Fundamental Studies on the Current-Voltage Curve in Polarography. II.*

Derivation of the Activation-Controlled Polarographic Waves of Simple Metal Ions from the Standpoint of Chemical Kinetics.

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In the previous paper⁽¹⁾ the authors derived the formula of the reversible current-voltage curve from the standpoint of chemical kinetics,

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(1) N. Tanaka and R. Tamamushi, This Bulletin, **22** (1949), 187.

and showed that the polarographic electrode potential can be defined by the Nernst's equation if the rate-determining step of the net electrode process is diffusion. In the present paper the authors analyse the relation between the current flowing and the electrode potential, when the rate-determining step is the activation process at the potential region where the rates of the forward and reverse reactions are nearly the same. By the same treatment as in the case of diffusion-control, some interesting results for the current-voltage relation are obtained. The theoretical curve which is analogous to the usual irreversible current-voltage curve is obtained under these conditions, and the meaning of the half-wave potential of such a wave is set down.

The Derivation of Equations.

Consider the net electrode process which contains the diffusion process and the electron-transfer reaction (the activation process) only. As the oxidation-reduction process, the reaction $M^{m+} + n\varepsilon \rightleftarrows M^{(m-n)+}$ is considered, in which M^{m+} and $M^{(m-n)+}$ symbolize the oxidant and the reductant, respectively. Let us assume that the reduction is the forward reaction and the oxidation is the reverse. In the absence of any external potential, the rates of the two reactions are represented as follows:

$$\begin{array}{ll} \text{forward :} & s\dfrac{kT}{h}e^{-\Delta F_1/RT} \equiv \kappa_1 \\ & \\ \text{reverse :} & s\dfrac{kT}{h}e^{-\Delta F_2/RT} \equiv \kappa_2 \ , \end{array} \qquad (1)$$

where s is the constant concerning the nature of the electrode surface, $\varDelta F_1$ and $\varDelta F_2$ are the free energies of activation and κ_1 and κ_2 are the abbreviations of the corresponding terms, respectively. If the particular potential V is applied to the electrode against the interior of the solution, the two rates must be written as follows:

$$\begin{array}{ll} \text{forward :} & \kappa_1 e^{-\frac{n\alpha VF}{RT}} \equiv \kappa_1 E_1 \\ & \\ \text{reverse :} & \kappa_2 e^{\frac{n(1-\alpha)VF}{RT}} \equiv \kappa_2 E_2 \end{array} \qquad (2)$$

αV is the fraction of the total applied potential V which will promote the forward reaction, and therefore $(1-\alpha)V$ will retard the reverse. If the activities of the oxidant and the reductant at the electrode surface are represented by $[A_O]$ and $[A_R]$, the current flowing by the electrode activation process is expressed by equation (3).

$$I = n\varepsilon\{\kappa_1 E_1[A_O] - \kappa_2 E_2[A_R]\} \qquad (3)$$

This current is carried by the diffusion process of oxidant, namely:

$$I = n\varepsilon K_O([C_O]^\circ - [C_O]) = n\varepsilon \frac{K_O}{f_O}([A_O]^\circ - [A_O]) = n\varepsilon K_O'([A_O]^\circ - [A_O]) \qquad (4)$$

or by that of reductant, namely:

$$I = n\varepsilon K_R([C_R] - [C_R]^\circ) = n\varepsilon \frac{K_R}{f_R}([A_R] - [A_R]^\circ) = n\varepsilon K_R'([A_R] - [A_R]^\circ) \qquad (5)$$

where $[A_O]^\circ$, $[A_R]^\circ$ are the activities of the oxidant and reductant in the body of the solution, $[C_O]$, $[C_R]$, $[C_O]^\circ$, $[C_R]^\circ$ are the concentrations of the oxidant and reductant at the electrode surface and in the body of the solution, and f_O, f_R symbolize the activity-coefficients of the corresponding terms. From equations (3), (4) and (5) the general relation between the current I and the electrode potential V is obtained:

$$I = n\varepsilon \frac{K_O' K_R'(\kappa_1 E_1 [A_O]^\circ - \kappa_2 E_2 [A_R]^\circ)}{\kappa_1 E_1 K_R' + \kappa_2 E_2 K_O' + K_O' K_R'} = n\varepsilon \frac{[A_O]^\circ - [A_R]^\circ \dfrac{\kappa_2 E_2}{\kappa_1 E_1}}{\dfrac{1}{K_O'} + \dfrac{1}{\kappa_1 E_1} + \dfrac{1}{K_R'} \dfrac{\kappa_2 E_2}{\kappa_1 E_1}} \qquad (6)$$

$$= n\varepsilon \frac{[A_O]^\circ \dfrac{\kappa_1 E_1}{\kappa_2 E_2} - [A_R]^\circ}{\dfrac{1}{K_O'} \dfrac{\kappa_1 E_1}{\kappa_2 E_2} + \dfrac{1}{\kappa_2 E_2} + \dfrac{1}{K_R'}} \qquad (6')$$

