Fundamental Studies on the Current-Voltage Curve in Polarography. III. The Equation for the Current-Voltage Curve of the Complex Ion—Especially for the Irreversible Wave(1)

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The polarographic literature contains numerous papers dealing with the behavior of complex metal ions, but all the discussion rests on the fact that the oxidation and reduction at the dropping mercury electrode is reversible, or the electrode process is controlled by the diffusion process.(3) In the present paper the polarographic wave, especially of the irreversible type, which is obtained by the oxidation and reduction of the complex metal ion at the dropping mercury electrode, is discussed from the viewpoint of the chemical kinetics.

Derivation of the General Formula

There are various possible types of the electrode reactions which involve complex metal ions, but in this treatment only the reaction, which consists of the oxidation and reduction from one ionic oxidation state to the other, is taken up as an example.

The oxidation-reduction of a complex metal ion may be represented by

$$\mathrm{MX}_p^{(n-pb)+}+a\varepsilon \rightleftarrows \mathrm{MX}_q^{(n-a-qb)+}+(p-q)\mathrm{X}^{-b}, \tag{1}$$

where X^{-b} is the complex-forming substance. In this reaction there may be various cases of the intermediate processes, but in the present paper the consideration will be restricted to the case when the reaction occurs through the following three steps.

(i) Decomposition of the complex ion,

$$\mathrm{MX}_p^{(n-pb)+} \underset{\kappa_2}{\overset{\kappa_1}{\rightleftarrows}} \mathrm{M}^{n+}+p\mathrm{X}^{-b}, \tag{2}$$

(ii) Oxidation-reduction reaction,

$$\mathrm{M}^{n+}+a\varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftarrows}} \mathrm{M}^{(n-a)+}, \tag{3}$$

(iii) Formation of the complex ion (reduced type),

$$\mathrm{M}^{(n-a)+}+q\mathrm{X}^{-b} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{MX}_q^{(n-a-qb)+}, \tag{4}$$

where M^{n+} and $\mathrm{M}^{(n-a)+}$ symbolize the simple or hydrated metal ions and the terms k_1, k_2, k_3 and k_4 represent the rate constants for each process, respectivly. κ_1E_1 and κ_2E_2 are the rate constants of the reduction (forward) and oxidation (reverse) processes and are represented by the equations:

$$\kappa_1E_1 = s\cdot\frac{kT}{h}e^{-\Delta F_1/RT}\,e^{-a\alpha VF/RT}$$

$$\kappa_2E_2 = s\cdot\frac{kT}{h}e^{-\Delta F_2/RT}\,e^{a(1-\alpha)VF/RT},$$

where ΔF_1 and ΔF_2 are the free energies of activation for the forward and reverse reactions, V is the potential difference between the dropping mercury electrode and the interior of the solution, a is the number of the electrons which participate in the reaction, and s is the proportionality constant concerning the nature of the electrode. The value of α is the portion of the total electrode potential which promotes the forward reaction. In the polarography, there exist the diffusion processes at the surface of the dropping mercury electrode besides the reactions mentioned above.

According to the same method as mentioned in the previous paper(4) the current flowing can be written as follows:

$$\begin{aligned}
I &= a\varepsilon K_{C\cdot O}([C_{C\cdot O}]^{\circ}-[C_{C\cdot O}])\\
&= a\varepsilon\frac{K_{C\cdot O}}{f_{C\cdot O}}([A_{C\cdot O}]^{\circ}-[A_{C\cdot O}])\\
&= a\varepsilon K'_{C\cdot O}([A_{C\cdot O}]^{\circ}-[A_{C\cdot O}])
\end{aligned} \tag{5}$$

$$\begin{aligned}
I &= a\sigma\varepsilon\,(k_1[A_{C\cdot O}]-k_2[A_O][A_X]^p)\\
&= a\varepsilon(k_1'[A_{C\cdot O}]-k_2'[A_O]),\\
&\qquad k_1'\equiv\sigma k_1,\ k_2'\equiv\sigma k_2[A_X]^p
\end{aligned} \tag{6}$$

