the published data.

It follows from equations 6 and 10 that the variation of $\rho$ with solvent is given by equation 11 where $\beta$ is a parameter. On the basis of data for the

$$\rho = \rho^w + \beta\mathbf{Y}_- \qquad (11)$$

system ethanol–water (Table III), equation 11 is valid to an excellent approximation, and for $\beta = 0.628$ the probable error of the fit is only 0.002. $\rho$ values for the other solvents have been used to estimate $\mathbf{Y}_-$ with the aid of equation 11. These tentative estimates are listed in Table III. For the solvent butanol-1, $\mathbf{Y}_-$ was also computed from data for aliphatic acids using equation 8. The value obtained in this way is in satisfactory agreement with the one based on equation 11 (see Table III), so that the present correlations do not seem to be limited in scope to the system ethanol–water.

**On the Determination of Degenerate Single Ion Activity Coefficients.**—If equation 6 is accepted, the way is open for the determination of log $f_H$ values and thus of other degenerate single ion activity coefficients. From the data reported in this article alone it is not possible to solve equations 6 for log $f_H$ since there is one more unknown than there are equations. However when values of $pK_A$ and of the activity function for other structural types become available, the number of independent equations increases more rapidly than the number of new unknowns, and solutions for $m_A$ and log $f_H$ become possible. This phase of the problem is being actively pursued.

**Acknowledgments.**—It is a pleasure to thank Professor L. P. Hammett in whose laboratory much of this work was done for his great hospitality, and to thank him and Professor D. Y. Curtin for many valuable discussions. One of us (E. G.) is grateful to the Frank B. Jewett Fellowship Committee for the award of a fellowship which has made this work possible.

TALLAHASSEE, FLA. RECEIVED MARCH 13, 1950

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[42] R. Kuhn and A. Wassermann, *Helv. Chim. Acta*, **11**, 1, 31, 44 (1928).

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

# Theory of Polarographic Currents Controlled by Rate of Reaction and by Diffusion[1]

BY PAUL DELAHAY

An equation is derived for polarographic currents controlled by rate of reaction and by diffusion. The Ilkovic equation corresponds to a special case of the more general equation reported in the present paper. The average limiting current is calculated. Variations of the limiting current with the head of mercury are discussed quantitatively. A simple graphic method for the computation of rate constants from experimental data is reported. The theory is applied to the reduction of weak acids. Experimental data confirming the theoretical conclusions are presented for pyruvic acid.

Two quantitative treatments of polarographic currents controlled by rate of reaction and by diffusion have been reported in the recent years. The theory of Brdicka and Wiesner,[2] although interesting, is based on rather arbitrary hypotheses as pointed out by Lingane.[3] The more rigorous treatment of Koutecky and Brdicka[4] involves elaborate mathematical operations. A new treatment is discussed in the present paper and some of the difficulties of previous theories are eliminated. New features of diffusion-rate controlled currents are also reported.

## Case of Linear Diffusion

**Boundary Condition.**—We consider the electrolytic reduction of two substances B and R which are transformed into one another according to the reaction B $\rightleftarrows$ R. We assume that R is reduced at less negative potentials than B, and that the concentration of R is negligible in comparison with that of B. Moreover, the potential of the electrode is adjusted in such a manner that only R is reduced. Under these conditions, B is transformed into R in the immediate neighborhood of the electrode as the reduction of R proceeds. If the transformation B $\rightleftarrows$ R is a first order reaction the number of moles B transformed into R at the surface of the electrode

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[1] Paper presented before the division of Physical and Inorganic Chemistry of the International Congress of Pure and Applied Chemistry held in New York in September, 1951.

[2] R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Commun.*, **12**, 138 (1947).

[3] J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

[4] J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 337 (1947).

is proportional to the concentration $C$ of B at the surface of the electrode. Thus one has for an area equal to 1 sq. cm.

