Studies on the Electrode Process in Polarography

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Preface

This paper is a review of the study on the theory of the current-voltage curve in polarography and the mechanism of the reduction process of hydrogen ion at the dropping mercury electrode, which was carried out by the present author, partly in collaboration with N. Tanaka, during 1948 and 1952. Our study on the current-voltage curve from the standpoint of the chemical kinetics might be considered as the first attempt to interpret theoretically the properties of so-called "irreversible" waves together with the works of H. Eyring—L. Marker—

T. C. Kwoh[1] and R. Goto—I. Tachi[2], and the application of our theoretical treatment to the reduction process of hydrogen ion brought some light into the mechanism of this electrode process.

Recently a great progress has been made in this field of polarography by some investigators, and some assumptions used in our theory have been criticized. Needless to say that these new theories are highly valuable in the analysis of the polarographic waves and the mechanism of the electrode reaction. Although, under such a circumstance, it would be very desirable to review the results of these theories, it is unfortunately out of the limit of the present paper. At any rate, it should be insisted here that, inspite of the new development of the theory and technique in polarography, many polarographic electrode processes still remain in total lack of any reasonable interpretation.

The present author should like to take this opportunity to thank Prof. San-ichiro Mizushima and Assist. Prof. Nobuyuki Tanaka for their great encouragement and valuable suggestions in the completion of this study.

Part I.   Theory of the Current-Voltage Curve

We owe to J. Heyrovsky and D. Ilkovic[3] the first theoretical interpretation of the current-voltage curve (c-v curve) in polarography. In 1935, they derived the formulae for the c-v curve under the assumption that the electrode potential of the dropping mercury electrode (DME) is represented by the Nernst equation and the current flowing is determined by the rate of diffusion of reducible or oxidizable substances. The Nernst equation, however, can be strictly applied only to the electrode where no current flows, in other words, where the condition of the thermodynamic reversibility is maintained. In polarography, the current is always flowing at the DME, and this means that the process at the DME is not in the equilibrium. This difference between the potentiometry and polarography makes the assumption of Heyrovsky and Ilkovic on the electrode potential of the DME somewhat doubtful. In fact, the application of their results has been limited only to the polarographic waves which are called to be " reversible ", and all other waves, called to be " irreversible ", have been set aside without any theoretical interpretation. Under this circumstance, it seems very valuable to analyse the c-v curve from a different viewpoint so that some theoretical interpretations can be given even to the irreversible waves.

The electrode process at the DME in polarography is a kind of complex electrochemical reactions consisting of many elementary processes. In the simplest case, this process involves the diffusion of the substances and the electron-transfer reaction (redox reaction) at the electrode, the

rate constant of the latter is a function of the electrode potential. By analysing the electrode precess at the DME by the method of the chemical kinetics[4], a new derivation of the formulae for the c-v curve can be carried out under the following assumptions:

    i) The overall process is in a stationary (or steady) state in a sense of the chemical kinetics.

    ii) The current flowing is represented by the rate of the redox reaction.

    iii) The migration current is negligible because of the presence of indifferent electrolytes in excess.

    The results of the theoretical consideration and some experimental evidences will be reviewed in the following sections.

1. Oxidation-Reduction of Simple (or Hydrated) Metal Ions[5]

i. Derivation of General Formulae

    Let us consider the simplest redox reaction represented by Eq. (I-1), in which no side reaction occurs at the electrode surface,

$$M^{m+} + n\varepsilon \overset{\rightarrow}{\underset{\leftarrow}{\rightleftarrows}} M^{(m-n)+} \qquad (I-1)$$

where M^{m+} and $M^{(m-n)+}$ are the oxidant and reductant of simple metal ion, respectively, and n is the number of electrons which participate in the redox reaction. Assume the existence of a potential barrier between the initial state, the oxidant M^{m+}, and the final state, the reductant $M^{(m-n)+}$. If the free energy difference of the initial and activated states and that of the final and activated states are represented by ΔF_1 and ΔF_2 respectively, the difference of ΔF_1 and ΔF_2 is the free energy difference of the initial and final states represented by ΔF_0.

    In the absence of any external potential, the rate constants of the forward and reverse processes are written as follows:

$$\text{forward}: \quad s\frac{kT}{h}e^{-\Delta F_1/RT} \equiv \kappa_1$$

$$\text{reverse}: \quad s\frac{kT}{h}e^{-\Delta F_2/RT} \equiv \kappa_2 \qquad (I-2)$$

where s is a constant concerning the nature of the electrode surface, k the Boltzmann constant, h the Planck constant, and T the absolute temperature. (Hereafter, the process from the left-hand side to the right-hand side of the reaction formula is called "forward" and the process from the right-hand to the left-hand is called "reverse"). If the particular potential V is applied to the electrode against the bulk of solution and V is assumed to act completely between the initial and final states of the redox reaction, the two rate constants must be written

as follows:

forward: $\kappa_1 e^{-n\alpha VF/RT} \equiv \kappa_1 E_1$

reverse: $\kappa_2 e^{n(1-\alpha)VF/RT} \equiv \kappa_2 E_2$

(I-3)

αV is the fraction of total applied potential V which promotes the forward reaction, and, therefore, $(1-\alpha)V$ retards the reverse.

The current flowing, I, is assumed to be determined by the rate of the electron-transfer reaction represented by Eq. (I-1). If the activities of the oxidant and reductant at the electrode surface are represented by $[A_o]$ and $[A_R]$, respectively, I is expressed by Eq. (I-4):

$$I = nF\{\kappa_1 E_1[A_o] - \kappa_2 E_2[A_R]\}$$ (I-4)

where F is the Faraday constant.

The redox reaction at the electrode surface is accompanied by the diffusion processes of the oxidant and reductant between the electrode surface and the bulk of solution, because of the change of activities of these substances at the electrode surface. When the overall process, consisting of these diffusion processes and the redox reaction at the electrode surface, is in a stationary state, the rates of diffusion processes are equal to that of the redox reaction. In such a case, the current flowing can also be represented by the diffusion process of the oxidant, namely:

$$I = nFK_o([C_o]^\circ - [C_o]) = nF\frac{K_o}{f_o}([A_o]^\circ - [A_o]) = nFK_o'([A_o]^\circ - [A_o])$$ (I-5)

$$K_o' \equiv K_o/f_o$$

or by that of the reductant, namely:

$$I = nFK_R([C_R] - [C_R]^\circ) = nF\frac{K_R}{f_R}([A_R] - [A_R]^\circ) = nFK_R'([A_R] - [A_R]^\circ)$$ (I-6)

$$K_R' \equiv K_R/f_R$$

where $[A_o]^\circ$ and $[A_R]^\circ$ are the activities of the oxidant and reductant in the bulk of 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 bulk of solution, and f_o and f_R are the activity-coefficients of the corresponding substances, respectively. K_o or K_R is a constant concerning the rate constant of each diffusion process.

From Eqs. (I-4), (I-5) and (I-6) the general equation for the current I and the electrode potential V is obtained:

$$I = nF\frac{K_o'K_R'(\kappa_1 E_1[A_o]^\circ - \kappa_2 E_2[A_R]^\circ)}{\kappa_1 E_1 K_R' + \kappa_2 E_2 K_o' + K_o'K_R'} = nF\frac{[A_o]^\circ - [A_R]^\circ\dfrac{\kappa_2 E_2}{\kappa_1 E_1}}{\dfrac{1}{K_o'} + \dfrac{1}{\kappa_1 E_1} + \dfrac{1}{K_R'}\dfrac{\kappa_2 E_2}{\kappa_1 E_1}}$$ (I-7)

$$=nF\dfrac{[A_o]^\circ\dfrac{\kappa_1 E_1}{\kappa_2 E_2}-[A_R]^\circ}{\dfrac{1}{K_o{}'}\dfrac{\kappa_1 E_1}{\kappa_2 E_2}+\dfrac{1}{\kappa_2 E_2}+\dfrac{1}{K_R{}'}} \qquad (I\text{-}7')$$

This equation could be analysed in more detail by using the concept of the rate-determining step of the complex reaction. Let us consider the magnitudes of the rate constants, $K_o{}'$, $K_R{}'$, $\kappa_1 E_1$ and $\kappa_2 E_2$ in Eqs. (I-7) and (I-7'). $K_o{}'$ and $K_R{}'$, which depend on the diffusion coefficients of the oxidant and reductant in the solution, might be regarded to be independent of the electrode potential and almost equal in their magnitudes. On the other hand, $\kappa_1 E_1$ and $\kappa_2 E_2$ are the functions of the electrode potential that is continuously changed in polarography. Therefore, these values should be compared in the particular potential region separately. In the present treatment, the total c-v curve is divided into three parts according to the value of V, i.e., $\kappa_1 E_1 \cong \kappa_2 E_2$ (Part A), $\kappa_1 E_1 > \kappa_2 E_2$ (Part B), and $\kappa_1 E_1 < \kappa_2 E_2$ (Part C).

ii. Diffusion-controlled Case

The "diffusion-controlled" case is defined as the case in which the conditions, $\kappa_1 E_1 \gg K_o{}'$ and $\kappa_1 E_1 \gg K_R{}'$, are maintained in the potential region where $\kappa_1 E_1 \cong \kappa_2 E_2$. By introducing these conditions into Eqs. (I-7) and (I-7'), Eq. (I-8) is obtained for the formula of the c-v curve in Part A:

$$I=nFK_o{}'K_R{}'\dfrac{[A_o]^\circ-[A_R]^\circ\dfrac{\kappa_2 E_2}{\kappa_1 E_1}}{K_R{}'+K_o{}'\dfrac{\kappa_2 E_2}{\kappa_1 E_1}} \qquad (I\text{-}8)$$

By rearranging Eq. (I-8) using the relation,

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

where V_0 equals $\Delta F_0/RT$, i.e., the normal oxidation-reduction potential of the system, the electrode potential V can be represented in terms of the experimentally determinable quantities as

$$e^{n(V-V_0)F/RT}=\dfrac{K_R{}'}{K_o{}'}\dfrac{nFK_o{}'[A_o]^\circ-I}{I+nFK_R{}'[A_R]^\circ} \qquad (I\text{-}9)$$

The limiting case, where the difference of V and V_0 is large, should be considered (Parts B and C). In Part B, $\kappa_1 E_1$ is much larger than $\kappa_2 E_2$ (V is much more negative than V_0), and the general equation is reduced to

$$I=nFK_o{}'[A_o]^\circ=nFK_o[C_o]^\circ\equiv(I_d)_o \qquad (I\text{-}10)$$

which shows that the current is independent of the electrode potential in this region. This represents nothing but the diffusion current of the cathodic wave. In Part C, $\kappa_2 E_2$ is much larger than $\kappa_1 E_1$ (V is much more positive than V_0), and the general equation is reduced to

$$I = -nFK_R'[A_R]^\circ = -nFK_R[C_R] \equiv (I_d)_R \qquad (I\text{-}11)$$

which represents the diffusion current of the anodic wave.

From Eqs. (I-9), (I-10) and (I-11), the equation,

$$e^{n(V-V_0)F/RT} = \frac{K_R'}{K_o'} \frac{(I_d)_o - I}{I - (I_d)_R} \qquad (I\text{-}12)$$

is obtained for the c-v curve in a form most generally used in polarography.

Eq. (I-12) is identical with the equation for the reversible wave which was derived by Heyrovsky and Ilkovic using the Nernst equation for the electrode potential of the DME. This result means that the "reversible" case in Heyrovsky-Ilkovic's treatment corresponds to the "diffusion-controlled" case in the present classification.

iii. Activation-controlled Case[6]

Derivation of the Formula.

The "activation-controlled" case is defined as the case in which the conditions, $\kappa_1 E_1 \ll K_o'$ and $\kappa_1 E_1 \ll K_R'$, are maintained in the potential region where $\kappa_1 E_1 \simeq \kappa_2 E_2$. As mentioned before, the whole c-v curve is divided into three parts according to the value of the electrode potential.

Part A. $\kappa_1 E_1 \simeq \kappa_2 E_2 \ldots$ By applying the conditions for the activation-controlled case to Eqs. (I-7) and (I-7'), the equation for the c-v curve in this potential region can be written as

$$I = nF\{\kappa_1 E_1[A_o]^\circ - \kappa_2 E_2[A_R]^\circ\} \qquad (I\text{-}13)$$

From this equation it can be said that the current flowing at such a potential is determined only by the rate of the electron-transfer process.

Part B. $\kappa_1 E_1 > \kappa_2 E_2 \ldots$ For convenience, this part is further divided into two regions.

(a) $\kappa_1 E_1 \simeq K_o' \ldots$ In this case, $\kappa_2 E_2/\kappa_1 E_1$ is nearly equal to zero. Under these conditions, the equation for the c-v curve in this potential region can be derived from Eq. (I-7), namely:

$$I = nF\frac{K_o'\kappa_1 E_1[A_o]^\circ}{K_o' + \kappa_1 E_1} \qquad (I\text{-}14)$$

(b) $\kappa_1 E_1 \gg K_o' \ldots$ In this case, $\kappa_2 E_2/\kappa_1 E_1$ obviously tends to zero. Hence, Eq. (I-7) is reduced to Eq. (I-10), which represents the limiting case and corresponds to the diffusion current in polarography.

From Eqs. (I-14) and (I-10), it can be said that, in 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 system under consideration.

Part C. $\kappa_1 E_1 < \kappa_2 E_2$....By the same treatment as for Part B, the equations for the anodic wave and anodic limiting current are obtained from Eq. (I-7') as follows:

(a) $\kappa_2 E_2 \simeq K_R'$

$$I = -nF\frac{K_R' \kappa_2 E_2 [A_R]^\circ}{K_R' + \kappa_2 E_2} \qquad (I-15)$$

(b) $\kappa_2 E_2 \gg K_R'$....The same equation as Eq. (I-11) is obtained for the limiting current.

These equations (I-13), (I-14), (I-15), (I-10) and (I-11) represent the whole c-v curve due to the electrode process which proceeds at the DME under the conditions described in this section.

Theoretical Analysis of the Curve.

The Electrode Potential where the Current is Equal to Zero.....In Part A of the c-v curve there must be such a point where the current flowing is zero, *i.e.*, $I=0$. From Eq. (I-13) the condition for this point is obtained as

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

or

$$\left[e^{n(V-V_0)F/RT}\right]_{I=0} = \frac{[A_o]^\circ}{[A_R]^\circ} \qquad (I-16)$$

This suggests the possibility that, if $[A_o]^\circ$ and $[A_R]^\circ$ are known and the potential $[V]_{I=0}$ is determined from the experimental curve, the normal oxidation-reduction potential V_0 of the system can be obtained from the experimental results. In effect, however, it will be somewhat difficult to determine the correct value of V_0 by this method, because the current flowing in this potential region is usually very small and the inclination of the curve at the point $[V]_{I=0}$ is also very small as shown later.