$$I = a\varepsilon(\kappa_1E_1[A_O]-\kappa_2E_2[A_R]) \tag{7}$$

$$\begin{aligned}
I &= a\varepsilon\sigma(k_3[A_R][A_X]^q-k_4[A_{C\cdot R}])\\
&= a\varepsilon(k_3'[A_R]-k_4'[A_{C\cdot R}]),\\
&\qquad k_3'\equiv\sigma k_3[A_X]^q,\ k_4'\equiv\sigma k_4
\end{aligned} \tag{8}$$

$$\begin{aligned}
I &= a\varepsilon K_{C\cdot R}([C_{C\cdot R}]-[C_{C\cdot R}]^{\circ})\\
&= a\varepsilon\frac{K_{C\cdot R}}{f_{C\cdot R}}([A_{C\cdot R}]-[A_{C\cdot R}]^{\circ})
\end{aligned}$$

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(3) J.J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

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R. Tamamushi and N. Tanaka, *Reports of the Radiation Chemistry Research Institue*, **4**, 20 (1949); this Bulletin, **22**, 227 (1949).

$$=a_\varepsilon K'_{C\cdot R}([A_{C\cdot R}]-[A_{C\cdot R}]^\circ) \qquad (9)$$

$$I=a_\varepsilon \frac{K_X}{p-q}([C_X]-[C_X]^\circ)$$

$$=a_\varepsilon \frac{K_X}{f_X(p-q)}([A_X]-[A_X]^\circ)$$

$$=a_\varepsilon \frac{K_X'}{p-q}([A_X]-[A_X]^\circ) \qquad (10)$$

In these equations,

$[C_{C\cdot O}]$, $[C_{C\cdot O}]^\circ$: the concentrations of the oxidized complex ion at the electrode surface and in the interior of the solution.

$[C_{C\cdot R}]$, $[C_{C\cdot R}]^\circ$: the concentrations of the reduced complex ion at the electrode surface and in the interior of the solution.

$[C_X]$, $[C_X]^\circ$: the concentrations of the complex-forming substance at the electrode surface and in the interior of the solution.

$[A_{C\cdot O}]$, $[A_{C\cdot O}]^\circ$, $[A_{C\cdot R}]$, $[A_{C\cdot R}]^\circ$, $[A_X]$, $[A_X]^\circ$: the activities for each of the corresponding terms.

$[A_O]$: the activity of the ion M^{n+} at the electrode surface.

$[A_R]$: the activity of the ion $M^{(n-a)+}$ at the electrode surface.

$f_{C\cdot O}$, $f_{C\cdot R}$, f_X: the activity-coefficients of the oxidized and reduced complex ions and of the complex-forming substance at the electrode surface.

σ: the constant concerning the nature of the electrode and others.

Let us consider the case when the rate of the reaction by which the reduced complex ion is formed from $M^{(n-a)+}$ is very rapid in comparison with the diffusion process of the ion.

From these relations, the general formula for the current I and the electrode potential V is obtained as below:

$$I/a_\varepsilon=\frac{K'_{C\cdot R}K'_{C\cdot R}(k_1'k_3'\kappa_1E_1[A_{C\cdot O}]^\circ-k_2'k'_4\kappa_2E_2[A_{C\cdot R}]^\circ}{k_2'k_3'K'_{C\cdot O}K'_{C\cdot R}+\kappa_1E_1k_3'K'_{C\cdot R}(k_1'+K'_{C\cdot O})+\kappa_2E_2k_2'K'_{C\cdot O}(k_4+K'_{C\cdot R})} \qquad (11)$$