Now let us consider the magitudes of K_O', K_R', $\kappa_1 E_1$ and $\kappa_2 E_2$ in equations (6) and (6′). K_O' and K_R', which depend on the diffusion coefficients of the oxidant and the reductant in the solution, may be generally regarded to be almost identical. On the other hand, $\kappa_1 E_1$ and $\kappa_2 E_2$ are the functions of the electrode potential V that is continuously changed in polarography. Therefore, the magnitudes of the above four values should be compared at the particular potential region separately. So, in the present treatment, the total current-voltage curve is divided into three parts according to the value of V, i. e., $\kappa_1 E_1 \simeq \kappa_2 E_2$ (Part A), $\kappa_1 E_1 > \kappa_2 E_2$ (Part B) and $\kappa_1 E_1 < \kappa_2 E_2$ (Part C).

Part A of the Current-Voltage Curve. If it is assumed that V equals V_0 when $\kappa_1 E_1$ just equals $\kappa_2 E_2$; V is nearly equal to V_0 in this potential region. From the condition for the activation-controlled reaction, the following relation is satisfied in this part, i. e.,

$$\kappa_1 E_1 \simeq \kappa_2 E_2 \ll K_O',\ K_R'. \qquad (7)$$

Applying this relation to equation (6) or (6′), the approximate equation of the current-voltage curve in this region can be obtained:

$$I/n\varepsilon = \kappa_1 E_1[A_O]^\circ - \kappa_2 E_2[A_R]^\circ \tag{8}$$

From this formula it can be seen that the current flowing at such an electrode potential is determined only by the rates of activation process.

Part B of the Current-Voltage Curve. In this potential region, the more negative the electrode potential V, the greater is the rate of the forward reaction $\kappa_1 E_1$, while the rate of the reverse reaction $\kappa_2 E_2$ tends to be negligibly small.

(a). $\kappa_1 E_1$ becomes almost equal to both of K_O' and K_R'.—Then, $\kappa_2 E_2/\kappa_1 E_1$ is very small and nearly equal to zero. Therefore, considering these relations, the equation for the current-voltage curve of this region can be derived from equation (6), namely:

$$I/n\varepsilon = \frac{[A_O]^\circ}{\dfrac{1}{K_O'} + \dfrac{1}{\kappa_1 E_1}} = \frac{K_O'\kappa_1 E_1[A_O]^\circ}{K_O' + \kappa_1 E_1} . \tag{9}$$

(b). $\kappa_1 E_1$ is greater than both of K_O' and K_R'.—In this case, obviously, $\kappa_2 E_2/\kappa_1 E_1$ tends to zero. Hence, from equation (6) the equation

$$I = n\varepsilon K_O'[A_O]^\circ = n\varepsilon K_O[C_O]^\circ \equiv (I_d)_O \tag{10}$$

is obtained, which represents the limiting case and corresponds to the limiting current in polarography.

From equations (9) and (10), it can be said that at Part B-(a) the current is dependent on the characters of the oxidant, but it is independent of those of the reductant, and that Part B-(a) corresponds to the reduction wave of the polarographic wave. Furthermore, the limiting current of such a case is expected to be defined by the Ilkovič's equation.

Part C of the Current Voltage Curve. In this region the rate of the reverse reaction increases as the electrode potential V is going to be more positive than V_0, while the rate of the forward reaction decreases to a negligibly small value. By the same treatment as for Part B, the equations for the anodic wave and the anodic limiting current are obtained from equation (6′) as follows:

(a). $\kappa_2 E_2$ becomes almost equal to both of K_O' and K_R'.

$$I/n\varepsilon = -\frac{[A_R]^\circ}{\dfrac{1}{K_R'} + \dfrac{1}{\kappa_2 E_2}} = -\frac{K_R'\kappa_2 E_2[A_R]^\circ}{K_R' + \kappa_2 E_2} \tag{11}$$

(b). $\kappa_2 E_2$ is greater than both of K_O' and K_R'.

$$I = -n\varepsilon K_R'[A_R]^\circ = -n\varepsilon K_R[C_R]^\circ \equiv (I_d)_R \tag{12}$$

These equations (8), (9), (10), (11) and (12) are expected to account for the total wave of oxidation-reduction process which proceeds at the polarographic electrode under the conditions above described.

