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Theory of Kinetic Polarographic Currents and Conversion of Rate Constants

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Equations are derived for polarographic currents controlled by the rate of a chemical reaction. Two cases are considered: (1) The current is controlled by the rate of a tautomeric transformation; (2) the current is controlled by the rate of recombination of hydrogen ion with the anion of a weak acid. The relationship between the present equations and a previous treatment of kinetic currents is discussed.

Introduction

Polarographic currents controlled by rate of reaction and by diffusion can be divided into two classes according to whether the chemical process controlling the current is a surface reaction or a reaction occurring at the surface of the electrode and in the bulk of the solution. Current for irreversible electrode processes belong to the first class.[1] Kinetic and catalytic currents are to be grouped in the second class. The theoretical treatment is different for each group of currents. In the first group, the rate of the electrode process is expressed as a function of a rate constant for an *heterogeneous* process. In the second group the rate of the reaction partially controlling the current is calculated in terms of conventional rate constants.[2] Nevertheless, it is sometimes convenient from a mathematical point of view to calculate kinetic currents in terms of heterogeneous rate constants,[3] and it is then necessary to convert heterogeneous rate constants to conventional rate constants. In the rather arbitrary method which was previously reported[3] this conversion was made by assuming that the reaction partially controlling the current occurs in a monolayer at the surface of the electrode. Further study led to new equations for kinetic currents and to a new method of converting rate constants. This matter is reported in the present paper.

The following two cases will be examined: (1) The current is controlled by the rate of a tautomeric transformation; (2) The current is controlled by the rate of recombination of hydrogen ion with the anion of a weak acid.

Kinetic Currents Controlled by the Rate of a Tautomeric Transformation

Current as a Function of Conventional Rate Constants.—Consider the electrolytic reduction of a substance R in equilibrium with a tautomeric form B. Furthermore assume that R is easier to reduce than B, and that the potential of the electrode is adjusted to a value at which only R is reduced. In the case of a plane electrode,[2] the change of concentration C_R between two planes at a distance x and $x + dx$ is

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} + k_f C_B - k C_R \qquad (1)$$

in which t is the time elapsed since the beginning of the electrolysis in sec., x the distance from the electrode in cm., D_R the diffusion coefficient of R in cm.^{2} sec.$^{-1}$, the C's are the concentrations in moles per cm.^{3}, k_f and k_b are the rate constants in sec.$^{-1}$ for the forward and backward reactions corresponding to the equilibrium

$$\mathrm{B} \rightleftarrows \mathrm{R} \qquad (2)$$

The first term on the right-hand side of (1) represents the change in concentration caused by diffusion of substance R. The second and third terms represent the change in concentration due to reaction (2). Note that by writing (1) one assumes that the activity coefficients of B and R are equal to unity.

In subsequent derivations it will be assumed that C_B is equal to the bulk concentration of substance B regardless of the distance from the electrode. This assumption is justified provided that k_f is sufficiently low[2] (see below). By replacing C_B in (1) by the bulk concentration C_B°, and introducing the equilibrium constant K for (2), one obtains the equation

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} + k_b(KC^\circ - C_R) \qquad (3)$$

Equation (3) is to be solved for the following initial and boundary conditions: for $t = 0$, $C_R = KC_B^\circ$; for $t > 0$ and $x = 0$, $C_R = 0$. A similar equation is encountered in the theory of catalytic waves,[2] and it is possible to write the current for the reduction of R at the dropping mercury electrode. However, the general equation previously reported[2] is not needed in the present treatment, and only the case in which K is much smaller than unity will be discussed. In this case the average current during drop life is[2]

$$i_{ave} = 0.6 \times 1.255 \times 10^6\, n m^{2/3} \tau^{2/3} C_B^\circ D_R^{1/2} K^{1/2} k_f^{1/2} \quad (4)$$

In equation (4), the current is in microamp., n is the number of electrons involved in the reduction of R, m the rate of flow of mercury in mg. sec.$^{-1}$, τ the drop time in sec., C_B° the bulk concentration of B in moles per liter, D_R the diffusion coefficient of R in cm^2. sec.$^{-1}$, K the equilibrium constant for (2) and k_f the rate constant for forward reaction (2) in sec.$^{-1}$.

By application of equation (4) it is possible to calculate, from experimental currents, the value of $K^{1/2}k_f^{1/2}$, and that of k_f if K is known. When applying (4) it should be kept in mind that the present derivation is valid only when k_fK is larger than 100 sec.$^{-1}$,[4] *i.e.*, when K is so small that equilibrium (2) is almost completely shifted toward the left.