$$\mathrm{d}N_\mathrm{B} = kC\,\mathrm{d}t \qquad (1)$$

where $k$ is the rate constant in cm. sec.$^{-1}$, and $C$ is in moles cm.$^{-3}$. The backward reaction R → B is neglected in equation 1 because the concentration of R at the electrode is negligible since R is reduced as soon as it is formed. The rate constant $k$ in equation (1) is expressed in cm. sec.$^{-1}$ whereas rate constants of first order homogeneous reactions are in sec.$^{-1}$. A conventional rate constant $k'$ can be introduced by writing equation 1 in the following manner

$$\mathrm{d}N_\mathrm{B} = k'C\delta\mathrm{d}t \qquad (2)$$

where $\delta$ represents the thickness (in cm.) of a monolayer of reducible substance at the surface of the electrode. The product $C\delta$ is thus the surface concentration of reducible substance in moles cm.$^{-2}$. As a first approximation, one may assume that $\delta$ represents the average distance between two ions or molecules of the reducible substance in solution. The distance $\delta$ is thus easily calculable on the basis of the concentration of reducible substance. However, the introduction of a surface concentration $C\delta$ is somewhat artificial and consequently we shall apply formula 1 rather than 2.

The number $\mathrm{d}N_\mathrm{B}$ of moles of B diffusing toward the electrode is proportional to the gradient of concentration at the surface of the electrode and to the diffusion coefficient $D$ of substance B. Thus one has for an area equal to 1 sq. cm.[5]

$$\mathrm{d}N_\mathrm{B} = D\left(\frac{\partial C}{\partial x}\right)_{x=0}\mathrm{d}t \qquad (3)$$

where $x$ is the distance from the electrode. Combining equations (1) and (3), one obtains the following boundary condition

$$D\left(\frac{\partial C}{\partial x}\right)_{x=0} = kC_{x=0} \qquad (4)$$

**Derivation of the Current.**—Concentration $C$ of substance B is the solution of the equation for linear diffusion and for the boundary condition corresponding to equation (4). An identical problem is studied in the theory of heat conduction and the solution reported in the literature[6] is applicable to the present case. The equation for $C$ thus obtained has been applied by Delahay and Jaffé[7] in their study of the kinetics of heterogeneous processes controlled by rate of reaction and by diffusion.

The current $i$ flowing through the electrolytic cell is proportional to the flux of substance at the electrode, to the charge exchanged per mole of substance reduced, and to the area of the electrode.[8] The flux at the electrode is calculated as follows. The equation giving the concentration as a function of $x$ and $t$ is differentiated with respect to $x$. The value $x = 0$ is introduced in the derivative $\partial C/\partial x$, and the resulting equation is multiplied by $D$. The equation thus obtained represents the flux at the electrode. By multiplying the flux by the charge involved in the electrode process and by the area of the electrode, one obtains the current. Thus

$$i = nFAC_0k\left[1 - \Phi\left(k\sqrt{\frac{t}{D}}\right)\right]\exp\frac{k^2t}{D} \qquad (5)$$

where $n$ is the number of electrons involved in the electrode process, $F$ is the faraday, $A$ is the area of the electrode in sq. cm., $C_0$ is the concentration of reacting substance in moles cm.$^{-3}$, $k$ is the rate constant in cm. sec.$^{-1}$, $D$ is the diffusion coefficient of the reacting substance in cm.$^2$ sec.$^{-1}$, $t$ is the time elapsed since the beginning of the electrolysis in sec., and $\Phi(k\sqrt{t/D})$ represents the error integral

$$\frac{2}{\sqrt{\pi}}\int_0^{k\sqrt{\frac{t}{D}}} e^{-z^2}\,\mathrm{d}z$$

Equation (5) shows that the current decreases in the course of time. At time $t = 0$ the current has a finite value equal to $nFAC_0k$, in contrast with the value $i = \infty$ for a current entirely controlled by diffusion.

By introducing the value $k = \infty$ in formula (5), one should obtain the equation for the case of a current entirely controlled by diffusion. It is easily shown that this is indeed the case by expanding the error integral into a semi-convergent series[9] and by introducing $k = \infty$ in the equation thus obtained.

## Case of the Dropping Mercury Electrode

In principle the method of calculation discussed in the previous section could be applied to the case of the dropping mercury electrode. However, the mathematical treatment becomes exceedingly intricate and it is much simpler to apply the following method. The area of the electrode in formula (5) is replaced by its value calculated in terms of the characteristics $m$ and $t$ of the dropping mercury electrode. Moreover, the error integral is expanded and the value $k = \infty$ is introduced in the equation thus obtained. The resulting formula is identical with the Ilkovic equation except for the numerical constant. The correct equation is obtained by multiplying by $\sqrt{7/3}$ the second member of the formula thus derived from (5). This is precisely the numerical coefficient which was used by Ilkovic[10] to adjust the results obtained by application of the equation of linear diffusion to the case of the dropping mercury electrode. Consequently, one obtains the equation for a finite value of $k$ by multiplying the second member of formula (5) by $\sqrt{7/3}$, and by introducing in the resulting equation the value of $A$ calculated in terms of $m$ and $t$. After numerical substitutions one obtains the equation