Dividing the numerator and denominator of the right-hand side of Eq. (11) by $K'_{C\cdot O}K'_{C\cdot R}\times k_1'k_3'\kappa_1E_1$, the relation

$$I/a_\varepsilon=\frac{[A_{C\cdot O}]^\circ-\dfrac{k_2'k_4'\kappa_2E_2}{k_1'k_3'\kappa_1E_1}[A_{C\cdot R}]^\circ}{\dfrac{k_2'}{k_1'\kappa_1E_1}+\left(\dfrac{1}{K'_{C\cdot O}}+\dfrac{1}{k_1'}\right)+\dfrac{k_2'k_4'\kappa_2E_2}{k_1'k_3'\kappa_1E_1}\left(\dfrac{1}{K'_{C\cdot R}}+\dfrac{1}{k_4'}\right)} \qquad (12)$$

is obtained. For convenience' sake, the abbreviations,

$$\begin{aligned} k_1'\kappa_1E_1/k_2' &\equiv[\kappa_1E_1],\\ k_4'\kappa_2E_2/k_3' &\equiv[\kappa_2E_2], \qquad (13)\\ [\kappa_2E_2]/[\kappa_1E_1] &\equiv[E], \end{aligned}$$

and $$[\kappa_1E_1]/[\kappa_2E_2]\equiv[E]',$$

are introduced into Eq. (12), resulting with the equations,

$$I/a_\varepsilon=\frac{[A_{C\cdot O}]^\circ-[E][A_{C\cdot R}]^\circ}{\dfrac{1}{[\kappa_1E_1]}+\left(\dfrac{1}{K'_{C\cdot O}}+\dfrac{1}{k_1'}\right)+[E]\left(\dfrac{1}{K'_{C\cdot R}}+\dfrac{1}{k_4'}\right)} \qquad (14)$$

$$=\frac{[E]'[A_{C\cdot O}]^\circ-[A_{C\cdot R}]^\circ}{\dfrac{1}{[\kappa_2E_2]}+\left(\dfrac{1}{K'_{C\cdot R}}+\dfrac{1}{k_4'}\right)+[E]'\left(\dfrac{1}{K'_{C\cdot O}}+\dfrac{1}{k_1'}\right)}, \qquad (14')$$

where $[\kappa_1E_1]$ and $[\kappa_2E_2]$ can be regarded as to represent the over-all rate constants of the reduction and oxidation processes at the electrode surface. That is, the over-all rate of the reduction process expressed by (1) is promoted by the terms k_1' and κ_1E_1 but retarded by the term k_2', and, therefore, it can be expressed by $k_1'\kappa_1E_1/k_2'$. Eqs. (14) and (14′) are the general formulae for the polarographic wave of the oxidation-reduction of the complex metal ion. It is mentioned here that if the solution is bufferized with regard to the complex-forming substance, then the quantity $[A_X]$ is equal to $[A_X]^\circ$ in these equations.

In the following section the analysis is set forth in two or three special cases, according to the equations described above.

When the Decomposition Rate of Complex Ion is Very Rapid

In the first place, if the rate of the decomposition of the complex ion at the electrode surface is very rapid in comparison with the rate of the diffusion of the ion, then the following conditions,

$$K'_{C.C}\ll k_1' \quad \text{and} \quad K_{O.R}\ll k_4'$$

are settled. By considering these conditions, Eqs. (14) and (14′) are reduced to

$$I/a_\varepsilon=\frac{[A_{C\cdot O}]^\circ-[E][A_{C\cdot R}]^\circ}{\dfrac{1}{[\kappa_1E_1]}+\dfrac{1}{K'_{C\cdot O}}+[E]\dfrac{1}{K'_{C\cdot R}}} \qquad (15)$$

$$=\frac{[E]'[A_{C\cdot O}]^\circ-[A_{C\cdot R}]^\circ}{\dfrac{1}{[\kappa_2E_2]}+\dfrac{1}{K'_{C\cdot R}}+[E]'\dfrac{1}{K'_{C\cdot O}}}. \qquad (15')$$

Now, two further cases, (A) the case when the diffusion process is rate-determing, and (B) the case when the process which contains the transfer of the electron between the electrode and the ion (activation process) is rate-determining, will be discussed.