Conversion of Rate Constants.—The current for the reduction of R was previously derived[3] by intro-

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[1] P. Delahay and J. E. Strassner, THIS JOURNAL, **73**, 5219 (1951).

[2] P. Delahay and G. L. Stiehl, *ibid.*, **74**, 3500 (1952).

[3] P. Delahay, *ibid.*, **73**, 4944 (1951).

[4] For a complete discussion, see ref. 2.

ducing the rate constant $(k_f)_h$ for an heterogeneous process. Under the conditions for which (4) is valid, one obtains an equation identical to (4) except for the last three terms on the right-hand side which are replaced by the rate constant $(k_f)_h$ for the heterogeneous process.[3,5] By identifying the current given by equation (4) with the current derived in terms of $(k_f)_h$, one obtains the following relationship between the rate constants k_f and $(k_f)_h$

$$k_f = \frac{1}{KD_R}(k^2{}_f)_h \qquad (5)$$

Application to the Ring ⇄ Aldehydo Equilibrium for Aldoses

The rate constant k_f for equilibrium (2) can be calculated from equation (5) provided that the equilibrium constant K and the diffusion coefficient D_R are known. Conversely, if trustworthy values of k_f can be obtained by assuming that the transformation B → R occurs essentially in a monolayer at the surface of the electrode, it is possible to calculate k_f from $(k_f)_h$ without having to apply (5). By equating the value of k_f obtained by the latter method[6] with that given by (5), one obtains an equation in which the only unknown is equilibrium constant K. This method of determining K was applied to various aldoses for which $(k_f)_h$ was previously determined,[5] and the corresponding equilibrium constants for the ring → aldehydo transformation are listed in Table I.

TABLE I

k_f, $(k_f)_h$ AND K FOR VARIOUS ALDOSES AT 25°

Aldose	k_f,[a] sec.$^{-1}$	$10^7 \times (k_f)_h$,[a] cm. sec.$^{-1}$	$10^8 \times K$
Arabinose	65.5	97.6	20
Xylose	52.0	77.5	16
Galactose	23.2	34.6	7
Mannose	14.7	21.9	4
Dextrose	6.4	9.5	2

[a] See ref. 5.

The diffusion coefficients of the aldoses of Table I were assumed to be equal to 0.67×10^{-5} cm.^{2} sec.$^{-1}$ which is the value one calculates from the polarographic data of Cantor and Peniston[7] for 5-hydroxymethylfurfural. Obviously, the above value of D is only approximate but this is immaterial since the values of K in Table I should be regarded as merely representing an order of magnitude because of the nature of the calculation. Nevertheless, approximate values of equilibrium constant K might be valuable since, as far as we know, no data on K are available.[8] From Table I it can be seen that the concentration of free aldehydo form for the various aldoses is extremely small. This accounts for the fact that the currents for the aldoses listed in Table I are entirely controlled by the rate of the ring → aldehydo transformation.[5,8]

Kinetic Currents Controlled by the Rate of Recombination of the Ions of a Weak Acid

Current as a Function of Conventional Rate Constants.—Consider the reduction of a weak HA which is reduced at less negative potentials than the corresponding anion A^-, and assume that the potential of the electrode is adjusted at a value at which only HA is reduced. Under these conditions, the current for the reduction of HA is determined by the diffusion of HA toward the electrode, and by the rate of recombination of ions H^+ and A^-.[9] If the reduction is carried out on a plane electrode, the change in the concentration of HA between two planes at distance x and $x + dx$ is

$$\frac{\partial C_{HA}}{\partial t} = D_{HA}\frac{\partial^2 C_{HA}}{\partial x^2} + k_r C_{H^+} C_{A^-} - k_d C_{HA} \qquad (6)$$

in which the C's are the concentrations in moles per cm.^{3}, D_{HA} is the diffusion coefficient of HA in cm.^{2} sec.$^{-1}$, k_r and k_d are the rate constants for the recombination and dissociation processes in (moles per cm.^{3})$^{-1}$ sec.$^{-1}$ and sec.$^{-1}$, respectively. In equation (6) hydronium ions are written as H^+ instead of H_3O^+. Actually, the recombination of H_3O^+ and A^- involves the liberation of one mole of water, and the third member on the right-hand side of (6) should be multiplied by the activity of water. This was not done in the present treatment for the sake of simplicity. Furthermore, the activity coefficients of all substances involved are assumed to be equal to unity.

