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

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

By Nobuyuki TANAKA and Reita TAMAMUSHI.

(Received December 13, 1948.)

In polarography, the formula of the current-voltage curve has been derived and the conception of the half-wave potential has been introduced by J. Heyrovský and D. Ilkovič⑴ in 1935. In this case, as the base of derivation, it was set down that the electrode potential is given by the Nernst's equation and the current is determined by the rate of diffusion of reducible or oxidizable substances. However, since the Nernst's equation, which is derived in thermodynamics, gives the static electrode potential, its application to polarography, in which the electrode potential seems to be dynamic, appears doubtful. Even if the application of the Nernst's equation to polarography is admitted as an approximation, the formula of the current-voltage curve obtained in that case is naturally confined to that of the " reversible wave ". The " irreversible wave " obtained in most cases in polarography is impossible to be treated theoretically with the formula based on the Nernst's equation.

The new derivation of the formula of the current-voltage curve in polarography has been carried out by the present authors from viewpoint of chemical kinetics.⑵ In other words the formula has been derived from the relation between the potential difference of electrode and solution and the current, independently of the Nernst's equation. In this treatment, the " irreversible wave " can be taken into consideration as well as the " reversible wave " and the Nernst's equation is proved to be fulfilled under particular conditions as the approximation.

The derivation of the formula has been carried out for the deposition of metals from the simple (or hydrated) metal ions, the oxidation-reduction of simple (or hydrated) metal ions, the reduction or the oxidation-reduction of organic compounds and the anodic current resulting from the dissolution of the dropping mercury electrode. Of these, in

---

* Presented at the meeting of the Chemical Society of Japan (the Analytical Chemistry Section) on July 1948.

(1) J. Heyrovsky and D. Ilkovič, *Collection Czechoslovak Chemical Communications*, **7** (1935), 198.

(2) Glasstone, Laidler and Eyring, "The Theory of Rate Processes", McGraw-Hill (1941); G. E. Kimball, *J. Chem Phys.*, **8** (1940), 199.

this paper, the former two under the conditions of the diffusion-control have been dealt with, in which, since the oxidation-reduction of simple (or hydrated) metal ions gives the more general formula, the formula for it is derived first and that for the deposition of metal is represented as one in particular conditions. The reduction or the oxidation-reduction of organic compounds is to be reported in the succeeding papers, as well as the electrode reaction of the complex metal ions and, further, the various electrode reactions under the conditions of the non-diffusion-control. As for the dissolution of the dropping mercury electrode the derivation of the formula has been furnished by Eyring⁽²⁾ in the more general case of the dissolution of metals.

Oxidation-reduction of simple (or hydrated) metal ions. Consider the net electrode reaction represented by the equation (1), in which adsorption, decomposition, polymerisation and the like are not assumed to occur at the electrode surface.

$$\mathrm{M}^{m+} + n\ominus \rightleftarrows \mathrm{M}^{(m-n)+}\,, \tag{1}$$

where M^{m+} and $\mathrm{M}^{(m-n)+}$ symbolize the oxidized and the reduced forms of simple (or hydrated) metal ions respectively. Consider a potential-energy barrier to exist between the initial state, the oxidized form M^{m+}, and the final state, the reduced form $\mathrm{M}^{(m-n)+}$. If the free energy difference of the initial and the activated states and that of the final and the activated states are represented by ΔF_1 and ΔF_2 respectively, the difference of ΔF_1 and ΔF_2 becomes the free energy difference of the initial and the final states, which is represented by ΔF_0.

Assume that the reaction in which the oxidized form is reduced at the electrode surface is the forward reaction and the reaction in which the reduced form is oxidized at the electrode surface is the reverse reaction, and that the potential difference between the electrode and the solution, V, acts completely between the initial and the final states of the electrode reaction. If α is the fraction of the potential V that is operative between the initial and the activated states, the potential αV will facilitate the forward reaction and $(1-\alpha)\,V$, retard the reverse reaction, and then the rates of the forward and the reverse reactions are represented by the equation (2)

$$\begin{aligned} &\text{forward reaction:} \quad s\cdot\frac{kT}{h}[A_O]\,e^{-\Delta F_1/RT}\,e^{-n\alpha VF/RT} \equiv [A_O]\,\kappa_1 E_1 \\ &\text{reverse reaction:} \quad s\cdot\frac{kT}{h}[A_R]\,e^{-\Delta F_2/RT}\,e^{n(1-\alpha)VF/RT} \equiv [A_R]\,\kappa_2 E_2\,, \end{aligned} \tag{2}$$

where s is the constant which depends on the nature of the electrode, $[A_O]$ and $[A_R]$ represent the activities of the oxidized and reduced forms at the electrode surface respectively, and κ_1, κ_2, E_1 and E_2 are the abbreviations of $s\frac{kT}{h}e^{-\Delta F_1/RT}$, $s\frac{kT}{h}e^{-\Delta F_2/RT}$, $e^{-n\alpha VF/RT}$ and $e^{n(1-\alpha)VF/RT}$ respectively. In the equation (2) it is also considered that in the reaction concerned the forward reaction is facilitated when the electrode potential becomes more negative.