Half-wave Potential.....There are two half-wave potentials in the whole c-v curve, *i.e.*, the half-wave potentials of the cathodic part and anodic part. By introducing Eq. (I-10) into Eq. (I-14), the equation,

$$\kappa_1 E_1 = \frac{K_o' I}{(I_d)_o - I}$$

or   (I-17)

$$V = -\frac{RT}{n\alpha F}\left(\frac{\Delta F_1}{RT} + \ln\frac{h}{skT}K_o' + \ln\frac{I}{(I_d)_o - I}\right)$$

can be obtained for the c-v curve of cathodic wave. At the half-wave

potential the current flowing is one half of the limiting current, namely:

$$I = (I_d)_o/2 \tag{I-18}$$

From Eqs. (I-17) and (I-18) the condition for the cathodic half-wave potential is derived as follows:

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

or   (I-19)

$$[V]_{\frac{(I_d)_o}{2}} = -\frac{RT}{n\alpha F}\left(\frac{\Delta F_1}{RT} + \ln\frac{h}{skT}K_o'\right)$$

Eq. (I-19) shows that the half-wave potential of the cathodic wave under the conditions of the activation-controlled case depends on the constant K_o' and the free energy of activation ΔF_1, and that it will be a particular constant for the oxidant concerned so long as the value of α remains constant.

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   (I-20)

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

The Log-plot Analysis (The Relation between $\log I/(I_l - I)$ and V).... From Eq. (I-17) it is obvious that the relation between $\log I/(I_l - I)$ 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, respectively. If this relation is plotted and the tangent of the line is determined, the value of α can be calculated. In the case when the redox reaction concerned involves one electron and the process is diffusion-controlled, the theoretical inclination of the above relation must be 0.059 volt at 25°C. If the experimental result deviates from this value, it might be concluded that the process does not proceed under the conditions of the diffusion-controlled.

First Derivative of the C-V Curve (Tangent of the Curve).... Differentiating Eqs. (I-13), (I-14) and (I-15) with respect to the electrode potential V, the tangents of the c-v curves of Parts A, B and C are represented as follows:

Part A.

$$\frac{dI}{dV} = -nF\frac{nF}{RT}\{\alpha[A_o]°\kappa_1 E_1 + (1-\alpha)\kappa_2 E_2[A_R]°\} \tag{I-21}$$

Part B.

$$\frac{dI}{dV} = -nF\frac{nF}{RT}\alpha K_o' \kappa_1 E_1 \frac{K_o'[A_o]^\circ}{(K_o' + \kappa_1 E_1)^2} \tag{I-22}$$

Part C.

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

From Eqs. (I-16) and (I-21) the tangent of the c-v curve at the point, $I=0$, can be obtained as

$$\left[\frac{dI}{dV}\right]_{I=0} = -nF\frac{nF}{RT}\kappa_1 E_1[A_o]^\circ \tag{I-24}$$

The tangent at the cathodic half-wave potential is derived by the application of Eq. (I-19) to Eq. (I-22):

$$\left[\frac{dI}{dV}\right]_{\frac{(I_d)_o}{2}} = -nF\frac{nF}{4RT}\alpha\kappa_1 E_1[A_o]^\circ = -nF\frac{n\alpha F}{4RT}K_o'[A_o]^\circ \tag{I-25}$$

Let us compare the two tangents (I-24) and (I-25) with each other. Dividing Eq. (I-25) by Eq. (I-24), Eq. (I-26) is obtained, unless the value of α is extremely small:

$$\frac{\left[\dfrac{dI}{dV}\right]_{\frac{(I_d)_o}{2}}}{\left[\dfrac{dI}{dV}\right]_{I=0}} = \frac{\alpha K_o'}{4[\kappa_1 E_1]_{I=0}} \gg 1 \tag{I-26}$$

From this result, it can be said that the cathodic wave is far steeper than the wave of Part A.

Second Derivative of the C-V Curve (Inflection Point of the Curve) ....By calculating the second derivatives of Eqs. (I-13), (I-14) and (I-15) with respect to the electrode potential V and by making these derivatives equal to zero, the conditions for the inflection points of the c-v curve are obtained as follows:

Part A.

$$\left[\frac{\kappa_2 E_2}{\kappa_1 E_1}\right]_{\text{infl. pt. A}} = \frac{\alpha^2}{(1-\alpha)^2}\frac{[A_o]^\circ}{[A_R]^\circ} \tag{I-27}$$

Part B.

$$[\kappa_1 E_1]_{\text{infl. pt. B}} = K_o' \tag{I-28}$$

Part C.

$$[\kappa_2 E_2]_{\text{infl. pt. C}} = K_R' \tag{I-29}$$

It is pointed out from these equations that the inflection point of

cathodic or anodic wave is identical with the corresponding half-wave potential.

From the results described above, it can be expected that these equations for the c-v curve under the conditions of the activation-controlled case will account for the nature of some types of so-called "irreversible" waves which have not yet been interpreted.

iv. Experiments to the Theory—Analysis of the Reduction Wave of Titanic Ion[7]

The oxidation-reduction wave of the mixture of titanous and titanic ions in the medium of hydrochloric acid has been studied by R. Strubl[8]. In this irreversible wave, the oxidation wave is separated from the reduction wave, and the half-wave potential of the former is different from that of the latter. It has also been shown by Kalousek's method[9] that the rate constant of the oxidation process of the reduction product of titanic ion in the medium of sulfuric acid might be very small in the potential region where the reduction wave appears[7]. These facts suggest that the overall electrode process of the reduction of titanic ion does not proceed under the conditions of the diffusion-controlled case, but under the conditions of the activation-controlled one.

A typical reduction wave of titanic ion is shown in Fig. 1, and a result of the log-plot analysis of the wave is shown in Fig. 2. The
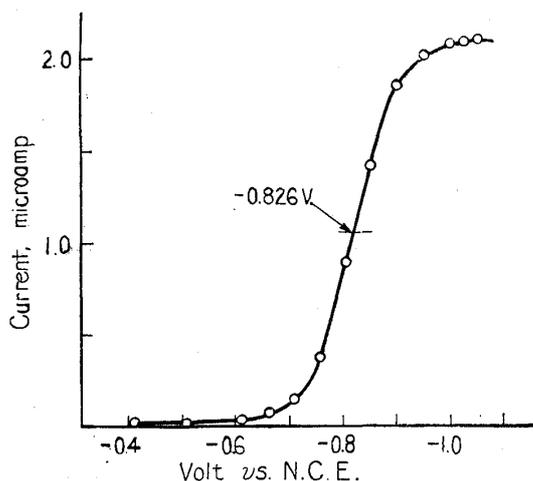
Fig. 1. Reduction wave of Ti^{4+}-ion in 0.065 N H_2SO_4.
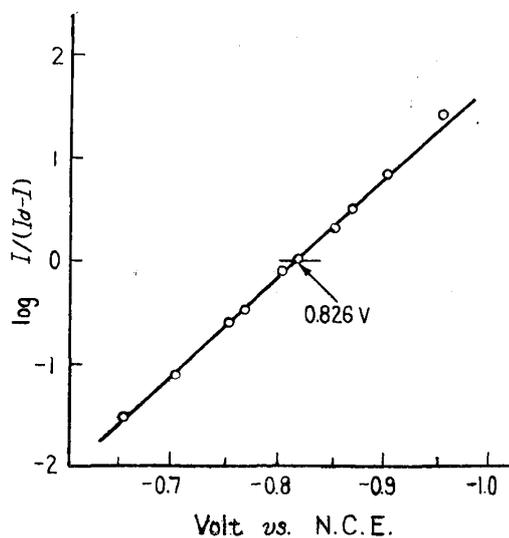
Fig. 2. Relation between $\log I/(I_d - I)$ and V.

latter gives a straight line, from the inclination of which the value of α can be calculated by using Eq. (I–17). It is found out that the limiting current of the reduction wave is proportional to the concentration of titanic ion and that the half-wave potential is constant independent of the concentration of titanic ion over the concentration range

from 0.125×10^{-3} to 1.000×10^{-3} mole per liter. All experimental results are summarized in Table 1. The good agreement between the experimental results and the results of the theoretical consideration will suggest that the basic assumptions in the present theory are essentially correct.

Table 1.

| Ti^{4+}-Concn., mole/l	I_d, amp	$V_{1/2}$, volt vs. N.C.E.	K_o, amp/mole/l	α
1.000×10^{-3}	2.04×10^{-6}	-0.828	2.10×10^{-8}	$0.58 \sim 0.56$
$\prime\prime$ $\prime\prime$	$2.02 \times$ $\prime\prime$	-0.827	$\prime\prime$ $\prime\prime$	$0.57 \sim 0.56$
$0.500 \times$ $\prime\prime$	9.95×10^{-7}	-0.826	$2.06 \times$ $\prime\prime$	0.62
$0.250 \times$ $\prime\prime$	$5.07 \times$ $\prime\prime$	-0.829	$2.11 \times$ $\prime\prime$	0.61
$0.125 \times$ $\prime\prime$	$2.44 \times$ $\prime\prime$	-0.820	$2.03 \times$ $\prime\prime$	0.67

It should be noted that the half-wave potential of the reduction wave changes with the change of concentration of indifferent electrolytes, such as sulfuric acid, hydrochloric acid, ammonium sulfate and potassium nitrate, in the solution. The experimental results are, though qualitatively, in accord with the change of the half-wave potential which is calculated on the consideration that the activity-coefficient of titanic ion changes with the change of the ionic strength of the solution. However, from the present study it can not be decided whether this change of the half-wave potential is only due to the change of the activity-coefficient of the titanic ion or not. It is probable that ζ-potential at the surface of the electrode would play an important role as discussed by A. Frumkin[10] in such an electrode process.

v. A Note on the " Reversibility " in Polarography

In polarography, such a wave, which can be interpreted by the equation derived by Heyrovsky and Ilkovic[3], has been called "reversible", and all the other waves, which show deviations from their equation, have been called "irreversible". This terminology comes from the fact that Heyrovsky-Ilkovic's equation is derived from the Nernst equation which rests on the assumption of the thermodynamic "reversibility". The process at the polarographic electrode, however, is not a thermodynamic one, but is a kinetic one as mentioned in the previous section. It has been shown in the kinetic treatment of the c-v curve that the Nernst equation can be applied to the electrode potential of the DME as an approximation if the conditions of the diffusion-controlled case prevail in the overall electrode process. This result is rather self-evident, because under such conditions the overall electrode process is in a state of partial equilibrium. Even in this case, however, the overall process might not be a "reversible process", because the electron-

transfer process is accompanied by diffusion processes which are not reversible, although the electron-transfer process itself represented by Eq. (I-1) might be a kind of "reversible changes" in a sense of Guggenheim[11].

In the chemical kinetics, the term "reversible" is used, as in the "reversible reaction", to distinguish a process which might reach a state of equilibrium from such processes which might go to apparent completion in one direction. But as H. S. Taylor has pointed out in his text-book on physical chemistry, "there is no reason to believe that any reaction is not reversible, at least for the purpose of theoretical considerations"[12]. Therefore, it should be noted that the term "reversible" in the chemical kinetics does not have any absolute meaning as in the thermodynamics.

Because of these reasons, the use of the words "reversible" and "irreversible" in polarography can not get rid of the lack of strictness and clarity. In this respect, the classification of the polarographic waves into "diffusion-controlled" and "activation-controlled" cases according to the rate-determining step of the overall process under a particular condition is undoubtedly in a preferable position.

In the following schematical table, the relation between $\kappa_1 E_1$, $\kappa_2 E_2$ and K_o' in the various potential regions is shown under the condition that there is no reductant in the bulk of solution. The correspondence between the type of the electrode process and the actual polarographic c-v curve can be seen from this table, e.g., the electrode process at the potential where $\kappa_1 E_1 \cong \kappa_2 E_2$ corresponds to the region of the reduction wave in the diffusion-controlled case, but such an electrode process corresponds to the region of the residual current in the activation-controlled case.

Table 2.

Type of electrode process	Diffusion-controlled case	Activation-controlled case
$\kappa_1 E_1 > \kappa_2 E_2$ Reduction	$\kappa_1 E_1 \gg K_o'$ Region of diffusion current	$\kappa_1 E_1 \gg K_o'$ Region of diffusion current
		$\kappa_1 E_1 \cong K_o'$ Rigion of reduction wave
$\kappa_1 E_1 \cong \kappa_2 E_2$ Equilibrium	$\kappa_1 E_1 \gg K_o'$ Region of reduction wave	$\kappa_1 E_1 \ll K_o'$ Region of residual current
$\kappa_1 E_1 < \kappa_2 E_2$ Oxidation	$\kappa_1 E_1 \ll K_o'$ Region of residual current	

Electrode potential → more negative

2. Oxidation-Reduction of Complex Metal Ions[13]

i. Derivation of General Formulae

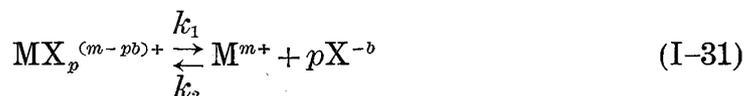There are various possible types of the electrode reactions which involve complex metal ions, but in the present treatment only the reaction which consists of the oxidation and reduction from one ionic oxidation state to the other, is taken up as an example.

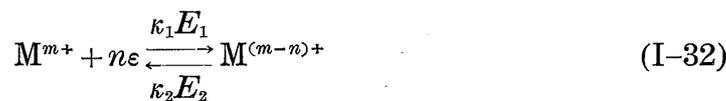The redox reaction of a complex metal ion may be represented by

$$MX_p^{(m-pb)+} + n\varepsilon \underset{\leftarrow}{\rightarrow} MX_q^{(m-pb-n)+} + (p-q)X^{-b} \tag{I-30}$$
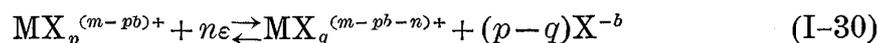
where X^{-b} is the complex-forming substance. For simplicity, the discussion is restricted to the case in which the above reaction occurs through the following steps:
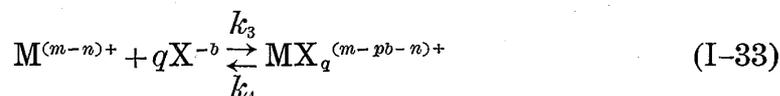
Decomposition of the complex ion,

$$MX_p^{(m-pb)+} \underset{k_2}{\overset{k_1}{\rightleftarrows}} M^{m+} + pX^{-b} \tag{I-31}$$

Redox reaction,

$$M^{m+} + n\varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftarrows}} M^{(m-n)+} \tag{I-32}$$

Formation of the complex ion (reduced form),

$$M^{(m-n)+} + qX^{-b} \underset{k_4}{\overset{k_3}{\rightleftarrows}} MX_q^{(m-pb-n)+} \tag{I-33}$$

M^{m+} and $M^{(m-n)+}$ are the simple (or hydrated) metal ions and k_1, k_2, k_3 and k_4 represent the rate constants for each process, respectively. The terms, $\kappa_1 E_1$, $\kappa_2 E_2$, ΔF_1, ΔF_2, V and α employed in the following treatment have the same meanings as described in the previous section.