By introducing the ionization constant K of acid HA ($K = k_d/k_r$), equation (6) becomes

$$\frac{\partial C_{HA}}{\partial t} = D_{HA}\frac{\partial^2 C_{HA}}{\partial x^2} + k_r K\left(\frac{C_{H^+} C_{A^-}}{K} - C_{HA}\right)\cdot \qquad (7)$$

Equation (7) is to be solved for the following initial and boundary conditions: for $t = 0$, $C_{HA} = (C_{H^+} C_{A^-})/K$; for $t > 0$ and $x = 0$, $C_{HA} = 0$. Applying results previously derived,[2] one can write the current for the reduction of HA at the dropping mercury electrode, provided that it is assumed that C_{A^-} and C_{H^+} do not vary with x and t. When $k_r K$ is larger than 100 sec.$^{-1}$, the average current during drop life is

$$i_{ave} = 0.6 \times 1.255 \times 10^6\, n m^{2/3} \tau^{2/3} C^0_{H^+} C^0_{A^-} D_{HA}{}^{1/2} (k_r{}^{1/2}/K^{1/2}) \qquad (8)$$

in which K is in moles per liter, k_r in (moles per liter)$^{-1}$ sec.$^{-1}$, $C^0_{H^+}$ and $C^0_{A^-}$ in moles per liter, and the other units are the same as in equation (4).

The rate constant k_r can be calculated from experimental currents by application of equation (8), provided that the ionization constant of acid HA is known. It should be emphasized that equation (8) is applicable only to cases in which the current is virtually controlled by the rate of the recombination process. Thus the experimental conditions should be such that the concentration of ions H^+ and A^- at the electrode surface are the same as the bulk concentrations $C^0_{H^+}$ and $C^0_{A^-}$.

Conversion of Rate Constants.—The equation for current i which is obtained by introducing in the derivation the rate constant $(k_r)_h$ for an heterogeneous process is identical to (8) except for the terms $(D_{HA} k_r/K)^{1/2}$ which are replaced by $(k_r)_h$.

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[5] P. Delahay and J. E. Strassner, THIS JOURNAL, **74**, 893 (1952).

[6] For a detailed discussion, see ref. 3.

[7] S. M. Cantor and D. P. Peniston, THIS JOURNAL, **62**, 2113 (1940).

[8] K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 64 (1947).

[9] R. Brdicka and K. Wiesner, *ibid.*, **12**, 138 (1947).

By equating the two values of the average current one obtains

$$k_r = \frac{K}{D_{HA}}(k_r^2)_h \qquad (9)$$

in which $(k_r)_h$ is in cm. (moles per liter)$^{-1}$ sec.$^{-1}$, k_r in (moles per liter)$^{-1}$ sec.$^{-1}$, and the other units are the same as in equation (4). From equation (9) one can convert $(k_r)_h$ to k_r provided that the ionization constant K and the diffusion coefficient D_{HA} are known.

Equation (9) is valid only when k_f and $(k_f)_h$ are obtained from currents which are essentially controlled by the rate of the recombination process. It follows that (9) is not necessarily valid when $(k_f)_h$ is obtained in an experiment in which the current is partially diffusion controlled. However, it seems that even so, results of the correct order of magnitude are obtained by applying (9) (see below).

Application to Pyruvic Acid

Comparison of Rate Constants.—The following data for pyruvic acid at 25°[10] were reported in a previous paper: $(k_r)_h = 5.78 \times 10^2$ cm. (moles per liter)$^{-1}$ sec.$^{-1}$, $K = 2.8 \times 10^{-3}$ mole per liter; diffusion coefficient of pyruvate ion: 0.44×10^{-5} cm.^{2} sec.$^{-1}$. On the basis of these data one can calculate k_r provided that it is assumed that the diffusion coefficient for pyruvic acid is the same as for pyruvate ion. By applying (9) one obtains $k_r = 2.12 \times 10^8$ (moles per liter)$^{-1}$ sec.$^{-1}$. The approximate value $k_r = 4.49 \times 10^8$ (moles per liter)$^{-1}$ sec.$^{-1}$ was previously obtained[10] by assuming that the recombination process occurs in a monolayer of ions at the surface of the electrode. Since the latter value is of the same order of magnitude as the value of k_r obtained from the more rigorous equation (9), one concludes that the recombination process essentially occurs in a monolayer at the surface of the electrode. This is understandable since the rate of the recombination process is much larger than the rate of the diffusion processes occurring at the electrode.