(A) Diffusion-controlled Case

The diffusion-controlled case will be defined as a case when the conditions, $[\kappa_1 E_1] \gg K'_{C\cdot O}$ and $[\kappa_1 E_1] \gg K'_{C\cdot R}$, are satisfied in the potential region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. Under these conditions the relation between the current and the electrode potential takes the forms:

$$I/a_\varepsilon = \frac{[A_{C\cdot O}]^\circ - [E]\,[A_{C\cdot R}]^\circ}{\dfrac{1}{K'_{C\cdot O}} + [E]\dfrac{1}{K'_{C\cdot R}}} \tag{16}$$

$$[E] = \frac{[A_{C\cdot O}]^\circ - \dfrac{I}{a_\varepsilon K'_{C\cdot O}}}{\dfrac{I}{a_\varepsilon K'_{C\cdot R}} + [A_{C\cdot R}]^\circ} \tag{17}$$

in the region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$.

Furthermore, as $[\kappa_1 E_1]$ becomes much larger than $[\kappa_2 E_2]$, the current is represented by

$$I = a_\varepsilon K'_{C\cdot O}[A_{C\cdot O}]^\circ = a_\varepsilon K_{C\cdot O}[C_{C\cdot O}]^\circ \equiv (I_d)_{C\cdot O}\,, \tag{18}$$

on the other hand, when $[\kappa_1 E_1]$ is smaller than $[\kappa_2 E_2]$,

$$I = -\,a_\varepsilon K'_{C\cdot R}[A_{C\cdot R}]^\circ = -\,a_\varepsilon K_{C\cdot R}[C_{C\cdot R}]^\circ \equiv (I_d)_{C\cdot R}\,. \tag{19}$$

These relations correspond to the limiting currents controlled by the diffusion process.

From Eqs. (17), (18) and (19) the following equation is derived:

$$[E] = \frac{K'_{C\cdot R}}{K'_{C\cdot O}}\,\frac{(I_d)_{C\cdot O} - I}{I - (I_d)_{C\cdot R}}\,, \tag{20}$$

which is quite the same as obtained from the Nernst's formula for the reversible wave.

The detailed discussion on the half-wave potential and the other properties of the wave has been set down by J. J. Lingane.(4)

(B) Activation-controlled Case

The activation-controlled case will be defined as a case when the conditions, $[\kappa_1 E_1] \ll K'_{C\cdot O}$ and $[\kappa_1 E_1] \ll K'_{C\cdot R}$, are satisfied in the potential region where $[\kappa_1 E_1]$ is nearly equal to $[\kappa_2 E_2]$. However, on the current-voltage curve, there may be a region in which the relation, $[\kappa_1 E_1] \gg [\kappa_2 E_2]$ or $[\kappa_1 E_1] \ll [\kappa_2 E_2]$, is satisfied, where the condition, $[\kappa_1 E_1] \ll K'_{C\cdot O}$ or $[\kappa_1 E_1] \ll K'_{C\cdot R}$ is not necessarily fulfilled. To analyse, therefore, the current-voltage curve, it must be divided into the following three parts according to the value of the electrode potential.

(I) $[\kappa_1 E_1] \cong [\kappa_2 E_2]$.—In this case when, according to the above definition, $[\kappa_1 E_1] \ll K'_{C\cdot O}$, Eq. (15) is reduced to the form,

$$I/a_\varepsilon = [\kappa_1 E_1]\,[A_{C\cdot O}]^\circ - [\kappa_2 E_2]\,[A_{C\cdot R}]^\circ. \tag{21}$$

From this equation, the condition for the point where the current is zero, is obtained as follows:

$$[E]_{I=0} = \frac{[A_{C\cdot O}]^\circ}{[A_{C\cdot R}]^\circ} \tag{22}$$

Eq. (21) means that the current in this part is fully defined by the rates of the activated reaction.