Since the magnitude of current flowing is determined by the difference of the two rates, the current, assumed to be cathodic, is

$$I = n\,\varepsilon\,\{[A_O]\,\kappa_1 E_1 - [A_R]\,\kappa_2 E_2\}. \tag{3}$$

On the other hand, since, in polarography, the current flowing depends almost entirely on the diffusion because of the existence of large excess of indifferent electrolytes, it can be represented by the diffusion equations for the oxidized and the reduced forms, as mentioned below:

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

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

$[C_O]$, $[C_R]$: concentrations of the oxidized and reduced ions at the electrode surface.
$[C_O]^\circ$, $[C_R]^\circ$: concentrations of the oxidized and reduced ions in the bulk of the solution.
$[A_O]^\circ$, $[A_R]^\circ$: activities of the oxidized and reduced ions in the bulk of the solution.
f_O, f_R: activity coefficients of the oxidized and reduced ions in the solution.
K_O, K_R: constants concerning the diffusion of the oxidized and reduced ions.

If it is assumed that the electrode reaction and the diffusion are kept in an equilibrium at the electrode surface, I, $[A_O]$ and $[A_R]$ can be written as the function of V, $[A_O]^\circ$ and $[A_R]^\circ$ using the equations (3), (4) and (5). The expression of $[A_O]$ is obtained as the equations (6) and (6′) and that of $[A_R]$, as the equations (7) and (7′).

$$[A_O] = \frac{K_O'[A_O]^\circ(\kappa_2 E_2 + K_R') + K_R'[A_R]^\circ \kappa_2 E_2}{K_R'\kappa_1 E_1 + K_O' K_R' + K_O' \kappa_2 E_2}$$

$$= \frac{[A_O]^\circ\left(\frac{1}{K_R'}\frac{\kappa_2 E_2}{\kappa_1 E_1} + \frac{1}{\kappa_1 E_1}\right) + \frac{1}{K_O'}[A_R]^\circ \frac{\kappa_2 E_2}{\kappa_1 E_1}}{\frac{1}{K_O'} + \frac{1}{\kappa_1 E_1} + \frac{1}{K_R'}\frac{\kappa_2 E_2}{\kappa_1 E_1}} \tag{6}$$

$$= \frac{[A_O]^\circ\left(\frac{1}{K_R'} + \frac{1}{\kappa_2 E_2}\right) + \frac{1}{K_O'}[A_R]^\circ}{\frac{1}{K_O'}\frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K_R'}} \tag{6'}$$

$$[A_R] = \frac{K'_O[A_O]^\circ \kappa_1 E_1 + K'_R[A_R]^\circ(\kappa_1 E_1 + K'_O)}{K'_R\kappa_1 E_1 + K'_O K'_R + K'_O\kappa_2 E_2}$$

$$= \frac{\frac{1}{K'_R}[A_O]^\circ + [A_R]^\circ\left(\frac{1}{K'_O} + \frac{1}{\kappa_1 E_1}\right)}{\frac{1}{K'_O} + \frac{1}{\kappa_1 E_1} + \frac{1}{K'_R}\frac{\kappa_2 E_2}{\kappa_1 E_1}} \qquad (7)$$

$$= \frac{\frac{1}{K'_R}[A_O]^\circ\frac{\kappa_1 E_1}{\kappa_2 E_2} + [A_R]^\circ\left(\frac{1}{K'_O}\frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2}\right)}{\frac{1}{K'_O}\frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K'_R}} \qquad (7')$$