$$i = 1255\ nm^{2/3}t^{2/3}C_0k\left[1 - \Phi\left(k\sqrt{\frac{t}{D}}\right)\right]\exp\frac{k^2t}{D} \qquad (6)$$

where $m$ is in mg. sec.$^{-1}$, $t$ in sec., $C_0$ in millimoles

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[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 17.

[6] P. Frank and R. von Misses, "Die Differential- und Integralgleichungen der Mechanik und Physik," Vol. II, Rosenberg, New York, N. Y., 1935, p. 579.

[7] P. Delahay and G. Jaffé, unpublished investigation.

[8] See ref. (5), p. 21.

[9] B. O. Pierce, "A Short Table of Integrals," 3rd Edition, Ginn and Co., Boston, Mass., 1929, p. 120.

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

per liter, $k$ in cm. sec.$^{-1}$, $D$ in cm.$^2$ sec.$^{-1}$, and $i$ in microamperes. $\Phi(k\sqrt{t/D})$ represents the error integral

$$\frac{2}{\sqrt{\pi}}\int_0^{k\sqrt{\frac{t}{D}}} e^{-z^2}\,dz$$

Formula (6) is the general equation for polarographic limiting currents controlled by diffusion and by rate of reaction. The Ilkovic equation corresponds to the particular case of formula (6) for which the rate constant is infinite. The equation reported by Koutecky and Brdicka[4] is of the same general form as equation (6).

As in the case of the Ilkovic equation one could take into account the corrections proposed by Lingane and Loveridge[11] and by von Strehlov and von Stackelberg.[12] However, these corrections will not be introduced in the present treatment.

### Average Limiting Current and Discussion

Equation (6) expresses the variations of current $i$ as a function of time during the life of a mercury drop. The average current is given by the equation

$$i_{\text{average}} = 1255\; nm^{2/3}C_0k\,\frac{1}{\tau}\int_0^{\tau} t^{2/3}\left[1 - \Phi\left(k\sqrt{\frac{t}{D}}\right)\right]\exp\frac{k^2t}{D}\,dt \quad (7)$$

where $\tau$ is the drop time in sec.

The integral appearing in formula (7) can be calculated by expanding the error integral, but it is much easier to determine the average current by graphic integration. The function appearing under the integral sign was plotted as a function of $\tau$ for different values of $kD^{-1/2}$, and the ratio $\gamma$ of the average value of the current to the maximum value was determined by graphic integration for different values of $\tau$. The average current is thus obtained by multiplying the second member of equation (6) by $\gamma$, which is directly read on the diagram of Fig. 1.

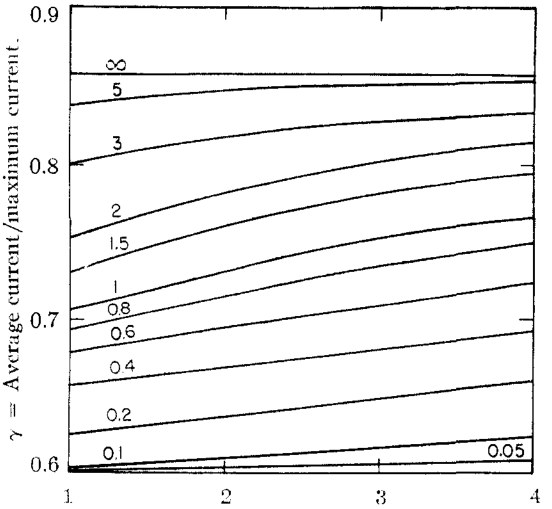

Fig. 1.—Variations of $\gamma$ as a function of drop time for different values of $kD^{-1/2}$. $kD^{-1/2}$ is expressed in sec.$^{-1/2}$.