(II) $[\kappa_1 E_1] \gg [\kappa_2 E_2]$.—In this part, the term $[E]$ becomes vanishingly small (and can be regarded as nearly equal to zero). As for convenience, this part is sub-divided into two cases.

(a) $[\kappa_1 E_1] \cong K'_{C\cdot O}$. — Here, the equation which represents the current-voltage curve is

$$I/a_\varepsilon = \frac{[A_{C\cdot O}]^\circ}{\dfrac{1}{[\kappa_1 E_1]} + \dfrac{1}{K'_{C\cdot O}}}\,, \tag{23}$$

or

$$[\kappa_1 E_1] = \frac{K'_{C\cdot O}\, I}{a_\varepsilon K'_{C\cdot O}[A_{C\cdot O}]^\circ - I} \tag{24}$$

From these equations it is obvious that the properties of the wave of this part are independent of the reverse reaction.

(b) $[\kappa_1 E_1] \gg K_{C.O}'$.—In this case the condition for the limiting current is obtained, i.e.,

$$I = a_\varepsilon K_{C.O}[C_{C.O}]^\circ \equiv (I_d)_{C.O}\,. \tag{18}$$

These equations, which are formally the same with those obtained for the oxidation-reduction of the simple metal ion(5), show the fact that the part (II) corresponds to the reduction wave with the characteristics of the "irreversible" one.

Introducing the condition for the limiting current into Eq. (24), the next formula is obtained,

$$[\kappa_1 E_1] = K'_{C.O}\,\frac{I}{(I_d)_{C.O} - I}\,, \tag{25}$$

or by solving this equation regarding the electrode potential, V, we obtain

$$V = \frac{RT}{a\alpha F}\left(\ln s\cdot\frac{kT}{h} + \ln \Gamma - \ln K'_{C.O}\right) - p\frac{RT}{a\alpha F}\ln[A_X] - \frac{RT}{a\alpha F}\ln\frac{I}{(I_d)_{C.O} - I} - \frac{\Delta F_1}{a\alpha F}, \tag{26}$$

where Γ represents the dissociation constant of the oxidized complex ion and is equal to k_1/k_2.

For the half-wave potential, the relations

$$[\kappa_1 E_1]_{\frac{(I_d)_{C.O}}{2}} = K'_{C.O} \tag{27}$$

and

$$[V]_{(I_d)_{C.O}} = \frac{RT}{a\alpha F}\left(\ln\cdot s\frac{kT}{h} + \ln\Gamma - \ln K'_{C.O}\right) - p\frac{RT}{a\alpha F}\ln[A_X] - \frac{\Delta F_1}{a\alpha F} \tag{28}$$

are obtained. Therefore, if α and the ionic strength of the solution are constant, the half-wave potential is the characteristic constant for each complex ion and is independent of the activity of the ion.

From Eq. (28) it can be said that the relation between $[V]_{\frac{(I_d)_{C.O}}{2}}$ and the activity of the complex-forming substance $[A_X]$ is a straight line, the tangent of which is $p\times 0.059/a\alpha$ volt at 25°. Hence, by determining the tangent of this relation and the values of a and α, the coordination number of this complex ion, p, will be calculated.

It must be noted, that if the net electrode process is diffusion-controlled the tangent of the above relation is $(p-q)\times 0.059/a$ volt, while the tangent of the activation-controlled one is $p\times 0.059/a\alpha$ volt and is independent of q.

Moreover, it is concluded from Eq. (25) that the relation between V and $\log I/(I_d-I)$ is a straight line whose tangent is $0.059/a\alpha$ volt (25°), if ΔF_1, p, α and $[A_X]$ remain constant. This means that the current-voltage curve is symmetrical about the half-wave potential. The value of α can be obtained from the measurement of the tangent of the above relation, if the value of a is known.