By taking into consideration the existence of diffusion processes of the concerning substances and by assuming the condition of the stationary state in the overall process, the current flowing can be written as follows:

$$I = nFK_{CO}([C_{CO}]^\circ - [C_{CO}]) = nF\frac{K_{CO}}{f_{CO}}([A_{CO}]^\circ - [A_{CO}])$$

$$= nFK_{CO}'([A_{CO}]^\circ - [A_{CO}]), \qquad K_{CO}' \equiv K_{CO}/f_{CO} \tag{I-34}$$

$$I = n\sigma F(k_1[A_{CO}] - k_2[A_o][A_X]^p) = nF(k_1'[A_{CO}] - k_2'[A_o]) \tag{I-35}$$

$$k_1' \equiv \sigma k_1, \qquad k_2' \equiv \sigma k_2[A_X]^p$$

$$I = nF(\kappa_1 E_1[A_o] - \kappa_2 E_2[A_R]) \tag{I-36}$$

$$I = n\sigma F(k_3[A_R][A_X]^q - k_4[A_{CR}]) = nF(k_3'[A_R] - k_4'[A_{CR}]) \tag{I-37}$$

$$k_3' \equiv \sigma k_3[A_X]^q, \qquad k_4' \equiv \sigma k_4$$

$$I=nFK_{CR}([C_{CR}]-[C_{CR}]^\circ)=nF\frac{K_{CR}}{f_{CR}}([A_{CR}]-[A_{CR}]^\circ)$$

$$=nFK'_{CR}([A_{CR}]-[A_{CR}]^\circ), \qquad K'_{CR}\equiv K_{CR}/f_{CR} \tag{I-38}$$

$$I=nF\frac{K_x}{p-q}([C_x]-[C_x]^\circ)=nF\frac{K_x}{f_x(p-q)}([A_x]-[A_x]^\circ)$$

$$=nF\frac{K_x'}{p-q}([A_x]-[A_x]^\circ), \qquad K_x'\equiv K_x/f_x \tag{I-39}$$

In these equations:

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

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

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

$[A]$: the activities for each of the corresponding terms.

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

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

f: the activity-coefficients for each of the corresponding terms.

σ: the constant concerning the nature of the electrode.

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

$$I=nF\frac{K'_{CO}K'_{CR}(k'_1k'_3\kappa_1E_1[A_{CO}]^\circ-k'_2k'_4\kappa_2E_2[A_{CR}]^\circ)}{k'_2k'_3K'_{CO}K'_{CR}+\kappa_1E_1k'_3K'_{CR}(k'_1+K'_{CO})+\kappa_2E_2k'_2{}'K'_{CO}(k'_4+K'_{CR})} \tag{I-40}$$

Dividing the numerator and denominator of the right-hand side of Eq. (I-40) by $K'_{CO}K'_{CR}k'_1k'_3\kappa_1E_1$, Eq. (I-40) can be reduced to,

$$I=nF\frac{[A_{CO}]^\circ-[E][A_{CR}]^\circ}{\dfrac{1}{[\kappa_1E_1]}+\left(\dfrac{1}{K'_{CO}}+\dfrac{1}{k'_1}\right)+[E]\left(\dfrac{1}{K'_{CR}}+\dfrac{1}{k'_4}\right)} \tag{I-41}$$

$$=nF\frac{\dfrac{1}{[E]}[A_{CO}]^\circ-[A_{CR}]^\circ}{\dfrac{1}{[\kappa_2E_2]}+\left(\dfrac{1}{K'_{CR}}+\dfrac{1}{k'_4}\right)+\dfrac{1}{[E]}\left(\dfrac{1}{K'_{CO}}+\dfrac{1}{k'_1}\right)} \tag{I-41'}$$

in which,

$$[\kappa_1E_1]\equiv\frac{k'_1\kappa_1E_1}{k'_2}, \qquad [\kappa_2E_2]\equiv\frac{k'_4\kappa_2E_2}{k'_3}, \qquad [E]\equiv\frac{[\kappa_2E_2]}{[\kappa_1E_1]}$$

$[\kappa_1E_1]$ and $[\kappa_2E_2]$ can be regarded as to represent the overall rate constants of the reduction and oxidation processes at the electrode surface represented by Eq. (I-30). It is mentioned here that if the solution is bufferized with respect to the complex-forming substance,

the quantity $[A_x]$ is equal to $[A_x]^\circ$ in these equations. Eqs. (I-41) and (I-41') are the general formulae for the polarographic wave due to the redox reaction of the complex metal ions under the mechanism described above.

ii. Formulae of the C-V Curve obtained when the Decomposition Rate of Complex Ions is Very Rapid

When the rate constant of the decomposition of the complex ion at the electrode surface is much larger than that of the diffusion process, i.e., $K'_{CO} \ll k'_1$ and $K'_{CR} \ll k'_4$, Eqs. (I-41) and (I-41') are reduced to

$$I = nF \frac{[A_{CO}]^\circ - [E][A_{CR}]^\circ}{\dfrac{1}{[\kappa_1 E_1]} + \dfrac{1}{K'_{CO}} + [E]\dfrac{1}{K'_{CR}}} \qquad (I-42)$$

$$= nF \frac{\dfrac{1}{[E]}[A_{CO}]^\circ - [A_{CR}]^\circ}{\dfrac{1}{[\kappa_2 E_2]} + \dfrac{1}{K'_{CR}} + \dfrac{1}{[E]}\dfrac{1}{K'_{CO}}} \qquad (I-42')$$

These equations are quite similar to Eqs. (I-7) and (I-7') in their forms, so that a similar treatment to the redox reaction of a simple metal ion can be carried out.

Diffusion-controlled Case.

This is a case in which the conditions, $[\kappa_1 E_1] \gg K'_{CO}$ and $[\kappa_1 E_1] \gg K'_{CR}$, are maintained in the potential region where $[\kappa_1 E_1] \cong [\kappa_2 E_2]$. Under these conditions the relation between the current and the electrode potential takes the form :

$$[E] = \frac{[A_{CO}]^\circ - \dfrac{I}{nFK'_{CO}}}{\dfrac{I}{nFK'_{CR}} + [A_{CR}]^\circ} \qquad (I-43)$$

in the potential region where $[\kappa_1 E_1] \cong [\kappa_2 E_2]$.

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

$$I = nFK'_{CO}[A_{CO}]^\circ = nFK_{CO}[C_{CO}]^\circ \equiv (I_d)_{CO} \qquad (I-44)$$

while, when $[\kappa_1 E_1]$ is much smaller than $[\kappa_2 E_2]$,

$$I = -nFK'_{CR}[A_{CR}]^\circ = -nFK_{CR}[C_{CR}]^\circ \equiv (I_d)_{CR} \qquad (I-45)$$

These relations represent the limiting currents which are controlled by the diffusion process.

From Eqs. (I-43), (I-44) and (I-45) the following equation is derived :

$$[E] = \frac{K'_{CR}}{K'_{CO}} \frac{(I_d)_{CO} - I}{I - (I_d)_{CR}} \tag{I-46}$$

This is quite the same as the formula which has been obtained for the reversible wave based on the Nernst equation.

The detailed discussion on the half-wave potential and the other properties of such a wave has been set down by J. J. Lingane[14].

Activation-controlled Case.

This is a case in which the conditions, $[\kappa_1 E_1] \ll K'_{CO}$ and $[\kappa_1 E_1] \ll K'_{CR}$, are maintained in the potential region where $[\kappa_1 E_1] \cong [\kappa_2 E_2]$. The theoretical treatment can be made in the same way as in the activation-controlled case of a simple metal ion.

Part A. $[\kappa_1 E_1] \cong [\kappa_2 E_2]$ ....In this potential region, Eq. (I-42) is reduced to

$$I = nF\{[\kappa_1 E_1][A_{CO}]^\circ - [\kappa_2 E_2][A_{CR}]^\circ\} \tag{I-47}$$

from which the condition for the point where the current is zero is obtained as

$$[E]_{I=0} = \frac{[A_{CO}]^\circ}{[A_{CR}]^\circ} \tag{I-48}$$

Part B. $[\kappa_1 E_1] > [\kappa_2 E_2]$

(a) $[\kappa_1 E_1] \cong K'_{CO}$ ....Here, the equation which represents the c-v curve is

$$[\kappa_1 E_1] = \frac{K'_{CO} I}{nF K'_{CO}[A_{CO}]^\circ - I} \tag{I-49}$$

From this relation, it is obvious that the properties of the wave in this region are independent of the oxidation process.

(b) $[\kappa_1 E_1] \gg K'_{CO}$ ....In this case, the same equation as Eq. (I-44) is obtained for the limiting current due to the reduction process.

By introducing the condition for the limiting current into Eq. (I-49), the following relations, which represent the c-v curve due to the reduction process, are obtained :

$$[\kappa_1 E_1] = K'_{CO} \frac{I}{(I_d)_{CO} - I} \tag{I-50}$$

or

$$V = \frac{RT}{n\alpha F}\left(\ln \frac{skT}{h} + \ln \Gamma - \ln K'_{CO}\right) - p\frac{RT}{n\alpha F}\ln[A_x]$$

$$- \frac{RT}{n\alpha F}\ln\frac{I}{(I_d)_{CO} - I} - \frac{\Delta F_1}{n\alpha F} \tag{I-51}$$

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

For the half-wave potential, the relations

$$[\kappa_1 E_1]_{\frac{(I_d)_{CO}}{2}} = K'_{CO} \qquad\qquad \text{(I-52)}$$

and

$$[V]_{\frac{(I_d)_{CO}}{2}} = \frac{RT}{n\alpha F}\left(\ln \frac{skT}{h} + \ln \Gamma - \ln K'_{CO}\right) - p\frac{RT}{n\alpha F}\ln [A_x] - \frac{\Delta F_1}{n\alpha F}$$

$$\text{(I-53)}$$

are obtained. If α, $[A_x]$ and the ionic strength of the solution are constant, the half-wave potential is a characteristic constant of each complex ion and is independent of the activity of this ion. This result is quite the same as in the case of a simple metal ion.

From Eq. (I-53) it can be said that the relation between $[V]_{\frac{(I_d)_{CO}}{2}}$ and the logarithm of activity of the complex-forming substance is a straight line, the tangent of which is $p \times 0.059/n\alpha$ volt at 25°C. Consequently, the coordination number of this complex ion, p, will be calculated by determining the tangent of this relation and the values of n and α. It is necessary to notice that if the overall electrode process is diffusion-controlled the tangent of the above relation is $(p-q) \times 0.059/n$ volt, while the tangent of the activation-controlled one is $p \times 0.059/n\alpha$ volt and is independent of q.

Eq. (I-50) shows that the relation between $\log I/(I_i - I)$ and V is a straight line whose tangent is $0.059/n\alpha$ volt at 25°C, provided ΔF_1, p, α and $[A_x]$ remain constant. The value of α can be obtained from the measurement of the tangent of this log-plot, if the value of n is known.

Quite the same discussion as described above can be applied to the case where $[\kappa_1 E_1] < [\kappa_2 E_2]$ (Part C), and it can be shown that this part corresponds to the oxidation wave.

All considerations on the activation-controlled case mentioned above are made under the assumptions that (i) $K'_{CO} \ll k'_1$ and $K'_{CR} \ll k'_4$, and (ii) $[\kappa_1 E_1] \ll K'_{CO}$ and $[\kappa_1 E_1] \ll K'_{CR}$ when $[\kappa_1 E_1] \cong [\kappa_2 E_2]$. From the first assumption, it is expected that the limiting current, being verified to be the same as the diffusion current by the above theoretical treatment, is represented by the Ilkovic equation. The second assumption means that the overall rate constant of the reduction process is much smaller than that of the diffusion of the ion at the electrode potential where the rate constants of the forward and reverse processes are nearly the same. The overall rate constant of the reduction process, $[\kappa_1 E_1]$, is accelerated by k'_1 and $\kappa_1 E_1$ but retarded by k'_2, which is clearly shown by the relation, $[\kappa_1 E_1] = k'_1 \kappa_1 E_1 / k'_2$. If the rate constant of the reaction corresponding to the transfer of electrons between the ion and electrode, $\kappa_1 E_1$, is assumed to be very rapid, k'_2 must be much larger than k'_1 and $\kappa_1 E_1$ in order to

fulfil the requirement of the second assumption, because k_1' is much larger than K_{co}' according to the first assumption. This condition will be established when the relating complex ion is very stable in the solution, *i.e.*, Γ is very small, and it can be said that the more stable the complex ion, the larger the irreversibility is, as far as the electrode process proceeds according to the mechanism mentioned above.

iii. *Formulae of the C-V Curve obtained when the Decomposition Rate is Slower than that of the Diffusion*

Let us consider the case, in which the conditions, $K_{co}' \gg k_1'$ and $K_{cR}' \gg k_4'$, are maintained. Eqs. (I-41) and (I-41') can be then reduced to

$$I = nF \frac{[A_{co}]^\circ - [E][A_{cR}]^\circ}{\dfrac{1}{[k_1 E_1]} + \dfrac{1}{k_1'} + [E]\dfrac{1}{k_4'}} \qquad \text{(I-54)}$$

$$= nF \frac{\dfrac{1}{[E]}[A_{co}]^\circ - [A_{cR}]^\circ}{\dfrac{1}{[k_2 E_2]} + \dfrac{1}{k_4'} + \dfrac{1}{[E]}\dfrac{1}{k_1'}} \qquad \text{(I-54')}$$

These equations are the same as Eqs. (I-42) and (I-42') except that the constants, K_{co}' and K_{cR}', in the latters are replaced by k_1' and k_4'. Therefore, a completely analogous consideration to the previous section can be made in the present case, providing both of k_1' and k_4' are the constants independent of the electrode potential.

Decomposition-controlled Case.

This case is defined as that which corresponds to the diffusion-controlled case in the previous section. The equation for the c-v curve in the potential region, where $[k_1 E_1] \cong [k_2 E_2]$, is represented by

$$I = nF \frac{[A_{co}]^\circ - [E][A_{cR}]^\circ}{\dfrac{1}{k_1'} + [E]\dfrac{1}{k_4'}} \qquad \text{(I-55)}$$

and the limiting currents are

$$I = nF k_1'[A_{co}]^\circ \equiv (I_k)_{co} \qquad \text{(I-56)}$$

$$I = -nF k_4'[A_{cR}]^\circ \equiv (I_k)_{cR} \qquad \text{(I-57)}$$

for the reduction and oxidation waves, respectively.

Activation-controlled Case.