The values of the error integral in formula (7) used in the preparation of Fig. 1 were taken from tables[13] for $kt^{1/2}D^{-1/2}$ smaller than 1. For larger values of $kt^{1/2}D^{-1/2}$ the error integral was expanded. In the latter case the accuracy was better than 0.5%.[14]

Figure 1 shows that $\gamma$ is practically equal to 0.60 when $kD^{-1/2}$ is smaller than 0.05. If $kD^{-1/2}$ is larger than 5, $\gamma$ is practically equal to 0.857 or $^6/_7$ which is the value corresponding to the Ilkovic equation. In the former case the limiting current is proportional to $t^{2/3}$, whereas it is proportional to $t^{1/6}$ in the latter case.

In order to simplify the application of formula (6) it is useful to apply the abridged equation

$$i_{\text{average}} = 1255\,\beta nm^{2/3}\tau^{2/3}C_0k \quad (8)$$

where function $\beta$ is defined by

$$\beta = \gamma\left[1 - \Phi\left(k\sqrt{\frac{\tau}{D}}\right)\right]\exp\frac{k^2\tau}{D} \quad (9)$$

The values of $\beta$, calculated by applying formula (9) and by using the diagram of Fig. 1, have been determined for different values of $kD^{-1/2}$. The results are shown in Fig. 2 in which $\beta kD^{-1/2}$ is plotted against drop time.

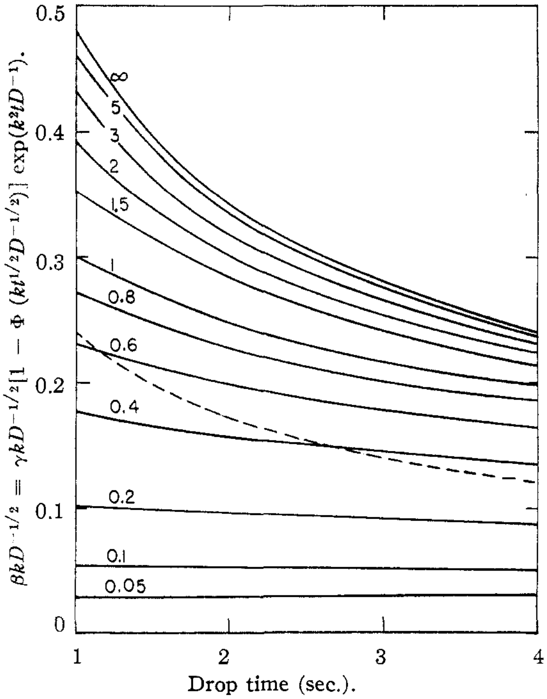

Fig. 2.—Variations of $\beta kD^{-1/2}$ as a function of drop time for different values of $kD^{-1/2}$. $kD^{-1/2}$ is expressed in sec.$^{-1/2}$. The dotted curve corresponds to $\beta kD^{-1/2}$ equal one-half its value for $k$ infinite.

When the rate constant $k$ is infinite, *i.e.*, when the Ilkovic equation is applicable, one has

$$\beta kD^{-1/2} = \frac{\gamma}{\sqrt{\pi\tau}} = \frac{0.483}{\sqrt{\tau}} \quad (10)$$

Figure 2 shows that equation (6) is almost identical to the Ilkovic equation for values of $kD^{-1/2}$

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

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

[13] E. Jahnke and F. Emde, "Tables of Functions," Teubner, Leipzig, 1938, p. 24.

[14] The error is smaller than the last term of the series which is considered in the calculation.

larger than 5. The limiting current is thus practically controlled by diffusion. On the other hand, $\beta$ is practically equal to 0.60 when $kD^{-1/2}$ is smaller than 0.05, and the current is then controlled by rate. For values of $kD^{-1/2}$ comprised between 0.05 and 5, both diffusion and rate determine the magnitude of the limiting current.

**Calculation of the Rate Constant from Experimental Data.**—The rate constant $k$ can be calculated from the experimental current $i$ by application of formula (6) using the values of $\gamma$ read on Fig. 1. However, this procedure is tedious since the last three factors in equation (6) are functions of the unknown rate constant $k$. The following graphic procedure is much simpler and gives accurate results.

The value of $\beta k$ is calculated from the average value of the experimental limiting current by application of formula (8). The corresponding value of the function $\beta k D^{-1/2}$ is calculated. The point having the drop time as abscissa and $\beta k D^{-1/2}$ as ordinate is located on the diagram of Fig. 2, and the value of $kD^{-1/2}$ for the curve passing through this point is determined by interpolation. The rate constant $k$ is calculated from the value of $kD^{-1/2}$. The value of the diffusion coefficient needed in this calculation may be determined by conventional methods[15] or it may be calculated from polarographic data obtained with substances which may be assumed to have approximately the same diffusion coefficient as the substance being investigated.