Substituting the equations (6) and (7) or (6′) and (7′) for $[A_O]$ and $[A_R]$ in the equation (3), I is written as follows:

$$I = \frac{n\,\varepsilon\, K'_O K'_R([A_O]^\circ\,\kappa_1 E_1 - [A_R]^\circ\kappa_2 E_2)}{K'_R\,\kappa_1 E_1 + K'_O K'_R + K'_O\,\kappa_2 E_2}$$

$$= n\,\varepsilon\frac{[A_O]^\circ - [A_R]^\circ\frac{\kappa_2 E_2}{\kappa_1 E_1}}{\frac{1}{K'_O} + \frac{1}{\kappa_1 E_1} + \frac{1}{K'_R}\frac{\kappa_2 E_2}{\kappa_1 E_1}} \qquad (8)$$

$$= n\,\varepsilon\frac{[A_O]^\circ\frac{\kappa_1 E_1}{\kappa_2 E_2} - [A_R]^\circ}{\frac{1}{K'_O}\frac{\kappa_1 E_1}{\kappa_2 E_2} + \frac{1}{\kappa_2 E_2} + \frac{1}{K'_R}}. \qquad (8')$$

Since $\frac{\kappa_2}{\kappa_1} = e^{-\Delta F_0/RT} = e^{-nV_0F/RT}$, where V_0 symbolizes the normal oxidation-reduction potential, the following relation is obtained.

$$\frac{\kappa_2 E_2}{\kappa_1 E_1} = e^{n(V-V_0)F/RT}$$

Now, the assumption that the oxidation-reduction reaction concerned is controlled completely by the diffusion will be introduced. When the rate of reduction of the oxidized form at the electrode surface is extremely large compared with the rate of diffusion of the oxidized form, that is, $\frac{1}{\kappa_1 E_1}$ is negligible compared with $\frac{1}{K'_O}$ and when the rate of oxidation of the reduced form at the electrode surface is extremely large compared with the rate of diffusion of the reduced form, that is, $\frac{1}{\kappa_2 E_2}$ is negligible compared with $\frac{1}{K'_R}$, the same equation for current, the equation (9), can be derived in both cases, but from the equation (8) in the former case and from the equation (8′) in the latter case.

$$I = n\,\varepsilon\,K'_O K'_R\,\frac{[A_O]^\circ - [A_R]^\circ e^{n(V-V_0)F/RT}}{K'_R + K'_O\,e^{n(V-V_0)F/RT}} \tag{9}$$

Further, the equation (10) is obtained by rearranging the equation (9).

$$e^{n(V-V_0)F/RT} = \frac{K'_R}{K'_O}\;\frac{n\,\varepsilon\,K'_O[A_O]^\circ - I}{I + n\,\varepsilon\,K'_R[A_R]^\circ} \tag{10}$$

The equations (9) and (10) express the relation of the electrode potential and the current, which are nothing but the formulae of the current-voltage curve in polarography.

The limiting case when the difference of V and V_0 is large should be considered. There are two cases, of which the one occurs when V is much more positive than V_0, and the other occurs when V is much more negative than V_0. In the first case $e^{n(V-V_0)F/RT}$, that is, $\frac{\kappa_2 E_2}{\kappa_1 E_1}$ becomes large and then $\frac{\kappa_1 E_1}{\kappa_2 E_2}$ becomes small; in other words $\frac{\kappa_1 E_1}{\kappa_2 E_2}$ is nearer to zero, the larger the difference of V ond V_0. Then, for the equation for the current, the equation (11) is obtained from the equation (8) or (8′) using the assumption of the diffusion-control:

$$I = -n\,\varepsilon\,K'_R[A_R]^\circ = -n\,\varepsilon\,K_R[C_R]^\circ \equiv (I_d)_R\,. \tag{11}$$

This represents nothing but the diffusion current for the anodic wave. Moreover it proves from the equation (7) or (7′) that $[A_R]$ is equal to zero in this condition.

In the second case, on the other hand, $e^{n(V-V_0)F/RT}$, that is, $\frac{\kappa_2 E_2}{\kappa_1 E_1}$ comes nearer to zero and then the equation for current is derived by the same manner as the equation (11).

$$I = n\,\varepsilon\,K'_O[A_O]^\circ = n\,\varepsilon\,K_O[C_O]^\circ \equiv (I_d)_O\,. \tag{12}$$

This expresses the diffusion current for the cathodic wave. In this case it proves from the equation (6) or (6′) that $[A_O]$ is equal or nearly equal to zero.

From the equations (11), (12) and (10), is obtained

$$e^{n(V-V_0)F/RT} = \frac{K'_R}{K'_O}\;\frac{(I_d)_O - I}{I - (I_d)_R}\,, \tag{13}$$

which is the formula of current-voltage curve employed most generally in polarography.

When $\kappa_1 E_1$ and $\kappa_2 E_2$ have a magnitude which is nearly the same and when they are both extremely large compared with K'_O and K'_R, from the equations (6) and (7) or (6′) and (7′) is obtained

$$e^{n(V-V_0)F/RT} = \frac{[A_O]}{[A_R]}. \tag{14}$$

This is the same as the Nernst's equation which expresses the static electrode potential.