Theoretical Analysis of the Curve.

In the following, the meaning of the half-wave potential, the tangent of the curve and the other important properties of the curve will be described in relation to the equations derived above.

The Electrode Potential where the Current is Equal to Zero. In Part A of the current-voltage curve there must be such a point where the current flowing is zero, i. e., $I = 0$. From equation (8) the relation between the electrode potential and the activities of the oxidant and the reductant in the body of the solution can be easily obtained as follows:

$$\left[\frac{\kappa_2 E_2}{\kappa_1 E_1}\right]_{I=0} = \frac{[A_O]^\circ}{[A_R]^\circ} \tag{13}$$

or

$$[e^{n(V-V_0)F/RT}]_{I=0} = \frac{[A_O]^\circ}{[A_R]^\circ}$$

in which the condition, $I = 0$, is satisfied. That is to say, the potential V, under the condition $I = 0$, may be determined only by the activities $[A_O]^\circ$ and $[A_R]^\circ$, and, furthermore, if $[A_O]^\circ$ is equal to $[A_R]^\circ$, this potential will represent the normal oxidation-reduction potential of the system. Therefore, if $[A_O]^\circ$ and $[A_R]^\circ$ are known and the potential $[V]_{I=0}$ are determined from the experimental curve, the normal oxidation-reduction potential V_0 can be obtained from the experimental result. In practice, since, in this potential region, the current flowing is usually very small and the inclination of the curve at the point $[V]_{I=0}$ is also very small as shown later, it will be somewhat difficult to determine the correct value of V_0 by this method.

Half-Wave Potential. There are two half-wave potentials in the total current-voltage curve, i. e., the half-wave potentials of the cathodic part and the anodic part. First, the relations for the cathodic half-wave potential will be derived, and then for the anodic one in the same way.

By substituting $(I_d)_O$ for $n\varepsilon K'_O[A_O]^\circ$ of equation (9), the equation,

$$\kappa_1 E_1 = \frac{K'_O I}{(I_d)_O - I}$$

or

$$V = -\frac{RT}{n\alpha F}\left(\frac{\Delta F_1}{RT} + \ln\frac{h}{kT}K'_O + \ln\frac{I}{(I_d)_O - I}\right), \tag{14}$$

is obtained. At the half-wave potential the current flowing is one half of the limiting current $(I_d)_O$, namely:

$$I = \frac{(I_d)_O}{2} \quad . \tag{15}$$

From equations (14) and (15) the condition for the cathodic half-wave potential is derived as follows:

$$[\kappa_1 E_1]_{\frac{(I_d)_O}{2}} = K_O'$$

or

$$[V]_{\frac{(I_d)_O}{2}} = -\frac{RT}{n\alpha F}\left(\frac{\Delta F_1}{RT} + \ln\frac{h}{kT}K_O'\right) \quad . \tag{16}$$

The equation (16) shows that the half-wave potential depends on the constant K_O', and that if the value of α is independent of the activity of the oxidant, it will be the particular constant for the oxidant concerned.

As for the anodic half-wave potential analogous equations can be obtained, i. e.,

$$[\kappa_2 E_2]_{\frac{(I_d)_R}{2}} = K_R'$$

or

$$[V]_{\frac{(I_d)_R}{2}} = \frac{RT}{n(1-\alpha)F}\left(\frac{\Delta F_2}{RT} + \ln\frac{h}{kT}K_R'\right) \quad . \tag{17}$$

The Relation between $\log(I/I_d - I)$ and V. From equations (14) and (17) it is obvious that the relation between $\log(I/I_d - I)$ and V must be linear and the absolute value of the tangent of this line is $RT/n\alpha F$ or $RT/n(1-\alpha)F$ according to the cathodic or anodic part. If this relation is plotted and the tangent of the line is determined, the value of α can be calculated. Although many investigators have often used this linear relation for the criterion of reversibility of polarographic wave, it is obvious that this may hold also in such a case when the electrode potential is not defined by the Nernst's equation. In the case when the oxidation-reduction reaction concerned is uni-valent, if the wave is reversible, the theoretical inclination of the above relation must be 0.059 volt at 25° C, hence, if the experimental result deviates from this value, we may conclude that the electrode activation process does not exist in an equilibrium state.