When $kD^{-1/2}$ is smaller than 0.05 the rate constant is directly computed from the limiting current by application of formula (8) in which $\beta$ is made equal to 0.60.

## Dependence of the Limiting Current on the Head of Mercury

The rate of flow of mercury $m$ is proportional to the head of mercury $H$ corrected for the back pressure.[16] The drop time is inversely proportional to $H$. Thus one has

$$m = m_0 H \tag{11}$$

$$\tau = \frac{\tau_0}{H} \tag{12}$$

where $m_0$ and $\tau_0$ are constants.

By introducing these values of $m$ and $\tau$ in equation (6) one obtains the instantaneous limiting current as a function of the head of mercury

$$i = 1255\, n m_0^{2/3} \tau_0^{2/3} C_0 k \left[1 - \Phi\left(k\sqrt{\frac{\tau_0}{HD}}\right)\right] \exp \frac{k^2 \tau_0}{HD} \tag{13}$$

Equation (13) has been applied to various cases for which $kD^{-1/2}$ is comprised between 0.05 and 1.4, $\tau_0$ being equal to 1000 sec. mm. Limiting currents have been calculated in per cent. of the current corresponding to a head of mercury of 400 mm. The results are shown in Fig. 3 for values of the head of mercury comprised between 400 and 800 mm. When $kD^{-1/2}$ is larger than 1.4 the current is practically proportional to $H^{1/2}$ as in the case of the Ilkovic equation. When $kD^{-1/2}$ is smaller than 0.05 the current is independent of the head of mercury.

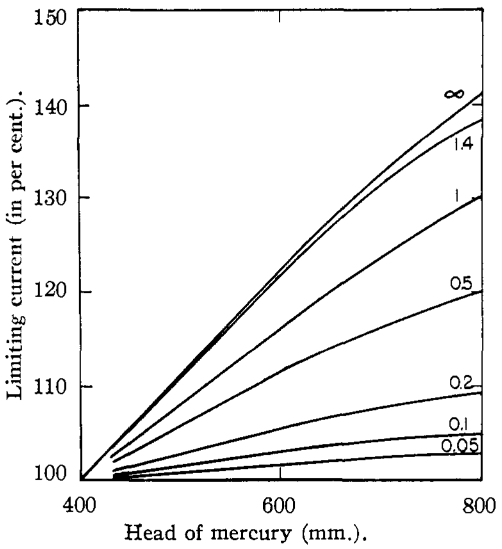

Fig. 3.—Variations of instantaneous limiting current as a function of the head of mercury for different values of $kD^{-1/2}$. $kD^{-1/2}$ is expressed in sec.$^{-1/2}$. Current is in per cent. of the value for H = 400 mm.

It should be pointed out that formula (13) gives the instantaneous limiting current. The average current is obtained by multiplying the second member of equation (13) by $\gamma$. However, $\gamma$ varies with $\tau$ (see Fig. 1), and consequently one should take into consideration the corresponding variations of $\gamma$ with the head of mercury. The values of $\gamma$ to be used are easily determined on the diagram of Fig. 1.

## Application to the Reduction of Weak Acids

We consider the case of a reducible weak acid HA, and we assume that the anion $A^-$ is reduced at more negative potentials than the undissociated acid HA. Two waves may be observed under these conditions. The first wave corresponds to the reduction of the undissociated acid, the second to the reduction of the anion. The limiting current of the first wave depends on the concentration of undissociated acid and on the rate of recombination of the ions $H^+$ and $A^-$, among other factors.[17] In the present treatment we shall assume that the $p$H of the supporting electrolyte is adjusted to a value corresponding to an almost complete dissociation of the acid. Moreover, the potential of the mercury drop is adjusted to a value at which only the undissociated acid is reduced. The number of moles of undissociated acid HA transformed at the surface of the dropping mercury electrode in time $dt$, per unit area, is

$$dN_{HA} = K[H^+][A^-]\,dt - K_d[HA]dt \tag{14}$$

where $[H^+]$, $[A^-]$ and $[HA]$ are the concentrations of the corresponding species in moles per cm.$^3$. $K$ and $K_d$ are the rate constants for the combination and for the dissociation process, respectively. The second term in the second member of equation (14) can be neglected since we assume that [HA] is neg-

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[15] A. Weissberger, "Physical Methods of Organic Chemistry," 2nd edition, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1941, p. 551.