It is of interest to compare the above values of k_r with that obtained by direct application of (8). It was previously reported[3] that the limiting current for the pyruvic acid wave was 0.42 microamp. for a 1.5×10^{-3} molar solution at pH 6.87 and 28°. This limiting current is only a small fraction of the diffusion current for pyruvic acid (5.78 microamp.) which was obtained under the same conditions at low pH's (4.2). Therefore, the limiting current for the pyruvic acid wave at pH 6.87 is essentially controlled by the rate of the recombination process, and equation (8) is applicable. This equation yields the value $k_r = 1.27 \times 10^8$ (moles per liter)$^{-1}$ sec.$^{-1}$ [11] which is of the same order of magnitude as the values of k_r obtained either by application of (9) (2.12×10^8) or by assuming that the reaction occurs in a monolayer at the electrode surface (4.49×10^8). It should be noted that the value 1.27×10^8 was calculated from data obtained at 28° whereas the other values of k_r are for 25°. Furthermore, concentration polarization slightly affects the value $k_r = 1.27 \times 10^8$, which is consequently too low.

Influence of Temperature.—It was previously reported that the variations of $(k_r)_h$ with temperature are essentially those predicted on the basis of Onsager's theory of ionic recombination.[10,12] This means that the energy of activation for k_r is virtually that which one calculates from experimental values of $(k_r)_h$. This can be explained on the basis of equation (9) as follows. The effect of temperature on rate constant $(k_r)_h$ is obtained by introducing in (9) energies of activation for the recombination process ($\Delta H_R^{\ddagger}$) and for the diffusion coefficient D_{HA} ($\Delta H_D^{\ddagger}$). Thus

$$k_r^\circ D_{HA} e^{-\Delta H_R^{\ddagger} + \Delta H_D^{\ddagger}/RT} = K(k_r^2)_h \qquad (10)$$

in which k_r° is defined by the equation

$$k_r = k_r^\circ e^{-\Delta H_R^{\ddagger}/RT} \qquad (11)$$

and D_{HA}° is defined similarly. It was previously shown[10] that $\Delta H_R^{\ddagger}$ is almost equal to the energy of activation for the diffusion of ion A$^-$, *i.e.*, almost equal to $\Delta H_D^{\ddagger}$. Furthermore, the temperature coefficient of ionization constant K is very small[13] and can be neglected in the present treatment. As a result, it follows from (10) that the energy of activation for k_r is approximately the same as that for $(k_r)_h$.

Conclusion

The present treatment of kinetic polarographic currents enables one to calculate conventional rate constants for the chemical process controlling the current. The derivation is more rigorous than a previous one[3] in which rate constants for heterogeneous processes were introduced. However, the equations derived in the present paper are applicable only when the limiting current is entirely controlled by the rate of the kinetic process.

ADDED IN PROOF.—After the completion of the present paper, the author's attention was called to a paper by Wiesner[14] in which an equation for the *thickness of the reaction layer* μ, previously introduced by Brdicka and Wiesner,[15] is derived. This expression for μ was obtained by identifying the thickness of the reaction layer "with the half mean path which can be traversed by the depolarizer within its mean life time."[16] By introducing Wiesner's value of μ in the original equation of Brdicka and Wiesner,[15] one obtains an equation which is identical to the above equation (4). This shows that it is possible to obtain the correct value of the limiting current (equation (4)) by introducing the quantity μ in the derivation; however, it is necessary to take into account the dependence of μ on the equilibrium constant K (see above) and the diffusion coefficient D, as Wiesner did.[14] Nevertheless, our derivation shows that the rigorous solution is obtained without introducing the notion of thickness of a reaction layer.[17]

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[10] P. Delahay and T. J. Adams, THIS JOURNAL, **74**, 1437 (1952).

[11] See ref. 3 for complete data.

[12] L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).

[13] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, p. 514.

[14] K. Wiesner, *Chem. Listy*, **41**, 6 (1947); see also K. Vesely and R. Brdicka, *Collection Czechoslov. Chem. Commun.*, **12**, 313 (1947).

[15] R. Brdicka and K. Wiesner, *Vestnik Kral Ces. Spol. Nauk*, No. 18 (1943); see also *Collection Czechoslov. Chem. Commun.*, **12**, 39 (1947).

[16] Quoted from J. Koutecky and R. Brdicka, *ibid.*, **12**, 337 (1947), see p. 340.

[17] See also ref. 16.