Quite the same discussion as described above can be applied to the case, $[\kappa_1E_1]\ll[\kappa_2E_2]$, and it can be shown that this part corresponds to the oxidation wave. In the following, only the results are cited.

(III) $[\kappa_1E_1]\ll[\kappa_2E_2]$.

(a) $[\kappa_2E_2]\cong K'_{C.R}$

$$I/a\varepsilon=\frac{-[A_{C.R}]^\circ}{\dfrac{1}{K'_{C.R}}+\dfrac{1}{[\kappa_2E_2]}}\tag{29}$$

and

$$[\kappa_2E_2]=\frac{-K'_{C.R}\,I}{a\varepsilon K'_{C.R}[A_{C.R}]^\circ-I}\tag{30}$$

(b) $[\kappa_2E_2]\gg K'_{C.R}$

$$I=-a\varepsilon K_{C.R}[C_{C.R}]^\circ\equiv(I_d)_{C.R}\tag{19}$$

From the above equations it is obvious that the oxidation wave is quite independent of the forward reaction.

All the consideration mentioned above about the activation-controlled case has been made, being based on the definitions, (1) $K'_{C.O}\ll k_1'$ and $K'_{C.R}\ll k_4'$ and (2) $[\kappa_1E_1]\ll K'_{C.O}$ and $[\kappa_1E_1]\ll K'_{C.R}$ when $[\kappa_1E_1]\cong[\kappa_2E_2]$, for which some discussions will be carried out. In the first place, the relation (1), shows that the decomposition rate of the complex ion is much larger than the rate of the diffusion of the ion. In this case, the limiting current will be the same as the diffusion current, and will be represented by the Ilkovič equation. In the second place, the relation (2) means that the rate of the activation process is much smaller than the rate of the diffusion of the ion at the electrode potential where the rate constants of the forward and reverse processes are nearly the same. According to Eq. (13), $[\kappa_1E_1]$ is represented by $k_1'\kappa_1E_1/k_2'$. This means that the over-all rate constant of the reduction process is accelerated by k_1' and κ_1E_1 but retarded by the term k_2'. κ_1E_1 is the rate constant of the reaction corresponding to the transfer of the electron between the ion and the electrode, and generally, it is regarded as to be very rapid. Moreover, by the condition (1) k_1' is much larger than $K'_{C.O}$, then k_2' must be much larger than k_1' and κ_1E_1 in order to fulfill the relation (2) This behavior will be satisfied when the relating complex ion is very stable in the solution, and it can be said that the more stable the complex ion, the larger the irreversibility is (and that it is reduced more difficultly) as far as the electrode process is carried out according to the mechanism mentioned above.

When the Decomposition Rate is Slower than that of the Diffusion

In this case when $K'_{C.O}\gg k_1'$ and $K'_{C.R}\gg k_4'$, the general equations, Eqs. (14) and (14′) assume the forms respectively,

$$I/a\varepsilon=\frac{[A_{C.O}]^\circ-[E][A_{C.R}]^\circ}{\dfrac{1}{[\kappa_1E_1]}+\dfrac{1}{k_1'}+[E]\dfrac{1}{k_4'}}\tag{31}$$

$$=\frac{[E]'[A_{C.O}]^\circ-[A_{C.R}]^\circ}{\dfrac{1}{[\kappa_2E_2]}+\dfrac{1}{k_4'}+[E]'\dfrac{1}{k_1'}}\tag{31'}$$

If we compare these equations with Eqs. (15) and (15′), it is easily seen that the only difference between them is the fact that $K'_{C.O}$ and $K'_{C.R}$ in (15) and (15′) are replaced by k_1' and k_4', respectively. Therefore, for the present case, the completely analogous consideration can be made as discussed above, if both k_1' and k_4' are the constants independent of the electrode potential. So that only the results obtained in the next section.