[16] See ref. (5), p. 67.

[17] See ref. 2.

ligible in comparison with [A$^-$]. Moreover, we assume that the supporting electrolyte is buffered and consequently the term [H$^+$] in equation (14) is constant. After these simplifications equation (14) becomes similar to equation (1) and the theory developed in the present paper is applicable to the reduction of weak acids. The constant $k$ of equation (1) is related to constant $K$ by the equation

$$k = K[\mathrm{H}^+]10^{-3} \qquad (15)$$

where $K$ is in cm. sec.$^{-1}$ (moles per liter)$^{-1}$ and [H$^+$] in moles per liter. It should be pointed out that $k$ defined by equation (1) does not depend on the units in which the concentration is calculated whereas $K$ defined by equation (14) depends on these units. Such a difference is to be expected since the rate constant $k$ is defined for a first order reaction whereas $K$ corresponds to a second order reaction.

***p*H of the Solution Exhibiting a Limiting Current Equal to One-half the Diffusion Current.**—When the $p$H of the supporting electrolyte is increased, the rate constant $k$ defined by equation (15) decreases. The corresponding decrease in the limiting current of the undissociated acid becomes noticeable when $kD^{-1/2}$ is smaller than 5 (see above). Thus, there is a value of $k$ for which the limiting current is equal to one-half the diffusion current which is obtained at low $p$H's. This value of $k$ should satisfy the condition

$$\beta k D^{-1/2} = 0.5 \times 0.483 \frac{1}{\sqrt{\tau}} \qquad (16)$$

which is derived from equation (10).

By combining equation (16) with formula (9), one obtains an equation which can be solved for $k$. However, it is easier to determine $k$ by the following graphic method. Values of $\beta k D^{-1/2}$ given by equation (16) are plotted against $\tau$ (dotted line in Fig. 2). The point on this curve having a given drop time as abscissa is located. The curve of the family represented in Fig. 2 which passed through this point is determined and the corresponding value of $kD^{-1/2}$ is calculated by interpolation. The $p$H corresponding to $i = id/2$ is calculated by application of formula (17) which is a modified form of equation (15).

$$(p\mathrm{H})_{1/2} = \log KD^{-1/2} - \log (kD^{-1/2})_{1/2} - 3 \qquad (17)$$

where $-\log(kD^{-1/2})_{1/2}$ is given in Table I.

TABLE I

Values of $kD^{-1/2}$ and $-\log$ ($kD^{-1/2}$) for $i = id/2$

| Drop time, sec. | $kD^{-1/2}$, sec.$^{-1/2}$ | $-\log$ ($kD^{-1/2}$) |
|---|---|---|
| 1 | 0.64 | 0.19 |
| 1.5 | .54 | .27 |
| 2.0 | .47 | .33 |
| 2.5 | .41 | .38 |
| 3.0 | .38 | .42 |
| 3.5 | .36 | .44 |
| 4.0 | .34 | .47 |

Formula (17) and Table I show that the variation of ($p$H)$_{1/2}$ with drop time is by no means negligible. The variation is especially noticeable for drop times shorter than 3 seconds.

## Experimental Verification in the Case of Pyruvic Acid

**Experimental.**—The supporting electrolytes used were Clark and Lubs biphthalate and monopotassium phosphate buffers prepared according to Kolthoff and Laitinen.[18] $p$H's were measured with a Beckman model G instrument using a saturated solution of monopotassium tartrate as a primary standard.[19] The concentration of pyruvic acid was calculated from the weight of dissolved acid. Waves were recorded with a Sargent polarograph model XXI. A conventional cell with a mercury pool as anode was used. The rate of flow of mercury $m$ = 1.53 mg. sec.$^{-1}$ (for a head of mercury of 538 mm.) was determined with a 1.5 volt difference of potential applied on the terminals of the cell. This voltage corresponds to a point in the upper plateau of the wave for the undissociated acid. The drop time determined under identical conditions was 3.85 sec. The temperature of the solution was 28.0 ± 0.1°. The oscillographic recording was made with a Du Mont cathode-ray instrument model 304 H. In this measurement the rate of flow of mercury was 2.00 mg. sec.$^{-1}$. A direct current pre-amplifier was used in order to reduce the ohmic drop in the circuit to a value of the order of 0.005 volt.