Index Potential V_i⁽²⁾. In the potentiometric study of the oxidation-reduction systems the term "index potential" has been used to specify the types of the titration curve. A similar quantity has been applied

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(2) L. Michaelis and M. P. Schubert, *Chem. Rev.*, **22** (1938), 437.

to analyse the type of polarographic wave. As the index potential V_i of the polarographic wave the quantity,

$$V_i = [V]_{\frac{3I_d}{4}} - [V]_{\frac{I_d}{2}} \quad \text{or} \quad [V]_{\frac{I_d}{2}} - [V]_{\frac{I_d}{4}}{}^{(3)} \qquad (18)$$

is given, where $[V]_{\frac{3I_d}{4}}$ and $[V]_{\frac{I_d}{4}}$ are the potentials at which the wave-heights are $3I_d/4$ and $I_d/4$ respectively. From equation (9) the condition for $[V]_{\frac{I_d}{4}}$ of the cathodic part is to be

$$[\kappa_1 E_1]_{\frac{I_d}{4}} = \frac{K_O'}{3}$$

or (19)

$$[V]_{\frac{I_d}{4}} = -\frac{\Delta F_1}{n\alpha F} - \frac{RT}{n\alpha F}\ln\left(\frac{h}{kT}\,\frac{K_O'}{3}\right) \quad .$$

Substracting equation (19) from equation (16) and rearranging, equation (20) is obtained, by which the value of α can be calculated.

$$\alpha = \frac{RT}{nF}\,\frac{\ln 3}{[V]_{\frac{I_d}{4}} - [V]_{\frac{I_d}{2}}} = \frac{0.059}{n}\,\frac{0.477}{[V]_{\frac{I_d}{4}} - [V]_{\frac{I_d}{2}}} \qquad (20)$$

This method of calculation of α is essentially identical with the method described above. However, the accuracy of this method is lower than the previous method, because equation (20) utilizes only two particular points of the experimental curve, while the previous method uses a series of points of the curve to determine α.

First Derivative of the Current-Voltage Relation.—Tangent of the Curve. Differentiating the equations (8), (9) and (11) with respect to the electrode potential V, the tangents of the curves of Parts A, B and C are represented as follows:

Part A

$$\frac{dI}{dV} = -n\varepsilon\frac{nF}{RT}\{\alpha[A_O]^\circ\kappa_1 E_1 + (1-\alpha)[A_R]^\circ\kappa_2 E_2\} \qquad (21)$$

Part B

$$\frac{dI}{dV} = -n\varepsilon\frac{nF}{RT}\alpha K_O'\kappa_1 E_1\frac{K_O'[A_O]^\circ}{(K_O'+\kappa_1 E_1)^2} \qquad (22)$$

Part C

$$\frac{dI}{dV} = -n\varepsilon\frac{nF}{RT}(1-\alpha)K_R'\kappa_2 E_2\frac{K_R'[A_R]^\circ}{(K_R'+\kappa_2 E_2)^2} \qquad (23)$$

From equations (13) and (21) the tangent of the curve at the point $I=0$ can be obtained.

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(3) R. Brdička, *Z. Electrochem.*, **47** (1941), 314.

$$\left[\frac{dI}{dV}\right]_{I=0} = -n\varepsilon\frac{nF}{RT}[A_O]^\circ\kappa_1E_1 \tag{24}$$

The tangent at the cathodic half-wave potential is derived by the application of equation (16) to equation (22):

$$\left[\frac{dI}{dV}\right]_{\frac{(I_d)_O}{2}} = -n\varepsilon\frac{nF}{4RT}\alpha\kappa_1E_1[A_O]^\circ = -n\varepsilon\frac{n\alpha F}{4RT}K_O'[A_O]^\circ \tag{25}$$

Now let us compare the two tangents (24) and (25) with each other. Dividing (25) by (24), equation (26) is obtained as follows, unless the value of α is very small:

$$\frac{\left[\frac{dI}{dV}\right]_{\frac{(I_d)_O}{2}}}{\left[\frac{dI}{dV}\right]_{I=0}} = \frac{\alpha K_O'}{4[\kappa_1E_1]_{I=0}} > 1\ . \tag{26}$$

From the result, it can be said that the cathodic wave is far steeper than the wave of part A. The same relations are to be held with between the anodic wave and the wave of Part A.