From Eqs. (I-47)-(I-53) the following relations can be obtained directly by introducing k_1' and k_4' in place of K_{co}' and K_{cR}'.

Part A. $[k_1 E_1] \cong [k_2 E_2]$

$$I = nF([\kappa_1 E_1][A_{CO}]^\circ - [\kappa_2 E_2][A_{CR}]^\circ)$$

This equation is the same as Eq. (I-47).

Part B. $[\kappa_1 E_1] > [\kappa_2 E_2]$

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

$$I = nF \frac{[A_{CO}]^\circ}{\dfrac{1}{k_1'} + \dfrac{1}{[\kappa_1 E_1]}} \qquad\qquad (I-58)$$

(b) $[\kappa_1 E_1] \gg k_1'$ ....In this case the limiting current, which is represented by Eq. (I-56), appears.

Part C. $[\kappa_1 E_1] < [\kappa_2 E_2]$ .... This part corresponds to the oxidation wave. The equations obtained will be omitted in the present treatment.

According to the results obtained above it is said that, when the rate constant of the decomposition process is much smaller than that of the diffusion, the limiting current is determined by the rate of the decomposition of the complex ion at the electrode surface and it is obviously smaller than the limiting current which is determined by the diffusion process. Such a limiting current determined by the kinetic term corresponds to the "kinetic current" mentioned by R. Brdicka and others[15].

iv. Experiments to the Theory—Reduction Wave of Nickel-thiocyanate Complex[16]

The results of the theoretical consideration on the redox reaction of a complex ion—especially, under the conditions of the activation-controlled case—have been applied to the analysis of the reduction wave of nickel-thiocyanate complex ion in the various media. In spite of the most complicated behaviours of the reduction wave of this complex ion, a possible mechanism on the reduction process at the DME has been suggested by such a treatment. This analysis is undoubtedly presenting an example how some properties of the so-called "irreversible" wave of a complex ion could be interpreted by the present method. The details of the results, however, are very complicated and are out of the scope of this paper.

3. Application of the Theory to Organic Substances— Reduction Wave of Pyruvic Acid[17]

The polarographic study on the pyruvic acid and phenylglyoxylic acid was carried out, at first, by O. H. Müller[18], and recently by R. Brdicka[15]. The latter has explained the appearance of the double-wave by introducing the conception of the "kinetic current". He assumed that, in the bulk of solution, the dissociated anions of these organic acids, A^-, and the corresponding undissociated molecules, HA, are kept

in the equilibrium according to the following equation,

$$A^- + H^+ \underset{k_4}{\overset{k_3}{\rightleftarrows}} HA \tag{I-59}$$

and that the undissociated molecules are reduced at a more positive potential than the dissociated anions. At the electrode surface, the undissociated molecule combines with the electrons giving the reduced ion, $R^=$, which reacts with the hydrogen ions getting the reduced molecule, RH_2, $i.e.$:

$$HA + 2\varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftarrows}} R^= \tag{I-60}$$

$$R^= + 2H^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} RH_2 \tag{I-61}$$

It is also assumed that the stationary state with respect to the undissociated molecule at the electrode surface is maintained by the diffusion process from the bulk of solution and by the recombination reaction at the electrode surface (the forward reaction of process (I-59)).

Using this assumption on the mechanism of the reduction process of pyruvic and phenylglyoxylic acids, the equations for the c-v curve of such a process will be derived first, and then the results obtained will be applied to the analysis of the change of the half-wave potential with the change of pH of the solution and to the calculation of the free energy of activation of process (I-60).

By the analogous method to the previous treatment, the relation between the current flowing and the electrode potential under the present conditions is derived as follows, provided the solution is well bufferized :

$$I = 2F \frac{[A_o]^\circ - [E][A_{RH_2}]^\circ}{\dfrac{1}{[\kappa_1 E_1]} + \left(\dfrac{1}{K_o'} + \dfrac{\rho}{k_3'}\right) + [E]\left(\dfrac{1}{K_R'} + \dfrac{1}{k_4'}\right)} \tag{I-62}$$

$$= 2F \frac{\dfrac{1}{[E]}[A_o]^\circ - [A_{RH_2}]^\circ}{\dfrac{1}{[\kappa_2 E_2]} + \left(\dfrac{1}{K_R'} + \dfrac{1}{k_4'}\right) + \dfrac{1}{[E]}\left(\dfrac{1}{K_o'} + \dfrac{\rho}{k_3'}\right)} \tag{I-62'}$$

$$[\kappa_1 E_1] \equiv \frac{k_3'}{k_3' + k_4'} \kappa_1 E_1 \,, \qquad [\kappa_2 E_2] \equiv \frac{k_2'}{k_1'} \kappa_2 E_2 \,, \qquad [E] \equiv \frac{[\kappa_2 E_2]}{[\kappa_1 E_1]} \tag{I-63}$$

$$\rho = \frac{I_k}{I}$$

$$I_k = 2F\sigma(k_3[A_{H^+}][A_A] - k_4[A_{HA}]) = 2F(k_3'[A_A] - k_4'[A_{HA}]) \tag{I-64}$$

$$k_3' \equiv \sigma k_3 [A_{H^+}] \,, \qquad k_4' \equiv \sigma k_4$$

$[A]^\circ, [A]$:   the activities of the corresponding substances represented by their subscripts in the bulk of solution and at the electrode surface.   The subscript " $_o$ " corresponds to the oxidized form.

$K' \equiv K/f$: K is a constant concerning the diffusion process and f is the activity-coefficient.

$k'_1 - k'_4$, $\kappa_1 E_1$, $\kappa_2 E_2$:   the terms concerning the rate constants of the corresponding processes.

σ :   the constant concerning the nature of the electrode.

Eqs. (I-62) and (I-62′) are quite analogous with those of the complex metal ion, Eqs. (I-41) and (I-41′).   The meaning of ρ in Eq. (I-64) will be discussed later.

Let us consider the special case in which the terms k'_2 and k'_3 are comparable with K'_o and K'_R in their magnitudes.   This case is subdivided into two cases, one of which corresponds to the activation-controlled one.   The condition for this case is that k'_2, k'_3, K'_o and K'_R are much larger than $[\kappa_1 E_1]$ and $[\kappa_2 E_2]$ at the potential region where $[\kappa_1 E_1] \cong [\kappa_2 E_2]$. Considering the various experimental results on pyruvic acid, the reduction process of this substance seems to proceed under the conditions of the activation-controlled, and the discussion will be limited only to this case.   By the same method as described before, the equations for the reduction wave can be obtained as follows:

Part A. $[\kappa_1 E_1] \cong [\kappa_2 E_2]$

$$I = 2F([\kappa_1 E_1][A_o]^\circ - [\kappa_2 E_2][A_{RH_2}]^\circ) \tag{I-65}$$

Part B. $[\kappa_1 E_1] > [\kappa_2 E_2]$
(a) $1/[\kappa_1 E_1] \cong 1/K'_o + \rho/k'_3$

$$I = 2F \frac{[A_o]^\circ}{\dfrac{1}{[\kappa_1 E_1]} + \left(\dfrac{1}{K'_o} + \dfrac{\rho}{k'_3} \right)} \tag{I-66}$$

(b) $1/[\kappa_1 E_1] \ll 1/K'_o + \rho/k'_3 \ldots$ In this case, the limiting current of the reduction wave is obtained as:

$$(I_l)_o = \frac{k'_3 (I_d)_o}{k'_3 + \rho K'_o} \tag{I-67}$$

Part C. $[\kappa_1 E_1] < [\kappa_2 E_2]$ .... This is the potential region for the oxidation wave, and all discussions on this part are omitted in this paper.

The limiting current is considered to be the sum of the term $(I_d)_{HA}$ due to the diffusion process of the undissociated molecule HA and the term I_k which is attributed to the recombination reaction (I-59), i.e.,

$$(I_l)_o = (I_d)_{HA} + I_k \tag{I-68}$$

By the definition of ρ, Eq. (I-64), the relation

$$\rho = \frac{I_k}{(I_l)_o} = \frac{(I_l)_o - (I_d)_{HA}}{(I_l)_o}$$

is derived. If $[A_{HA}]^\circ$ is the activity of the undissociated molecule in the bulk of solution, the term $(I_d)_{HA}$ can be written as,

$$(I_d)_{HA} = 2FK_o'[A_{HA}]^\circ$$

Taking into consideration that in the bulk of solution the dissociation equilibrium is maintained, ρ can be represented as below by means of the relations mentioned above:

$$\rho = \frac{(I_l)_o - (I_d)_o \dfrac{[A_{H^+}]}{[A_{H^+}] + \Gamma}}{(I_l)_o} \qquad (I\text{-}69)$$

$$(I_d)_o = 2FK_o'[A_o]^\circ$$

Γ means the dissociation constant of the molecule, HA, and is equal to k_4/k_3. When $(I_d)_o$, $(I_l)_o$, Γ and $[A_{H^+}]$ are known, the value of ρ can be calculated by Eq. (I-69). By introducing this equation into Eq. (I-67), the equation, which is quite the same as has been set down by R. Brdicka[15] for the kinetic current, can be derived.

Rate Constant of the Recombination Reaction.

From Eq. (I-67) k_3' is obtained as

$$k_3' = \sigma k_3 [A_{H^+}] = \frac{K_o' \rho (I_l)_o}{(I_d)_o - (I_l)_o} \qquad (I\text{-}70)$$

According to R. Brdicka, K. Wiesner[19] and J. Koutecky[15] the constant σ can be represented by the following relation:

$$\sigma = q \cdot \mu \cdot 10^{-3}{}^* \qquad (I\text{-}71)$$

$$\mu = \sqrt{\frac{D}{k_3 \Gamma}} \qquad (I\text{-}72)$$

where
  q: the surface area of the DME in cm².
  μ: the thickness of the reaction layer at the electrode surface in cm.
  D: the diffussion coefficient of the depolarizer.
From Eq. (I-72), the relation for k_3,

$$k_3 = \frac{(\mu k_3)^2 \Gamma}{D} \sec^{-1}(\text{mole}/l)^{-1} \qquad (I\text{-}73)$$

is obtained. Since the value of (μk_3) is calculated from Eqs. (I-70) and (I-71), the value of the rate constant, k_3, can be determined by Eq. (I-73) from the experimental results.

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  * In this case the unit of the concentration is mole per liter.

Relation between $\log I/((I_i)_o - I)$ *and* V, *and Half-wave Potential.*

Eq. (I–66) shows that the log-plot analysis should be a straight line whose tangent is $0.059/2\alpha$ volt at 25°C, if the value of α is constant.

By introducing the relation, $I = (I_i)_o/2$, for the current at the half-wave potential, Eq. (I–74) can be derived for the half-wave potential from Eq. (I–66) together with relation (I–63) and the definition of Γ, *i.e.*:

$$V_{1/2} = const - \frac{RT}{2\alpha F} \ln \frac{\sigma k_3([A_{H^+}] + \Gamma)}{\sigma k_3[A_{H^+}] + \rho K_o'}$$

$$const = \frac{RT}{2\alpha F}\left(\ln \frac{skT}{h} - \ln K_o' - \frac{\Delta F_1}{RT}\right)$$

(I–74)

Now, let us consider the relation between $V_{1/2}$ and pH of the solution. Representing the half-wave potentials corresponding to the hydrogen ion concentrations $[A_{H^+}]_a$ and $[A_{H^+}]_b$ by $(V_{1/2})_a$ and $(V_{1/2})_b$, respectively, the change of the half-wave potential with the change of pH can be represented by,

$$(V_{1/2})_a - (V_{1/2})_b = \Delta V_{1/2} = \frac{RT}{2\alpha F} \ln \frac{([A_{H^+}]_b + \Gamma)(\sigma k_3[A_{H^+}]_a + K_o'\rho_a)}{([A_{H^+}]_a + \Gamma)(\sigma k_3[A_{H^+}]_b + K_o'\rho_b)}$$

(I–75)

It is evident from Eqs. (I–74) and (I–75) that, when the value of pH is sufficiently large, the value of $V_{1/2}$ is independent of pH and reaches a constant value (Fig. 3). This fact is considered to be characteristic of the reduction wave obtained under the present conditions.

Calculation of the Change of the Half-wave Potential and the Value of ΔF_1.

The theoretical results derived above are applied to the experimental data on the reduction waves of pyruvic and phenylglyoxylic acids obtained by Brdicka[15]. The log-plots of these waves are straight lines and from the tangents of these lines the values of α are calculated to be 0.28 and 0.34–0.54 for pyruvic and phenylglyoxylic

Fig. 3. Relation of the half-wave potential and pH of the reduction wave of pyruvic acid: ○, the values calculated from Eq. (89); △, the experimental values obtained by R. Brdicka.

acids, respectively. Only the discussion on the reduction wave of pyruvic acid will be carried out in the following, because it is quite doubtful
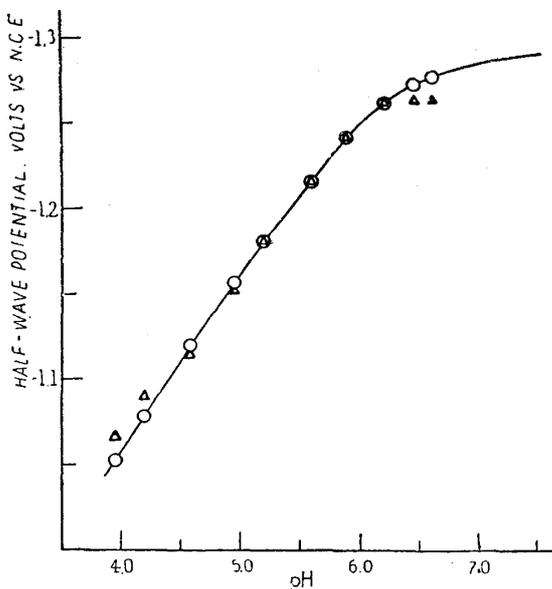
whether Eqs. (I–74) and (I–75) can be applicable or not to the present purpose, unless α remains constant.

After having been determined the value of α, the term μk_3 is calculated by Eqs. (I–70) and (I–71), the mean value of which is 3.2×10^3 over the range of pH 4.95–6.81. For the value of Γ, 4×10^{-3} is used and the other terms are calculated from Brdicka's data. By using these values, the change of $V_{1/2}$ with that of pH is calculated from Eq. (I–75), the results of which are compared with the experimental data obtained by Brdicka (Table 3 and Fig. 3). The half-wave potential of the wave at pH$=5.20$ (-1.180 volts) is used as the standard in the present calculation. Table 3 shows that the theoretical results are in good agreement with the experimental results.