**Variation of Limiting Current with *p*H.**—The waves obtained at various $p$H were essentially the same as those reported in the literature.[20,21] Below a $p$H approximately equal to 4.5 one wave of constant height is observed. This wave corresponds to the reduction of the undissociated acid. Between $p$H 4.5 and 7 the height of this wave decreases and a second wave, due to the reduction of the anion, appears. Above $p$H 7 only the wave corresponding to the reduction of the anion is observed. Limiting currents for the undissociated acid at different $p$H are listed in Table II. The corresponding values of $kD^{-1/2}$, also given in Table II, were determined as follows.

TABLE II

AVERAGE LIMITING CURRENTS FOR UNDISSOCIATED PYRUVIC ACID AS A FUNCTION OF $p$H

| $p$H | $i$, $10^{-6}$ amp. | $kD^{-1/2}$, sec.$^{-1/2}$ | $KD^{-1/2} \times 10^{-8}$ sec.$^{-1/2}$ (moles per liter)$^{-1}$ |
|---|---|---|---|
| 4.20 | 5.78 | . . . | . . |
| 5.20 | 5.21 | 1.7 | 2.70 |
| 5.89 | 3.35 | 0.43 | 3.33 |
| 5.95 | 2.45 | .26 | 2.32 |
| 6.11 | 1.04 | .083 | 1.07 |
| 6.32 | 0.79 | .060 | 1.25 |
| 6.56 | .65 | .045 | 1.63 |
| 6.87 | .42 | .031 | 2.30 |
| | | Average | 2.08 |

The limiting currents for the undissociated acid were calculated in per cent. of the diffusion current observed at low $p$H, *i.e.*, at $p$H 4.2. The corresponding values of $\beta k D^{-1/2}$ and $kD^{-1/2}$ were directly read on the diagram of Fig. 2. The values of $kD^{-1/2}$ were calculated from $kD^{-1/2}$ by application of formula (15).

The fluctuations in the values of $KD^{-1/2}$ of Table II are probably caused by local variations of the hydrogen ion concentration in the immediate vicinity of the electrode. In the calculation of $KD^{-1/2}$ from $kD^{-1/2}$ one assumes that the hydrogen ion concentration at the surface of the electrode is the same as the bulk concentration. This would be true if the dissociation or the recombination of the ions of the buffer mixture were instantaneous. Since this is certainly not the case, as it has been pointed out by Koutecky and Brdicka,[22] variations of $KD^{-1/2}$ are observed. The variations of $p$H, which account for the fluctuations of

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[18] I. M. Kolthoff and H. A. Laitinen, "*p*H and Electro Titrations," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 35.

[19] J. J. Lingane, *Anal. Chem.*, **19**, 810 (1947).

[20] R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 212 (1947).

[21] O. H. Müller and J. P. Baumberger, THIS JOURNAL, **61**, 590 (1939).

[22] See ref. 3.

$KD^{-1/2}$, can be calculated from (15) on the basis of the average value of $KD^{-1/2}$. The $p$H corresponding to the largest value of $KD^{-1/2}$ (Table II) is 5.68 whereas the experimental value is 5.89. The $p$H corresponding to the lowest value of $KD^{-1/2}$ (Table II) is 6.40 whereas the experimental $p$H is 6.11. From these data one concludes that local variations of $p$H at the surface of the mercury drop are of the order of 0.3 $p$H unit. This figure represents only an order of magnitude because of the approximative character of calculations based on the assumption that the average value of $KD^{-1/2}$ of Table II is the correct value of $KD^{-1/2}$. In further calculations we shall use the actual value of $KD^{-1/2}$ obtained at a given $p$H rather than the average value.

**Value of $(p\mathrm{H})_{1/2}$.**—On the basis of the extreme values of $KD^{-1/2}$ listed in Table II one obtains the following values of $(p\mathrm{H})_{1/2}$ by application of formula (17): $(p\mathrm{H})_{1/2} = 5.49$ for $KD^{-1/2} = 1.07 \times 10^8$ and $(p\mathrm{H})_{1/2} = 5.98$ for $KD^{-1/2} = 3.33 \times 10^8$. These values are in fairly good agreement with the experimental value $(p\mathrm{H})_{1/2} = 5.91$.