Second Derivatives of the Current-Voltage Relation.—Inflection Point of the Curve. By deriving the second derivatives of equations (8), (9) and (11) with respect to the electrode potential V and by making these derivatives equal to zero, the inflection points of the current-voltage curves are obtained. The three following relations are obtained for the conditions of the inflection points of the waves, i. e.,

Part A $$\left[\frac{\kappa_2E_2}{\kappa_1E_1}\right]_{\text{infl. pt A.}} = \frac{\alpha^2}{(1-\alpha)^2}\frac{[A_O]^\circ}{[A_R]^\circ} \tag{27}$$

Part B $$[\kappa_1E_1]_{\text{infl. pt. B.}} = K_O' \tag{28}$$

Part C $$[\kappa_2E_2]_{\text{infl. pt. C.}} = K_R' \tag{29}$$

It is pointed out from these equations that the inflection point of cathodic or anodic wave is identical with the corresponding half-wave potential. Consequently it is concluded that there may be three inflection points in the total region of the polarographic oxidation-reduction wave.

The Tracing of the Theoretical Curve Using the Equations Derived Above. As an example, let us assume some hypothetical values of ΔF_1, ΔF_2, α, $[A_O]^\circ$, $[A_R]^\circ$, K_O' and K_R' as follows, and trace the theoretical curve according to the obtained equations (8), (9) and (11) (Fig. 1).

$$\Delta F_1 = 15.0 \times 10^4 \,\text{joule}, \qquad \Delta F_2 = 13.1 \times 10^4 \,\text{joule},$$
$$[A_O]^\circ = [A_R]^\circ = 1.04 \times 10^{-3} \,\text{mol}/l., \qquad K_O' = K_R' = 1.8 \times 10^{-8} \,\text{amp./mol}/l.,$$
$$\alpha = 0.6, \qquad n = 1.$$

Under these conditions the following values are obtained for $[V]_{\frac{(I_d)_O}{2}}$, $[V]_{\frac{(I_d)_R}{2}}$ and $[V]_{I=0}$, i. e.,

$$[V]_{\frac{(I_d)_O}{2}} = -0.569 \text{ volt vs. hydrogen electrode.}$$
$$[V]_{\frac{(I_d)_R}{2}} = +0.353 \quad ,, \quad ,, \quad ,, \quad ,,$$
$$[V]_{I=0} = -0.200 \quad ,, \quad ,, \quad ,, \quad ,,$$

From Fig. 1 it can be said that the theoretical curve is essentially the same, at least qualitatively, as some types of irreversible waves obtained in polarography, and that the equations cited above will account for the natures of the polarographic waves which have not yet been interpreted.

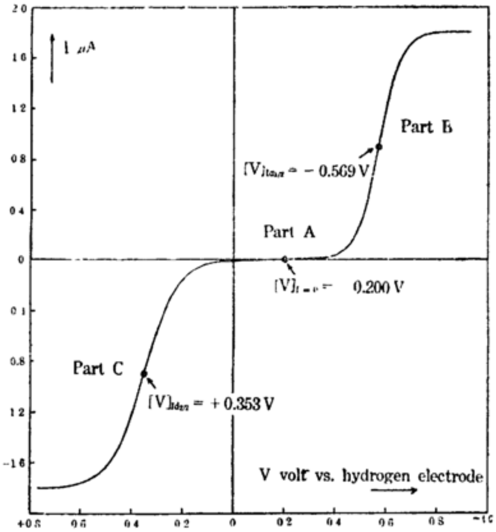

Fig. 1. Theoretical Curve.

Summary.

In this paper the authors have derived the equations of the polarographic current-voltage curve from the standpoint of chemical kinetics, assuming that the net electrode process is activation-controlled. The results obtained are summarized as follows:

(1) Half-wave potential is the constant of the substance concerned, and is independent of its activity.

(2) The potential where the current is equal to zero is only defined by the activities of the oxidant and the reductant in the body of the solution.

(3) The inflection point of the cathodic or anodic wave agrees with its half-wave potential.

(4) The relation between $\log (I/I_d - I)$ and V of the cathodic or anodic wave is a straight line.

(5) The values of ΔF_1, ΔF_2 and α are possible to be calculated from the experimental data.

(6) The theoretical curve is essentially the same as the experimental curve of the irreversible type.

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