Table 3.

pH	$\Delta V_{1/2}$ calc., mV	$\Delta V_{1/2}$ obs., mV	pH	$\Delta V_{1/2}$ calc., mV	$\Delta V_{1/2}$ obs., mV
3.95	127	114	5.59	-35	-35
4.19	102	90	5.91	-60	-60
4.58	61	65	6.24	-79	-80
4.95	24	28	6.48	-89	-80
5.20	—	—	6.64	-93	—

Introducing the vales of α, μk_3, ρ and others into Eq. (I–74), the value of the free energy of activation of the forward process of reaction (I–60), ΔF_1, can be calculated. In the case of pyruvic acid the results obtained over the range of pH 4.95–6.48 are shown in Table 4. The constancy of the value of ΔF_1 suggests that the theoretical treatment discussed in this section is essentially correct.

Table 4.

pH	$V_{1/2}$, volt	ΔF_1, kcal
4.95	-1.152	22.7
5.20	-1.180	22.7
5.59	-1.215	22.9
5.91	-1.240	22.9
6.24	-1.260	22.9
6.49	-1.260	22.7
		mean value 22.8

Part II. Mechanism of the Reduction Process of Hydrogen Ion[20]

The study of the reduction wave of hydrogen ion at the DME is not only very important in the field of polarography, but also it seems to be highly valuable from the general standpoint of the study of hydrogen overvoltage, because the DME has some advantages over the

usual stationary electrodes.   It is well known that at the DME a very good reproducibility can be obtained in the redox processes of many metal ions and organic substances because of its continuous renewal of the surface.   The use of the DME, therefore, makes it possible to ignore the historical effect of the electrode, and it can be expected that some obstacles in experiments, which appear in the use of the stationary electrodes, are eliminated.

The mechanism of the reduction process of hydrogen ion at the DME was mainly investigated by J. Tomes[21], J. Novak[22] and J. Heyrovsky[23] in 1937, and recently by J. Kuta[24].   The experimental results obtained by them, however, seem to be too complicated to be satisfactorily explained by the theory of Heyrovsky and Ilkovic[3] on the polarographic c-v curve.   As shown in the previous part, the basic assumption on the electrode potential made by Heyrovsky and Ilkovic in their derivation of the equation for the c-v curve can only be applicable to the electrode process which is diffusion-controlled.   It is quite doubtful whether the conditions of the diffusion-controlled case prevail or not in the reduction process of hydrogen ion at the DME.   Therefore, we could not go further into the mechanism of this reduction process as far as we stick on the theory of Heyrovsky and Ilkovic.

The great advances in the experimental technique and theoy of polarographic waves have been made during these ten years.   The use of the cathode-ray oscillograph[25] and the method of Kalousek[9] have made it possible to examine the so-called " reversibility "* of the electrode process.   A new concept of the polarographic limiting current including the " kinetic current " has been introduced by R. Brdicka and others[15], and the revised Ilkovic equation for the diffusion current has been derived by several investigators[26].   In collaboration with N. Tanaka, the present author had introduced a derivation of the equation for the c-v curve from the standpoint of the chemical kinetics, the details of which have been discussed in the previous part.   These facts might throw a new light on the analysis of the mechanism of the reduction process of hydrogen ion at the DME.

In the following sections, the theoretical consideration will be carried out first on the various possible mechanisms, and, then, the experimental properties of the reduction wave of hydrogen ion will be discussed in comparison with the theoretical results.
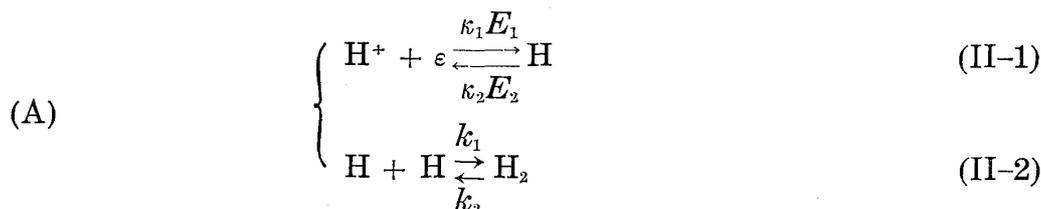
1.   General Remarks on the Hydrogen Overvoltage

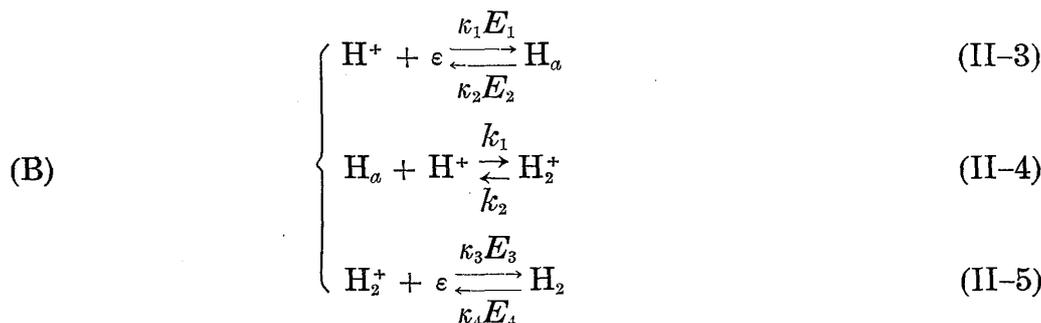Many theories have been presented to interpret theoretically Tafel's equation[27],

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* See Part I-1-v.

$$\eta = a - b \log i \ ,$$

where η is the overvoltage at the current density i, and a and b are the constants. These theories can be classified into three types—namely, (i) the slow discharge theory, (ii) the recombination theory, and (iii) the electrochemical theory—according to the rate-determining step. In the slow discharge theory[28] the rate-determining step is the discharge process of hydrogen ion (II-1), while in the recombination theory[29] the process of the formation of molecular hydrogen (II-2) is the slowest step.

(A)

$$H^+ + \varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftarrows}} H \tag{II-1}$$

$$H + H \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_2 \tag{II-2}$$

In the electrochemical theory of J. Horiuchi and others[30], the following reduction process is assumed:

(B)

$$H^+ + \varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftarrows}} H_a \tag{II-3}$$

$$H_a + H^+ \underset{k_2}{\overset{k_1}{\rightleftarrows}} H_2^+ \tag{II-4}$$

$$H_2^+ + \varepsilon \underset{\kappa_4 E_4}{\overset{\kappa_3 E_3}{\rightleftarrows}} H_2 \tag{II-5}$$

H_a: the hydrogen atom adsorbed on the electrode surface.

in which the rate-determining step is process (II-5). The mechanism which is assumed by Heyrovsky to interpret the polarographic c-v curve of hydrogen ion is similar to that of the electrochemical theory, but in this case "molarization" process (II-4) is the rate-determining step[23].

In general, the hydrogen atom which is produced, H or H_a, will disappear from the electrode surface by various processes, i.e., recombination process (II-2), molarization process (II-4), the diffusion process of H itself, and so on. As far as the reduction process is concerned, the problem which of these processes is predominant will be determined by the magnitudes of the forward rates of these processes. For example, if the rate constant of the forward process of (II-2) is larger than those of the diffusion process of the hydrogen atom from the electrode surface and the other processes, process (II-2) will be the predominant reaction to consume the hydrogen atom produced. On the other hand, if the diffusion process of the hydrogen atom is much faster than the rates of the other processes, the hydrogen atom will disappear from the electrode surface mainly by the diffusion of itself.

It is assumed throughout the following discussion that the overall electrode process is in a stationary state. It is to be mentioned here that the electrode potential is used in the present treatment instead of the overvoltage.

2. Derivation of the Equations for C-V Curve

i. Mechanism (A)

One Hydrogen Ion participates in Process (II-1).

Let us assume the electrode process as represented by (A). The rate constants, k_1E_1, k_2E_2, k_1 and k_2, have their usual meanings. This process is accompanied by the diffusion processes of the hydrogen ion and the molecular hydrogen produced between the electrode surface and the bulk of solution. By the same consideration discussed in the previous part, the current flowing can be represented as follows under the condition of stationary state:

$$I=FK_{H^+}([C_{H^+}]^\circ-[C_{H^+}])=FK'_{H^+}([A_{H^+}]^\circ-[A_{H^+}]) \tag{II-6}$$

$$K'_{H^+}\equiv K_{H^+}/f_{H^+}$$

$$I=2FK_{H_2}([C_{H_2}]-[C_{H_2}]^\circ)=2FK'_{H_2}([A_{H_2}]-[A_{H_2}]^\circ) \tag{II-7}$$

$$K'_{H_2}\equiv K_{H_2}/f_{H_2}$$

$$I=F(k_1E_1[A_{H^+}]-k_2E_2[A_H]) \tag{II-8}$$

$$I=2F(k'_1[A_H]^2-k'_2[A_{H_2}]) , \qquad k'_1\equiv\sigma k_1 , \qquad k'_2\equiv\sigma k_2 \tag{II-9}$$

where

$[C]^\circ, [C]$:　the concentrations of the substances represented by their subscripts in the bulk of solution and at the electrode surface, respectively.

$[A]^\circ, [A]$:　the activities of the substances represented by their subscripts in the bulk of solution and at the electrode surface, respectively.

$K'\equiv K/f$:　K is the constant concerning the diffusion process, and f the activity-coefficient.

σ :　the constant concerning the nature of the electrode.

We can neglect the existence of the migration current in the following treatment, because of the presence of the excess of supporting electrolyte in the polarographic studies.

From Eqs. (II-6), (II-7), (II-8) and (II-9), the general equation for the c-v curve due to the discharge of hydrogen ion under mechanism (A) can be expressed as,

$$I = F\kappa_1 E_1\left(\frac{FK'_{H^+}[A_{H^+}]^\circ - I}{FK'_{H^+}}\right) - F\kappa_2 E_2\left(\frac{\Gamma}{2FK'_{H_2}}\left(2FK'_{H_2}[A_{H_2}]^\circ + \frac{K'_{H_2}}{k'_2}I + I\right)\right)^{1/2}$$

$$\Gamma \equiv k_2/k_1 \tag{II-10}$$

Diffusion-controlled Case.... The diffusion-controlled case is defined as the case, in which $\kappa_1 E_1$ and $\kappa_2 E_2 \Gamma^{1/2}$ are much larger than K'_{H^+}, K'_{H_2}, or k'_2 at the electrode potential where $\kappa_1 E_1 \cong \kappa_2 E_2 \Gamma^{1/2}$. Under this condition, Eq. (II-10) can be reduced to

$$\left(\frac{\kappa_2 E_2}{\kappa_1 E_1}\right)^2 = \frac{2}{F}\frac{K'_{H_2}}{(K'_{H^+})^2}\frac{1}{\Gamma}\frac{(FK'_{H^+}[A_{H^+}]^\circ - I)^2}{2FK'_{H_2}[A_{H_2}]^\circ + \frac{K'_{H_2}}{k'_2}I + I} \tag{II-11}$$

When the activity of the hydrogen molecule in the bulk of solution is equal to zero, the following equation for the reduction wave can be obtained from Eq. (II-11), by introducing relation (II-13) for the limiting current, *i.e.*:

$$V = const - \frac{RT}{F}\ln\frac{I}{(I_l - I)^2} \tag{II-12}$$

$$I_l = FK'_{H^+}[A_{H^+}]^\circ \tag{II-13}$$

From this equation it is shown that the relation between V and $\log I/(I_l - I)^2$ is linear and that the condition for the half-wave potential is represented by

$$V_{1/2} = const' + \frac{RT}{F}\ln I_l \tag{II-14}$$

This equation means that the half-wave potential is not independent of the limiting current but it shifts to a more positive one as the limiting current increases.

Activation-controlled Case.... In this case it is assumed that $\kappa_1 E_1$ is much smaller than K'_{H^+} at the electrode potential where $\kappa_1 E_1 \cong \kappa_2 E_2 \Gamma^{1/2}$. In this potential region the current flowing is negligibly small. When the electrode potential becomes more negative, the current due to the reduction process appears. Under this condition, the second term of the right-hand side of Eq. (II-10) can be neglected in comparison with the first term and the reduction current can be represented by

$$I = F\kappa_1 E_1\frac{FK'_{H^+}[A_{H^+}]^\circ - I}{FK'_{H^+}} \tag{II-15}$$

$$I_l = FK'_{H^+}[A_{H^+}]^\circ$$

This relation is quite the same as that for the reduction of a simple metal ion in the activation-controlled case, the characteristics of which have been discussed in the previous part.

Two Hydrogen Ions participate in Process (II–1).

If we assume that each of two hydrogen ions takes an electron simultaneously and the hydrogen atoms thus produced combine with each other to form a hydrogen molecule at the electrode surface, the following equation for the discharge reaction should be used instead of process (II–1), *i.e.*:

$$2H^+ + 2\varepsilon \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftharpoons}} 2H \tag{II-1'}$$

According to this process the current flowing is represented by

$$I = 2F(\kappa_1 E_1 [A_{H^+}]^2 - \kappa_2 E_2 [A_H]^2) \tag{II-16}$$

Using Eq. (II–16) instead of Eq. (II–8), the general equation for the c–v curve can be obtained as:

$$I = 2F\kappa_1 E_1 \left(\frac{FK'_{H^+}[A_{H^+}]^\circ - I}{FK'_{H^+}} \right)^2 - 2F\kappa_2 E_2 \left(\frac{\varGamma}{2FK'_{H_2}} \left(2FK'_{H_2}[A_{H_2}]^\circ + \frac{K'_{H_2}}{k'_2} I + I \right) \right) \tag{II-17}$$

*Diffusion-controlled Case....*The results obtained in this case are quite the same as Eqs. (II–12), (II–13) and (II–14).

*Activation-controlled Case....*In this case the following relation for the reduction wave is derived from Eq. (II–17):

$$V = const - \frac{RT}{\alpha F} \ln \frac{I}{(I_i - I)^2} \tag{II-18}$$

$$I_i = FK'_{H^+}[A_{H^+}]^\circ$$

This relation shows that the half-wave potential becomes more positive as I_i increases.

ii. Electrochemical Mechanism

According to the electrochemical theory, the reduction mechanism of hydrogen ion is represented by Process (B). In this case, besides Eqs. (II–6) and (II–7) due to the diffusion processes, the current flowing can be written as follows:

$$I = F(\kappa_1 E_1 [A_{H^+}] - \kappa_2 E_2 [A_{Ha}]) \tag{II-19}$$

$$I = F(k'_1 [A_{Ha}][A_{H^+}] - k'_2 [A_{H_2}^+]) \tag{II-20}$$

$$k'_1 \equiv \sigma k_1, \quad k'_2 \equiv \sigma k_2$$

$$I = F(\kappa_3 E_3 [A_{H_2}^+] - \kappa_4 E_4 [A_{H_2}]) \tag{II-21}$$

$$\kappa_3 E_3 \equiv s \frac{kT}{h} e^{-\varDelta F_3/RT} e^{-\beta VF/RT}$$

$$\kappa_4 E_4 \equiv s \frac{kT}{h} e^{-\varDelta F_4/RT} e^{(1-\beta)VF/RT}$$

ΔF_3 and ΔF_4 are the free energies of activation of the forward and reverse reactions of process (II-5), respectively, and β has a similar meaning to α.