(A) Decomposition-controlled Case

This case obviouly corresponds to the diffusion-controlled case in the previous section. Hence, the equation for the current-voltage curve in the region where $[\kappa_1E_1]$ is nearly equal to $[\kappa_2E_2]$ is represented by

$$I/a\varepsilon=\frac{[A_{C.O}]^\circ-[E][A_{C.R}]^\circ}{\dfrac{1}{k_1'}+[E]\dfrac{1}{k_4'}},\tag{32}$$

and the limiting currents are

$$I = a\varepsilon k_1' [A_{C.O}]^\circ \equiv (I_k)_{C.O} \qquad (33)$$

$$I = -a\varepsilon k_4' [A_{C.R}]^\circ \equiv (I_k)_{C.R} \qquad (34)$$

for the reduction and oxidation waves, respectively.

(B) Activation-controlled Case

From Eqs. (19)$\sim$(30) the following relations can be obtained directly by introducing k_1' and k_4' in place of $K'_{C.O}$ and $K'_{C.R}$.

(I) $[\kappa_1 E_1] \cong [\kappa_2 E_2]$

$$I/a\varepsilon = [\kappa_1 E_1][A_{C.O}]^\circ - [\kappa_2 E_2][A_{C.R}]^\circ \qquad (35)$$

(II) $[\kappa_1 E_1] \gg [\kappa_2 E_2]$

(a) $[\kappa_1 E_1] \cong k_1'$

$$I/a\varepsilon = \frac{[A_{C.O}]^\circ}{\dfrac{1}{k_1'} + \dfrac{1}{[\kappa_1 E_1]}} \qquad (36)$$

(b) $[\kappa_1 E_1] \gg k_1'$

$$I = a\varepsilon k_1' [A_{C.O}]^\circ \equiv (I_k)_{C.O} \qquad (33)$$

(III) $[\kappa_1 E_1] \ll [\kappa_2 E_2]$

(a) $[\kappa_2 E_2] \cong k_4'$

$$I/a\varepsilon = \frac{-[A_{C.R}]^\circ}{\dfrac{1}{k_4'} + \dfrac{1}{[\kappa_2 E_2]}} \qquad (37)$$

(b) $[\kappa_2 E_2] \gg k_4'$

$$I = -a\varepsilon k_4' [A_{C.R}]^\circ \equiv (I_k)_{C.R} \qquad (34)$$

According to the consequences obtained above it is said that, when the decomposition-rate of the complex ion is slower than the rate of the diffusion, the limiting current is defined by the rate of the decomposition of the ion at the electrode surface and it is necessarily smaller than the limiting current which is defined by the diffusion process. This limiting current caused by the kinetic term probably corresponds to the "kinetic current" mentioned by Brdička and others.(5)

The kinetic current can be distinguished from the diffusion current by its dependence on the temperature change and the geometrical characteristics of the dropping mercury electrode and so on.

Summary

The fundamental equations for the current-voltage curve of the complex ion, especially for the irreversible type, have been derived under the assumption that the over-all oxidation-reduction proccess at the electrode surface follows the mechanism represented by (1) $\sim$(4). Moreover, the two cases, of which one is based on the assumption that the decomposition-rate is much larger than the rate of the diffusion, and the other corresponds to the case when the relation between the two rates is reverse, have been discussed and it has been pointed that the limiting current of the former is the same as the diffusion current, but the limiting current of the latter corresponds to the kinetic current. It has been concluded that, if the electrode process is activation-controlled, the wave which has many properties of the irreversible one appears. The meaning of the half-wave potential of such a wave has been analyzed, and from the results it has been found that the value of the half-wave potential would be the parameter for the degree of difficulty of the oxidation-reduction process of the complex ion, even if the corresponding wave is irreversible. It should be noted here, that all the discussion cited above rests on the fact that the complex-forming substance exists in a sufficient quantity.

It is likely that the treatment for the oxidation-reduction reaction of the complex ion is essentially the same as for the discussion about the organic compounds.

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