Finally the following must be emphasized. In the direct derivation of the formula of the current-voltage curve in polarography that is based on chemical kinetics, two fundamental assumptions are taken: the one is that the electrode reaction at the electrode surface and the diffusion are strictly kept in an equilibrium, and the other is that the rates of all of the possible intermediate steps in the oxidation-reduction reaction are so much more rapid than the diffusion that the current at any point on the polarographic wave is diffusion-controlled. However, to attain the equations (9) and (10), it is not absolutely necessary that both rates of the electrode reactions of the oxidized and the reduced forms are much larger than the rates of diffusions of corresponding forms. In other words, if the rate of diffusion of oxidized form can be rate-determining, it makes no difference whether on the reduced form the rate of electrode reaction is larger than the rate of diffusion or smaller. The converse is also true. This is obvious by the fact that the same equation, the equation (9), can be derived from the equations (8) and (8′) in the corresponding cases. To obtain the Nernst's equation, on the other hand, it is absolutely necessary that both rates of the electrode reactions of the oxidized and the reduced forms have the magnitude nearly the same as each other, and they are much larger than the rates of the diffusions of the corresponding forms.

Deposition of metals from simple (or hydrated) metal ions. In this case the following reaction should be considered instead of the equation (1).

$$\mathrm{M}^{n+} + n\ominus \rightleftarrows \mathrm{M(Hg)}, \tag{15}$$

where M^{n+} symbolizes the simple (or hydrated) metal ion of n valences and M(Hg), amalgam of the metal deposited by the electrode reaction.

If the activities of the metal ion and the metal in amalgam at the electrode surface are represented by $[M^+]$ and $[M]$ respectively and the activities of the metal ion in body of solution and the metal in body of the dropping mercury electrode, by $[M^+]^\circ$ and $[M]^\circ$, $[M^+]$, $[M]$, $[M^+]^\circ$ and $[M]^\circ$ correspond to $[A_O]$, $[A_R]$, $[A_O]^\circ$ and $[A_R]^\circ$ respectively in the equations (2) to (14) described above. Therefore, the equations for the deposition of metal can be obtained by substituting $[M^+]$, $[M]$, $[M^+]^\circ$ and $[M]^\circ$ for $[A_O]$, $[A_R]$, $[A_O]^\circ$ and $[A_R]^\circ$ respectively in those equations. In this case K'_R signifies a constant concerning the diffusion of the metal in mercury.

If the case when pure mercury is employed for the dropping mercury electrode is taken up, the activity of the metal in body of the dropping mercury electrode, $[M]^\circ$, can be regarded as zero, and hence $[A_R]^\circ$ can be substituted by zero. As the result of this substitution, the following equations are obtained for the formula of the current-voltage curve in polarography, corresponding to the equations (9) and (10).

$$I = \frac{n\,\varepsilon\,K'_O\,K'_R\,[M^+]^\circ}{K'_R + K'_O\,e^{n(V-V_0)F/RT}} \tag{16}$$

$$e^{n(V-V_0)F/RT} = \frac{K'_R}{K'_O}\,\frac{n\,\varepsilon\,K'_O[M^+]^\circ - I}{I} \tag{17}$$

As to the equation for diffusion current, in the case of the oxidation-reduction reaction two equations are obtained; the one, for cathodic, and the other for anodic. In this case, however, for the diffusion current only one equation, the equation (18), is given, since $(I_d)_R$, that is, the equation (11) becomes zero because $[M]^\circ$ which corresponds to $[A_R]^\circ$ in the equation (11) is zero.

$$I = n\,\varepsilon\,K'_O[M^+]^\circ \equiv I_d\,. \tag{18}$$

Summary.

The formula of the current-voltage curve in polarography has been derived from the view-point of chemical kinetics and independently of the Nernst's equation. As a result, it has been clearly shown that if the condition of the diffusion-control is fulfilled the formula which had been derived from the Nernst's equation has been obtained in the various types of the electrode reaction. Of these types both the oxidation-reduction of the simple (or hydrated) metal ions and the deposition of the metals from the simple (or hydrated) metal ions have been dealt with in the present paper.

It is also suggested that the "irreversible wave" which cannot be treated theoretically based on the Nernst's equation can possibly be dealt with by the similar derivation as mentioned here.

The authors take this opportunity of acknowledging their gratitude to Director San-ichiro Mizushima for his kind advice and encouragement throughout this study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the authors' thanks are due.

Radiation Chemistry Research Institute,
Tokyo University.