Rate-determining Step is Process (II-5).

If we assume that process (II-5) is the slowest step of processes (II-3), (II-4) and (II-5) in the potential region where the reduction wave appears, Eq. (II-22) for the c-v curve can be derived from Eqs. (II-6), (II-7), (II-19), (II-20) and (II-21):

$$I = F\left\{ \kappa_3 E_3 \frac{k_1' \kappa_1 E_1[(FK_{H^+}'[A_{H^+}]^\circ - I)^2 - K_{H^+}' I(FK_{H^+}'[A_{H^+}]^\circ - I)] - F(K_{H^+}')^2 \kappa_2 E_2 I}{F^2 k_2'(K_{H^+}')^2 \kappa_2 E_2} \right.$$
$$\left. - \kappa_4 E_4 \frac{2FK_{H_2}'[A_{H_2}]^\circ + I}{2FK_{H_2}'} \right\} \qquad \text{(II-22)}$$

By taking into account the condition of the activation-controlled case, the second term of the right-hand side of Eq. (II-22) can be neglected in the potential region of the reduction wave, because $\kappa_4 E_4 \simeq 0$ under this condition, and Eq. (II-22) can be reduced to Eq. (II-23):

$$I = F' \kappa_3 E_3 \frac{\dfrac{1}{(K_{H^+}')^2}[(FK_{H^+}'[A_{H^+}']^\circ - I)(FK_{H^+}'[A_{H^+}]^\circ - I - K_{H^+}' I)] - F \dfrac{1}{k_1'} \dfrac{\kappa_2 E_2}{\kappa_1 E_1} I}{F^2 \dfrac{k_2'}{k_1'} \dfrac{\kappa_2 E_2}{\kappa_1 E_1}}$$

$$\text{(II-23)}$$

Furthermore, it seems reasonable to assume that $\kappa_2 E_2/\kappa_1 E_1$ is very small in this potential region and that I is much larger than $K_{H^+}' I$. By assuming these facts Eq. (II-23) can be simplified as,

$$I = \kappa_3 E_3 \frac{1}{(K_{H^+}')^2} \frac{(FK_{H^+}'[A_{H^+}]^\circ - I)^2}{F\Gamma \dfrac{\kappa_2 E_2}{\kappa_1 E_1}} \qquad \text{(II-24)}$$

When the electrode potential is sufficiently negative, the limiting current, which is represented by Eq. (II-13), appears. From these equations the following equations for the c-v curve and the half-wave potential are derived, *i.e.*:

$$V = const - \frac{RT}{(1+\beta)F} \ln \frac{I}{(I_l - I)^2} \qquad \text{(II-25)}$$

and

$$V_{1/2} = const' + \frac{RT}{(1+\beta)F} \ln I_l \qquad \text{(II-26)}$$

These results are qualitatively similar to those obtained from Eqs. (II-12) and (II-14).

Rate-determining Step is Process (II-3).

Let us consider the case in which the rate constant of the reverse

reaction of process (II-3), $\kappa_2 E_2$, is negligibly small in comparison with that of the forward reaction, $\kappa_1 E_1$, in the potential region of the reduction wave, and that the rate constants of the forward reactions of processes (II-4) and (II-5) are sufficiently large. In this case the adsorbed hydrogen atom, H_a, produced in process (II-3) will instantaneously react with H^+ and an electron to give a molecular hydrogen. Under this condition the reduction current can be represented by the equation,

$$I = \kappa_1 E_1 \frac{I_l - I}{K'_{H^+}}$$

$$I_l = F K'_{H^+} [A_{H^+}]^\circ$$

This result is quite the same as that of the reduction of a simple metal ion in the activation-controlled case. As far as the reduction process is concerned, processes (II-4) and (II-5) do not play any role in the present case, but, if the oxidation process of H_2 is considered, these processes have an important effect on the c-v curve.

iii. Slow Discharge Mechanism of the Adsorbed Hydrogen Ion

Let us assume that only the hydrogen ions adsorbed on the electrode surface can be neutralized. This assumption seems plausible because it has been pointed out by J. Weiss that only H_3O^+ ion on or very near to the surface of the electrode can discharge[31]. The structure of the double layer near the electrode is considered to consist of two energy barriers, one of which is between the solution side, S, and the adsorbed state, A, and the other is between the adsorbed state and the electrode side, E (Fig. 4).

As mentioned before, there may be various processes which will take place after the neutralization of hydrogen ion, e.g., the recombination of hydrogen atoms, the combination reaction of hydrogen atom and hydrogen ion, etc. However, if it is assumed that the rate constant of the oxidation process, i.e., the process from E to A, is negligibly small in comparison with that of the process from A to E in the potential

Fig. 4. The energy barrier between the electrode and the solution.

region of the reduction wave, the equation for the reduction wave is not influenced by the processes which follow the neutralization reaction. For convenience, let us call this mechanism "the slow discharge mechanism of the adsorbed hydrogen ion".

Under these conditions the overall electrode process of the discharge of hydrogen ion is represented as follows:
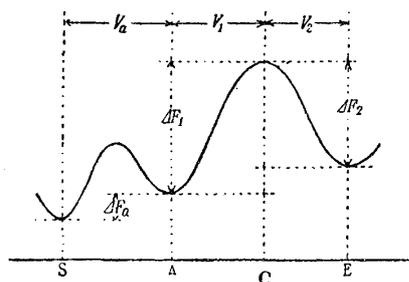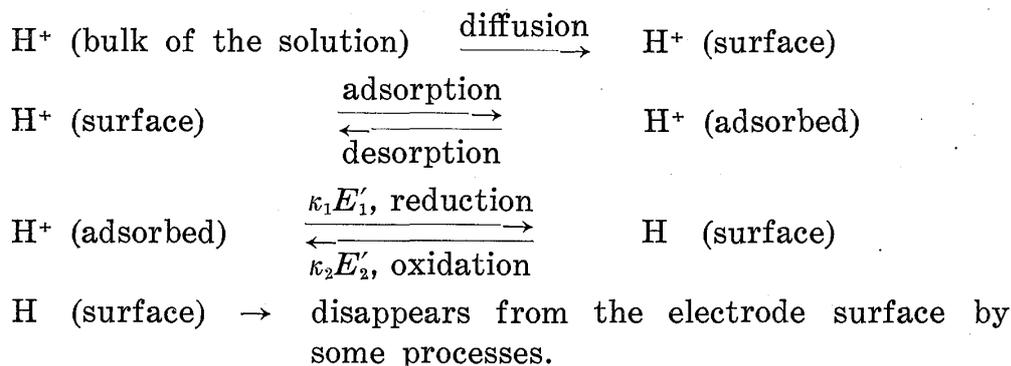
H$^+$ (bulk of the solution) $\xrightarrow{\text{diffusion}}$ H$^+$ (surface)

H$^+$ (surface) $\underset{\text{desorption}}{\overset{\text{adsorption}}{\rightleftarrows}}$ H$^+$ (adsorbed)

H$^+$ (adsorbed) $\underset{\kappa_2 E'_2,\ \text{oxidation}}{\overset{\kappa_1 E'_1,\ \text{reduction}}{\rightleftarrows}}$ H (surface)

H (surface) $\rightarrow$ disappears from the electrode surface by some processes.

According to these processes the current flowing can be written by the next equations:

$$I = FK'_{H^+}([A_{H^+}]^{\circ} - [A_{H^+}]) , \quad K'_{H^+} \equiv K_{H^+}/f_{H^+} \tag{II-26}$$

$$I = F(\kappa_1 E'_1[A_{H_a^+}] - \kappa_2 E'_2[A_H]) \tag{II-27}$$

$$\kappa_1 E'_1 \equiv s \frac{kT}{h} e^{-\Delta F_1/RT} e^{-V_1 F/RT} \quad .$$

$$\kappa_2 E'_2 \equiv s \frac{kT}{h} e^{-\Delta F_2/RT} e^{V_2 F/RT}$$

where ΔF_1 and ΔF_2 are the free energies of activation of the redox process, V_1 means the difference of the electrical potential between the activated state, C, and the adsorbed state, A, and V_2 means the difference of the electrical potential between the electrode surface, E, and the activated state, C, respectively (Fig. 4). $[A_{H_a^+}]$ is the activity of the hydrogen ion adsorbed on the electrode surface. According to the assumption mentioned above, we can neglect the second term of the right-hand side of Eq. (II-27) in the potential region of the reduction wave, and, therefore, Eq. (II-27) can be reduced to the following as an approximation,

$$I = F\kappa_1 E'_1[A_{H_a^+}] \tag{II-28}$$

Now, let us assume that the adsorption equilibrium of the Freundlich adsorption isotherm type prevails between the adsorbed ion and the ion in the solution side. If the effect of the electrical potential difference, V_a, between the adsorbed state, A, and the solution side, S, is taken into consideration, this equilibrium can be represented by

$$[A_{H_a^+}] = \gamma[A_{H^+}]^{\nu} \exp\left(-\frac{V_a F}{RT}\right) \tag{II-29}$$

$$\nu \leq 1$$

where γ and ν are the constants of adsorption.

From Eqs. (II-6), (II-28) and (II-29) the equation for the c-v curve can be obtained as

$$\kappa_1 E_1' \exp\left(-\frac{V_a F}{RT}\right) = \frac{(FK_{H^+}')^\nu}{F\gamma} \frac{I}{(FK_{H^+}'[A_{H^+}]^\circ - I)^\nu} \tag{II-30}$$

by which it is easily shown that at a sufficiently negative potential the limiting current, which is represented by Eq. (II-13), appears. If the relation between the electrode potential, V, and the terms, V_1, V_2 and V_a,

$$V = V_1 + V_2 + V_a, \qquad V_1 + V_a = \alpha' V$$

α' : a proportional constant,

and Eq. (II-13) are introduced into Eq. (II-30), the following equation is obtained for the reduction wave:

$$V = const - \frac{RT}{\alpha'F} \ln \frac{I}{I_l - I} + \frac{RT}{\alpha'F}(\nu - 1) \ln (I_l - I) \tag{II-31}$$

in which

$$const = \frac{RT}{\alpha'F}\left(-\frac{\Delta F_1}{RT} + \ln \gamma + \ln s + \ln \frac{kT}{h} + \ln F - \nu \ln (FK_{H^+}')\right)$$

Table 5.

Mechanism	Chemical Formula	Formula for C–V Curve	Log-plot	$V_{1/2}$ vs. I_l	I_l
A–(I)					
Diff.	$\begin{cases} H^+ + \varepsilon \rightleftarrows H \\ \end{cases}$	$V = const - \frac{RT}{F} \log \frac{I}{(I_l - I)^2}$	unsym. (L)	pos.	I_d
Act.	$H + H \rightleftarrows H_2$	$V = const - \frac{RT}{\alpha F} \log \frac{I}{I_l - I}$	sym.	indep.	$\prime\prime$
A–(II)					
Diff.	$\begin{cases} 2H^+ + 2\varepsilon \rightleftarrows 2H \\ \end{cases}$	$V = const - \frac{RT}{F} \log \frac{I}{(I_l - I)^2}$	unsym. (L)	pos.	$\prime\prime$
Act.	$2H \rightleftarrows H_2$	$V = const - \frac{RT}{\alpha F} \log \frac{I}{(I_l - I)^2}$	unsym. (L)	pos.	$\prime\prime$
Electrochem.					
(I)[a]	$\begin{cases} H^+ + \varepsilon \rightleftarrows H_a \\ H_a + H^+ \rightleftarrows H_2^+ \end{cases}$	$V = const - \frac{RT}{(1+\beta)F} \log \frac{I}{(I_l - I)^2}$	unsym. (L)	pos.	$\prime\prime$
(II)[b]	$H_2^+ + \varepsilon \rightleftarrows H_2$	$V = const - \frac{RT}{\alpha F} \log \frac{I}{I_l - I}$	sym.	indep.	$\prime\prime$
Slow Disch. Ads. H^+ Ion	$\begin{cases} H_a^+ + \varepsilon \rightleftarrows H \\ H + H \rightleftarrows H_2 \end{cases}$	$V = const - \frac{RT}{\alpha'F} \log \frac{I}{(I_l - I)^\nu}$	unsym. (U)	neg.	$\prime\prime$

Diff.: The diffusion-controlled type.   Act.: The activation-controlled type.

unsym. (L): The lower half of the wave is steeper than the upper half.

unsym. (U): The upper half of the wave is steeper than the lower half.

sym.: There is a center of symmetry at half-wave potential, $i.e.$, the relation between $\log I/(I_l - I)$ and V is linear.

pos.: $V_{1/2}$ shifts to more positive with the increase of I_l.

neg.: $V_{1/2}$ shifts to more negative with the increase of I_l.

indep.: $V_{1/2}$ is independent of I_l.

a: Rate-determining step is process (II-5).

b: Rate-determining step is process (II-3).

It is quite clear that the relation between $\log I/(I_l - I)$ and V is not linear in this case. By using the definition for the half-wave potential, i.e., $I = I_l/2$, the condition for the half-wave potential can be represented by

$$V_{1/2} = const' + \frac{RT}{\alpha'F}(\nu - 1) \ln I_l \qquad \text{(II-32)}$$

$$const' = \frac{RT}{\alpha'F}\left(-\frac{\Delta F_1}{RT} + \ln \gamma + \ln s + \ln \frac{kT}{h} \right.$$

$$\left. + \ln F - \nu \ln (FK'_{H^+}) - (\nu - 1) \ln 2 \right)$$

The half-wave potential changes to a more negative potential as the limiting current increases, because the term $(\nu - 1)$ is usually negative.

All results on the properties of the c-v curve of hydrogen ion, which have been discussed so far under the various mechanisms of the reduction process, are summarized in Table 5.