**Variation of the Limiting Current with the Head of Mercury.**—Formula (13) was verified in the case of pyruvic acid at $p$H 5.95. The actual value $kD^{-1/2}$ given in Table II was used in the calculation. The results are listed in Table III for different values of the head of mercury corrected for the back pressure.

TABLE III

VARIATIONS OF AVERAGE LIMITING CURRENT WITH THE HEAD OF MERCURY FOR PYRUVIC ACID AT $p$H 5.95

| $H$, mm. | Experimental average current, $10^{-6}$ amp. | Calcd. av. current, $10^{-6}$ amp. |
|---|---|---|
| 240 | 2.02 | 2.11 |
| 364 | 2.17 | 2.33 |
| 521 | 2.45 | 2.47 |
| 683 | 2.64 | 2.66 |

The agreement between calculated and experimental values is fairly good if one takes into account the error caused by local variations of $p$H at the surface of the mercury drop. The difference between the values 2.45 and 2.47 microamperes for H = 521 mm. results from approximations in numerical calculations. The same value should have been obtained since the value 2.45 microamperes was used in the calculation of $kD^{-1/2}$.

**Variation of Limiting Current with Time.**—Equation (6) was verified by recording the current during the life of a drop for the solution of pyruvic acid at $p$H 5.95.

Figure 4 shows that the agreement between the experimental curve and the calculated points is excellent. The following values were used in the calculation: $m = 2.00$ mg. sec.$^{-1}$, $kD^{-1/2} = 0.26$ sec.$^{-1/2}$ and $C_0 = 1.50$ millimoles per liter. The ratio $\gamma$ of the average current to the maximum current determined by graphic integration of the experimental curve is 0.65. This is in good agreement with the theoretical value 0.66 read in Fig. 1.

**Calculation of Conventional Rate Constant K′.**—As it was pointed out in a previous section it is possible to convert the rate constant $K$ of equation (15) into a conventional constant $K'$, expressed in sec.$^{-1}$ (moles per liter)$^{-1}$, by dividing $K$ by the quantity $\delta$ (see formula 2). As a first approximation one may consider $\delta$ as equal to the average distance of two molecules of pyruvic acid in solution. In the present case one calculates $\delta = 10^{-6}$ cm. on the basis of the concentration $C_0 = 1.5$ millimoles per liter. The diffusion coefficient for pyruvic acid calculated by application of the Ilkovic equation to the diffusion current measured at low $p$H was $0.36 \times 10^{-5}$ cm.$^2$ sec.$^{-1}$. Using these data and the values of $KD^{-1/2}$ of Table II one obtains the extreme values $2.0 \times 10^{11}$ and $6.0 \times 10^{11}$ sec.$^{-1}$ (moles per liter)$^{-1}$ for $K'$. It should be pointed out that only the order of magnitude of $K'$ can be obtained because of the uncertainty of the value of $\delta$.

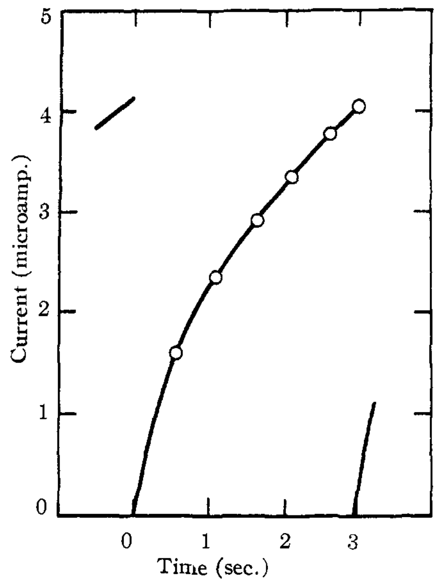

Fig. 4.—Oscillographic recording of current during the life of a drop for pyruvic acid in buffer of $p$H 5.95. Dots are calculated points.

## Conclusion

The theory reported in the present paper accounts for the characteristics of polarographic currents controlled by rates of reaction and by diffusion. The Ilkovic equation corresponds to a special case of a more general formula taking into account rate and diffusion effects. This theory and its implications can be verified to a certain extent by studying the reduction of a weak acid such as pyruvic acid.

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