3. Experimental Properties of the Reduction Wave of Hydrogen Ion

A well-defined reduction wave of hydrogen ion as shown in Fig. 12 is obtained in the system of dilute HCl in 0.1 N KCl solution. The apparatus used in this study is a manually operating polarograph similar to that used by J. J. Lingane and I. M. Kolthoff[32]. The electrode potential of the DME* against a reference electrode (N. C. E.) is measured by a potentiometer, and the current flowing is measured by an over-damped galvanometer. A specially designed all-glass polarographic cell as shown in Fig. 5 is used to avoid the contamination from the rubber connections. The reference electrode and the anode are connected with the cell-solution by h-type sat. KCl-agar-bridges. The part be of a h-type bridge is filled with sat. KCl-agar and the cell-solution is sucked into
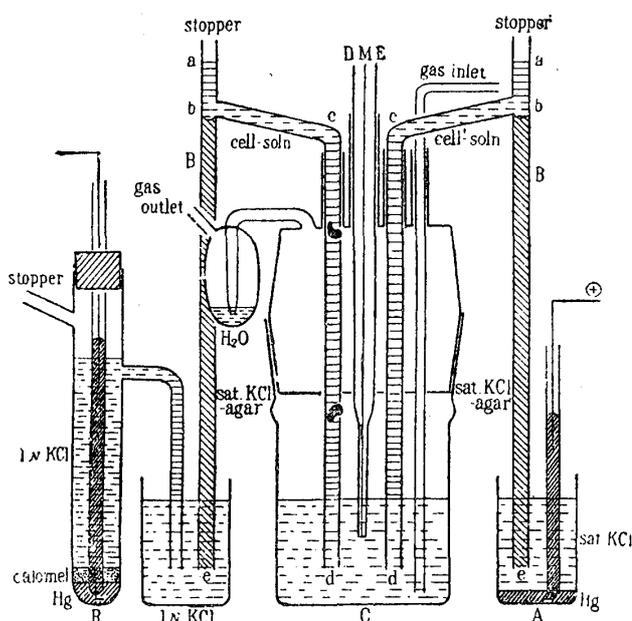

Fig. 5. All-glass polarographic cell assembly: A, anode; B, h-type sat. KCl-agar-bridge; C, polaro-graphic cell; R, reference electrode (N. C. E.).

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* The capillary constant of the DME used throughout the experiment was 1.028 mg$^{2/3}$ sec$^{-1/2}$ at the height of the mercury reservior of 53 cm.

the side-tube **abcd** to make a junction at point **b**. By this method the effect of the high concentration of KCl in agar on the cell-solution can be reduced to a negligible amount.

The relation between the limiting current, I_l, and the concentration of hydrogen ion, $[C_{H^+}]^\circ$, is a straight line as shown in Fig. 6 over the concentration range from 0.039 to 1.95 millimoles per liter. This relation is represented by the equation,

$$I_l = a[C_{H^+}]^\circ$$
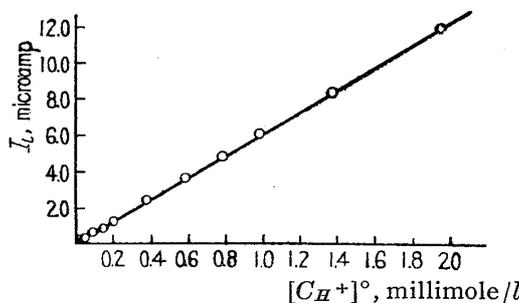
$a = 6.04$ microamp/millimole/l

(II-33)

Fig. 6. The relation between I_l and $[C_{H^+}]^\circ$ at 25°C.

Fig. 7 shows the relation between I_l and the effective hydrostatic pressure applied to the DME, P, which is represented by

$$I_l = 0.76\sqrt{P} + 2.0 \qquad (II-34)$$

if we express P in cm Hg and I_l in microamp. It is well known that the kinetic current is independent of the effective pressure, P. According to the recent theory on the diffusion current[26], it is represented by the equation,
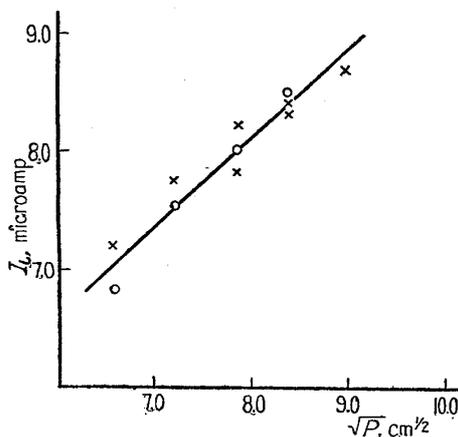
Fig. 7. The relation between I_l and $\sqrt{P}$: O, data obtained by the manual apparatus; ×, data obtained by the Heyrovsky-Shikata type polarograph.

$$I_d = 605nCD^{1/2}m^{2/3}t^{1/6}\left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right)$$

(II-35)

where

n : the number of electrons which participate in the redox reaction.

C : the concentration of depolarizer in the bulk of solution in millimole per liter.

D : the diffusion coefficient of the depolarizer in the medium under investigation in cm² per sec.

m : the weight of mercury flowing from the DME in mg per sec.

t : the drop-time in sec.

A is a constant and equal to 39 or 17 according to Lingane-Loveridge and Kambara-Tachi or Strehlov-Stackelberg, respectively. This equation, which is called as the revised Ilkovic equation, requires that the relation between I_d and P is described by,

$$I_d = a_0 + a_1\sqrt{P} \qquad (II-36)$$

where a_0 and a_1 are constants. The experimental result, represented by Eq. (II–34), is quite similar to the theoretical relation (II–36). This suggests that the limiting current of hydrogen ion in the present system is not a kinetic current but a diffusion current.

This conclusion is also confirmed by the temperature coefficient of the limiting current. The temperature coefficient of the limiting current, if it would be a diffusion current, can be calculated from the Ilkovic equation by assuming that the temperature coefficient of the diffusion coefficient is obtained from that of the limiting ionic conductance, λ°, by means of the Nernst equation. The result is represented by the equation[33],

$$\left[\frac{1}{I_d}\frac{dI_d}{dT}\right]_{298} = 0.0053 + \left[\frac{1}{2\lambda^\circ}\frac{d\lambda^\circ}{dT}\right]_{298} \quad *$$

According to B. B. Owen and F. H. Sweeton[31], the temperature coefficient of λ° of hydrogen ion at 25°C is equal to 0.015, from which the temperature coefficient of I_l of hydrogen ion, provided it is assumed to be a diffusion current, is calculated to be nearly equal to 0.013 at 25°C. The result obtained from the revised Ilkovic equation differs from that of the Ilkovic equation only by the following additional term,

$$\frac{d\log(1+AD^{1/2}m^{-1/3}t^{1/6})}{dT} \simeq \frac{AD^{1/2}m^{-1/3}t^{1/6}}{1+AD^{1/2}m^{-1/3}t^{1/6}}\left\{\frac{1}{2}\left(\frac{1}{\lambda^\circ}\frac{d\lambda^\circ}{dT}+\frac{1}{T}\right)-\frac{1}{3m}\frac{dm}{dT}\right\}$$

in which the temperature coefficient of the drop-time is neglected. By considering this additional term, the temperature coefficient of I_d of hydrogen ion is 0.015, if $A=39$ and $\left[\frac{1}{m}\frac{dm}{dT}\right]_{298} \simeq 0.0037$ are used.

Table 6 and Fig. 8 show the experimental results on the temperature

Table 6. Temperature Coefficient of I_l.

Temp. τ, °C	I_l, microamp	$dI_l/d\tau$, microamp/°C	$(1/I_l)(dI_l/d\tau)$, %	$d\log I_l/d\tau$, %
$[C_{H^+}]^\circ = 0.78$ millimole/l				
5	3.74	0.0866	2.32	1.01
15	4.46	0.0612	1.37	0.61
25	5.03	0.0526	1.05	0.43
35	5.44	0.0316	0.58	0.24
45	5.72	0.0240	0.42	0.17
$[C_{H^+}]^\circ = 1.95$ millimole/l				
5	9.25	0.15	1.62	0.68
15	10.6	0.12	1.13	0.52
25	11.7	0.11	0.94	0.44

* In this case, the temperature coefficient means the value which is obtained by dividing the slope of the relation between I_l and T at 25°C, $(dI_l/dT)_{298}$, by I_l at 25° (Table 6, column 4).

coefficient of I_l of hydrogen ion in a medium of 0.1 N KCl solution over the temperature range of 0 to 50°C. From these data the temperature coefficient of I_l is found to be nearly equal to 0.010 at 25°C, which is in comparatively good agreement with the theoretical value obtained under the assumption that the limiting current of hydrogen ion is a diffusion current. If this might be a kind of kinetic currents, the temperature coefficient should be much larger than those in Table 6.

Fig. 8. The effect of temperature on I_l: a, I_l vs. τ; b, $\log I_l$ vs. τ. $[C_{H^+}]° = 0.78$ millimole/l.

From the above discussion, it is almost doubtless that the limiting current of hydrogen ion in the present system is a diffusion current. The next question is whether this diffusion current of hydrogen ion is represented by the Ilkovic equation or better by the revised one. From the Ilkovic equation, it is expected that the diffusion current constant, $I_l/m^{2/3}t^{1/6}$, should be independent of $m^{-1/3}t^{1/6}$. Experimental result, as illustrated in Fig. 9, clearly sh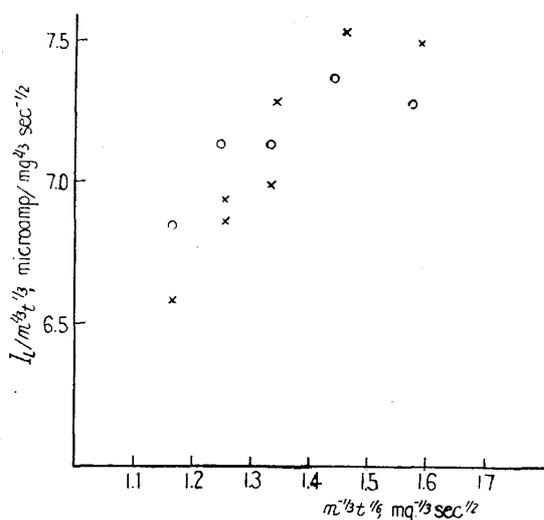ows that this is not the case in the present system, and suggests that the revised Ilkovic equation could be a better approximation. The value of A in Eq. (II-35) can be obtained from the slope of this relation (Fig. 9). If the value, 8.0×10^{-5} cm²/sec, is used for D_{H^+} in 0.1 N KCl solution, A is calculated to be equal to about 35, which is quite reasonable.

The diffusion coefficient of hydrogen ion in 0.1 N KCl solution, which was used in the above calculation, is computed by the Onsager's limiting law for the diffusion coefficient[35]. As the concentration of the diffusing ion is generally very small in comparison with that of the supporting electrolyte whose composition is sensibly constant in the polarographic study, the diffusion coefficient of hydrogen ion under the present condition can be represented as follows according to this law:

Fig. 9. The relation between the diffusion current constant and $m^{-1/3}t^{1/6}$.

$$D_{H^+} = \frac{\lambda°_{H^+} RT}{|Z_{H^+}| F^2} \times 10^{-7} - \frac{\lambda°_{H^+} |Z_{H^+}| v^2 \varepsilon}{3D} \times 10^{-9} \sqrt{\frac{4\pi}{1000\,DRT}} (-\sqrt{d(\omega_{H^+})}) \sqrt{\Gamma}$$
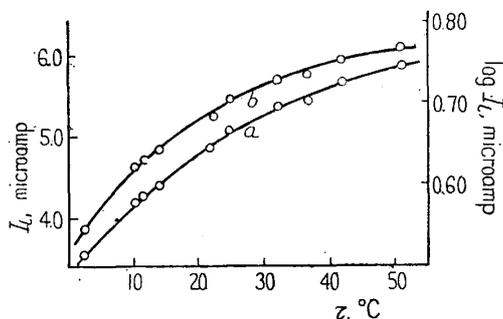
$$d(\omega_{H^+}) = \left(\frac{|Z_{H^+}|}{|Z_{K^+}| + |Z_{Cl^-}|}\right)\left(\frac{|Z_{K^+}|\lambda^\circ_{K^+}}{|Z_{H^+}|\lambda^\circ_{K^+} + |Z_{K^+}|\lambda^\circ_{H^+}} + \frac{|Z_{Cl^-}|\lambda^\circ_{Cl^-}}{|Z_{H^+}|\lambda^\circ_{Cl^-} + |Z_{Cl^-}|\lambda^\circ_{H^+}}\right)$$

$$\Gamma = C_{H^+}Z^2_{H^+} + C_{K^+}Z^2_{K^+} + C_{Cl^-}Z^2_{Cl^-} \simeq C_{K^+}Z^2_{K^+} + C_{Cl^-}Z^2_{Cl^-}$$

in which λ° is the ionic conductance of the corresponding ion, Z the valency, C the concentration in mole per liter, D the dielectric constant, v the velocity of light, and ε the electric charge.

Although the agreement between the theoretical predictions of the Onsager's limiting law and the experimental results was stated not to be exact and only reasonably satisfactory by L. J. Gosting and H. S. Harned[35], it seems more appropriate to use this limiting law rather than to use the Nernst equation for the diffusion coefficient of the individual ion in the polarographic study.

If we assume the value, 8.0×10^{-5} cm²/sec, thus obtained for D_{H^+}, the number of electrons, which participate in the redox process of hydrogen ion, is obtained as follows from Eq. (II–33):

$n = 1.09$ (from the Ilkovic equation)

$n = 0.72$ (from the revised equation, $A = 39$)

$n = 0.89$ (from the revised equation, $A = 17$)

This result proves the assumption that n is equal to one in the reduction process of hydrogen ion at the DME.

Inversely, if we assume that n is equal to one, the polarographic diffusion coefficient of the hydrogen ion in 0.1 N KCl solution can be calculated by the Ilkovic equation or the revised one, $i.e.$:

$D_{H^+} = 9.5 \times 10^{-5}$ cm²/sec   (from the Ilkovic equation)

$D_{H^+} = 4.8$ ''   ''   (from the revised equation, $A = 39$)

$D_{H^+} = 6.6$ ''   ''   (from the revised equation, $A = 17$)

So far, the properties of the limiting current have been mainly discussed. However, the properties of the reduction wave, $e.g.$, the log-plot analysis of the c-v curve, the nature of the half-wave potential, are more important in analysing the mechanism of the reduction process. Now the question arises as to whether the overall electrode process, which produces the reduction wave of hydrogen ion in the present system, would be activation-controlled or diffusion-controlled. This may be replied by the application of the Kalousek's method[9]. It has been known that an apparent oxidation current appears when the Kalousek's method is applied to such a reduction process like of Pb^{2+} ion in KOH solution which is considered to be diffusion-controlled. In the case of the reduction wave of hydrogen ion, however, no oxidation current can be observed. This excludes the possibility of the existence of any electrochemically active hydrogen species at the surface of the

electrode, which can be easily oxidized. If the reduction product could be easily oxidized at the potential region of the reduction wave and would not escape from the electrode surface instantaneously, the oxidation current should appear as in the case of Pb^{2+}-ion, when the Kalousek's method is applied. Under this circumstance, it seems possible to conclude that the overall electrode process of hydrogen ion in 0.1 N KCl solution at the DME is a kind of the activation-controlled type.

This conclusion is also supported by the relatively large temperature coefficient of the half-wave potential, namely it changes to more positive by about 0.003 volt per degree as the temperature of the cell-solution increases over the range of 0 to 50°C (Fig. 10 and Table 7). If the overall process would be diffusion-controlled, the temperature coefficient of the half-wave potential expected should be much smaller[36].
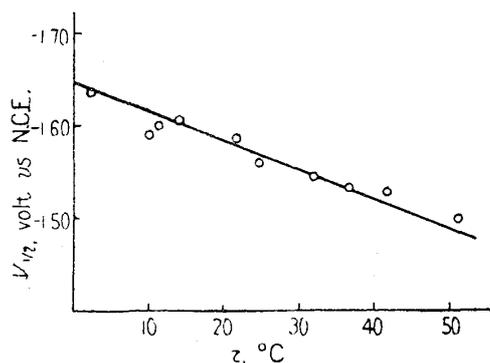

Fig. 10. The effect of temperature on $V_{1/2}$. $[C_{H^+}]° = 0.78$ millimole/l.

Table 7. The Effect of Temperature on the Reduction Wave of the Hydrogen Ion

Temp. τ, °C	I_l, microamp	$V_{1/2}$, volt vs. N.C.E.	α'	ν	$\overrightarrow{\Delta F}$, kcal
$[C_{H^+}]° = 0.78$ millimole/l					
2.2	3.50	−1.636	0.56	0.76	32.3
10.2	4.18	1.589	0.50	0.64	31.1
11.2	4.24	1.598	0.57	0.68	32.7
14.0	4.37	1.605	0.48	0.71	29.8
21.7	4.83	1.585	0.58	1.0	32.0
24.7	5.05	1.561	0.53	1.0	30.1
31.7	5.33	1.544	0.53	0.73	31.5
36.5	5.43	1.533	0.58	1.0	32.0
41.7	5.64	1.527	0.46	0.49	30.3
50.9	5.84	1.498	0.54	0.68	32.3
$[C_{H^+}]° = 1.95$ millimole/l					
1.5	8.56	1.638	0.46	0.67	28.9
20.5	11.2	1.591	0.49	0.75	29.8
27.8	12.0	1.567	0.47	0.52	30.1
36.5	12.3(?)	1.550(?)	0.45(?)	0.61(?)	29.1(?)
45.2	13.4(?)	1.530(?)	0.64(?)	0.77(?)	35.3(?)

When we refer to Table 5 in the previous section, it is quite obvious that the relation between the limiting current and the half-wave potential and the log-plot analysis are crucial in deciding the mechanism of the reduction process. The half-wave potential of hydrogen ion becomes more negative as the concentration of hydrogen ion

Table 8. The Effect of the Concentration of the Hydrogen
Ion on the Reduction Wave

$[C_{H^+}]°$, millimole/l	I_l, microamp	$V_{1/2}$, volt vs. N.C.E.	$α'$	$ν$	$\overrightarrow{ΔF}$, kcal
0.039	0.136	−1.540			
0.078	0.390	1.545			
0.137	0.738	1.546	0.59		32.0
0.195	1.04	1.559	0.66		34.9
〃	1.22	1.553	0.49		28.7
〃	1.07	1.555	0.52		29.6
0.390	2.31	1.562	0.46	0.58	29.4
〃	2.32	1.565	0.42	0.39	29.1
0.585	3.60	1.561	0.53	0.74	31.5
0.780	4.79	1.572	0.51	0.69	30.6
〃	4.66	1.568	0.58	0.76	33.0
〃	4.76	1.568	0.48	0.47	30.8
0.975	6.03	1.574	0.45	0.59	29.6
1.37	8.24	1.587	0.46	0.52	29.6
〃	8.10	1.570	0.44	0.56	28.7
1.95	11.4	1.577	0.50	0.49	31.1
〃	11.8	1.581	0.42	0.63	29.8

in the bulk of solution, $[C_{H^+}]°$, or I_l, becomes larger over the concentration range of 0.039 to 1.95 millimoles per liter (Fig. 11 and Table 8). From the straight line as shown in Fig. 11, the relation between $V_{1/2}$ and I_l is found to be represented by
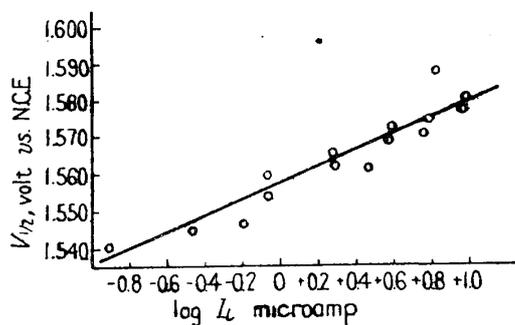
$$V_{1/2} = -1.687 - 0.022 \log I_l$$

Fig. 11. The relation between $V_{1/2}$ and $\log I_l$.

where I_l is in amp and $V_{1/2}$ in volt.

The relation between $\log I/(I_l - I)$ and V is not linear and an apparent deviation from a straight line appears in the more negative potential region than the half-wave potential as shown in Fig. 12. This result means that the upper half of the reduction wave is steeper than the lower half. This deviation, however, is not clear when the concentration of hydrogen ion is less than about 0.5 millimole per liter.

These results are not in agreement with those obtained by the previous investigators. J. Tomes[21] reported that $V_{1/2}$ of hydrogen ion of the dilute solution of HCl in 1 N KCl or $CaCl_2$ solution became to be more positive with the increase of the diffusion current according to the relation $ΔV_{1/2}/Δ \log I_d = 0.028$ volt. Quite recently, it was mentioned by J. Kuta[24] that $V_{1/2}$ of hydrogen ion in the system, HCl or H_2SO_4 in 0.1 N solutions of supporting electrolytes (KCl, KBr, K_2SO_4 and $BaCl_2$), is independent of the concentration of the acid. As for the log-plot of

the c-v curve, he stated that this relation was a straight line whose tangent is nearly equal to $2RT/F$. It must be noted that, although the results on the relation between $V_{1/2}$ and I_d obtained by J. Tomes and by the present author are in considerable contradiction, the same deviation in the log-plot analysis as mentioned above was also observed by Tomes, which was represented by the following relation :

$$(V_{1/4} - V_{1/2}) - (V_{1/2} - V_{3/4})$$
$$= + 0.006 \text{ volt}$$

in which $V_{1/4}$ and $V_{3/4}$ meant the electrode potentials where $I = 1/4 \ I_d$ and $I = 3/4 \ I_d$, respectively. J. Kuta attributed the discrepancy between his results and those of J. Tomes to the possibility of the existence of maximum of the second kind in 1 N solution of the supporting electrolyte. At any rate, further investigation on the c-v curve of hydrogen ion in the solutions of various supporting electrolytes is necessary to make clear these points.
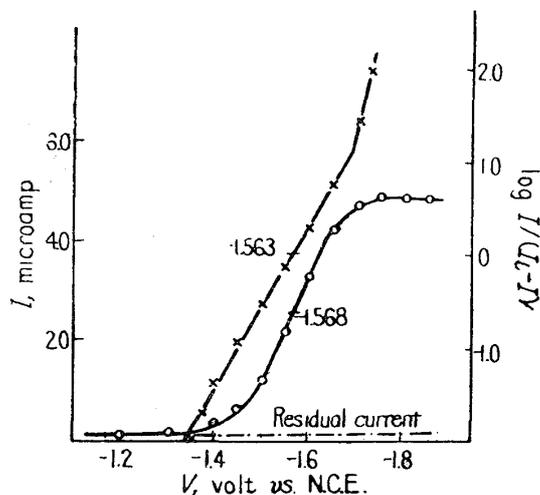

Fig. 12.   Polarogram of the hydrogen ion of dil. HCl in 0.1 N KCl solution and the log-plot analysis of the wave. $[C_{H^+}]^\circ = 0.78$ millimole/l.

4. Discussion

The properties of the reduction wave of hydrogen ion in 0.1 N KCl solution are summarized as follows :

(i) The limiting current is controlled by the diffusion process, i.e., it is a diffusion current.

(ii) One electron participates in the redox reaction of a hydrogen ion.

(iii) The overall electrode process in the potential region of the reduction wave might be activation-controlled.

(iv) The half-wave potential becomes more negative as the limiting current increases.

(v) The log-plot of the reduction wave is not a straight line. The upper half of the wave is steeper than the lower half.

By referring to Table 5, it is concluded that these results could only be interpreted by assuming the " slow discharge mechanism of the adsorbed hydrogen ion " for the electrode process.

The equations for the c-v curve and the half-wave potential under this mechanism, Eqs. (II-31) and (II-32), have been already discussed in the previous section. The values of the constants, α' and ν, can be

obtained from the experimental data on the c-v curve by writing Eq. (II-31) in the form of Eq. (II-37) and by determining a_0, a_1 and a_2 in this equation by the least square method:

$$- V_0 = a_0 + a_1 A + a_2 B$$

$$A \equiv \frac{RT}{F} \ln \frac{I}{I_i - I}, \qquad B \equiv \frac{RT}{F} \ln (I_i - I) \qquad \text{(II-37)}$$

$$a_1 \equiv \frac{1}{\alpha'}, \qquad a_2 \equiv \frac{1-\nu}{\alpha'}, \qquad a_0 = const$$

Now, let us analyse the constant, a_0, in Eq. (II-37) more closely. This involves the free energy of activation of the forward process of the redox reaction, ΔF_1, and the constant γ in the equation of the adsorption isotherm, Eq. (II-29). According to the theoretical derivation of the Freundlich adsorption isotherm[37], γ and ν can be represented as follows:

$$\gamma = \exp \left(\frac{f'(T)}{RT} + \frac{1}{i} - 1 \right) \qquad \text{(II-38)}$$

$$\nu = \frac{1}{i} \qquad \text{(II-39)}$$

i is a constant in the equation of state of the adsorbed layer, namely, $FA = iRT$, in which F is the surface pressure and A is the surface area. $f'(T)$ is a function of temperature and can be considered to be equal to the free energy of adsorption, $-\Delta F_a$ (Fig. 4). If we neglect the term $1/i - 1$ against $f'(T)/RT$, Eq. (II-38) is reduced to

$$\gamma = \exp \left(-\frac{\Delta F_a}{RT} \right) \qquad \text{(II-38')}$$

From Eqs. (II-31) and (II-38'), the following equation is obtained for the constant a_0:

$$a_0 = -\frac{\overrightarrow{\Delta F}}{\alpha' F} - \frac{\nu RT}{\alpha' F} \ln (FK'_{H^+}) + \frac{RT}{\alpha' F} \ln F + \frac{RT}{\alpha' F} \ln s + \frac{RT}{\alpha' F} \ln \frac{kT}{h} \qquad \text{(II-40)}$$

$$\overrightarrow{\Delta F} = \Delta F_1 + \Delta F_a$$

where $\overrightarrow{\Delta F}$ is the difference of the free energy between the activated state of the redox process, H^+ (adsorbed) $\rightleftarrows$ H (surface), and the solution side, S, in Fig. 4, and can be considered as the free energy of activation of the overall discharge process of hydrogen ion, H^+ (solution) $\rightarrow$ H (surface). If we assume that FK'_{H^+} is nearly equal to FK_{H^+}, the terms α', ν and FK_{H^+} in Eq. (II-40) can be obtained from the experimental data. The constant, s, can be approximately represented by the relation[19],

$$s \cong q \cdot \mu \cdot 10^{-3}$$

$$q = \frac{3}{5} \times 0.85 \times m^{2/3} t^{2/3} \; (\text{cm}^2)$$

in which m is the weight of mercury flowing from the DME in g per sec and t the drop-time of one drop in sec. In the above relation q means the mean surface area of the DME, and μ the thickness of the reaction layer at the electrode surface in cm which is assumed to be approximately equal to 10^{-7} cm according to R. Brdicka[19]. Using these values, $\overrightarrow{\Delta F}$ can be calculated from the constant, a_0, obtained from Eq. (II–37). In this case, the current is expressed in amp and the value of the electrode potential referred to a normal calomel electrode is used.

The numerical values of α', ν and $\overrightarrow{\Delta F}$ calculated from c-v curves obtained under various conditions are shown in Tables 7 and 8. The values of α' are in the range of 0.4 and 0.6, but those of ν diverge over the range of 0.4 to 1.0. If we consider that ν is the exponent in the equation for the adsorption equilibrium and may be influenced by a slight change of the condition of the electrode surface and solution, such a divergence in the values of ν seems to be rather reasonable. The fairly good constancy of the values of $\overrightarrow{\Delta F}$, which are obtained under the various conditions, can be considered as one of the supports which prove the correctness of the present assumption on the discharge process of hydrogen ion. The value of $\overrightarrow{\Delta F}$ can be also determined by the relation between $V_{1/2}$ and $\log I_l$ according to Eq. (II–32). As $(\nu - 1)/\alpha'$ is obtained from Eq. (II–32), both of α' and ν can be settled provided either one of them is known. If we assume that α' is nearly equal to 0.5, the value of $\overrightarrow{\Delta F}$ is calculated by this method to be equal to about 30 kcal/mole, which is in good agreement with the values mentioned in Tables 7 and 8.

In the end of this discussion, a brief consideration about the effect of the effective pressure applied to the DME, P, on the half-wave potential will be set down. In 1937, J. Novak[22] reported that the double increase of P caused a shift of $V_{1/2}$ to a more negative potential by 13 millivolts, while recently J. Kuta[24] found that this shift was equal to 18 millivolts. This change of $V_{1/2}$ with the change of P can be expected from Eq. (II–32). In this equation, the terms, $\log I_l$ and $\log (FK'_{H^+})$ are the functions of P, but the term $\log s$ is independent of P because s is proportional to $m^{2/3} t^{2/3}$ which is independent of P. As mentioned before, the limiting current of hydrogen ion in the present system is proportional to the square root of P (Eq. (II–34)). Under these conditions, the following relation between $V_{1/2}$ and P can be derived from Eq. (II–32):

$$V_{1/2} \cong const\ (P) - \frac{RT}{2\alpha'F} \ln P \tag{II-41}$$

in which $const(P)$ is a constant independent of P. As α' is in between 0.4 and 0.6, it can be said from Eq. (II-41) that $V_{1/2}$ shifts to a more negative potential by about 18 millivolts with the double increase of P, which is in accordance with Kuta's experimental result. In this discussion it is assumed that α' and ν are independent of P.

From the discussion carried out so far, it is obvious that all the property of the c-v curve of hydrogen ion in 0.1 N KCl solution can be satisfactorily interpreted by assuming the mechanism of the reduction process as follows: First, the hydrogen ion is adsorbed on the surface of the DME, and, next, the adsorbed hydrogen ion is reduced to the hydrogen atom under the condition of the activation-controlled process. In this case it is assumed that the equilibrium state represented by the Freundlich adsorption isotherm exists between the hydrogen ion in the neighbourhood of the electrode surface and the adsorbed hydrogen ion in the adsorbed layer. The results obtained by the application of the kinetic treatment of the c-v curve to the hydrogen wave give us the conclusion that the discharge process of hydrogen ion of dilute hydrochloric acid in 0.1 N KCl solution will proceed according to the "slow discharge mechanism of the adsorbed hydrogen ion".

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