On the Mechanism of the Reduction Process of the Hydrogen Ion at the Dropping Mercury Electrode. I. Theoretical Part

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Introduction

The study of the irreversible reduction wave of the hydrogen ion at the dropping mercury electrode (D. M. E.) 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 D. M. E. has the following characteristics in comparison with the usual stationary electrode. It is well known that at the D. M. E. a very good reproducibility can be obtained with many metal ions and organic substances because of its continuous renewal of the surface. The use of the D. M. E. 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 electrode, are eliminated.

The mechanism of the reduction process of the hydrogen ion at the D. M. E. was investigated by J. Tomes,(2) J. Novak(3) and J. Heyrovsky(4) in 1937. The experimental results obtained by them, however, seem to be too complicated to be satisfactorily explained by the former theory on the polarographic current-voltage curve which assumes that the electrode potential of the D. M. E. can be represented by the Nernst equation.(5) Furthermore, it is doubtful whether the Nernst equation could be used in the polarographic reduction process of the hydrogen ion.

The great advances in the experimental technique and theory of polarography have been made during these ten years. By the use of the cathode-ray oscillograph(6) and the method of Kalousek(7) it became possible to examine the reversibility of the electrode process at the D. M. E. A new concept of the polarographic limiting current which is controlled by the adsorption process(8) or the rate of the reaction(9) was introduced by R. Brdicka and others, and the revised Ilkovic equation for the diffusion current was derived by several investigators.(10) In collaboration with Dr. N. Tanaka the present author derived the formulas for the current-voltage curve in polarography from the standpoint of chemical kinetics and presented an interpretation for the experimental results concerning the irreversible polarographic waves.(11)

Under these circumstances it seems to be promising to investigate the reduction process of the hydrogen ion at the D. M. E. from the same theoretical viewpoint as in the previous work.(11) This paper treats the theoretical part of the study; the formulas for the current-voltage curve of the hydrogen ion discharge under the various reaction mechanisms are derived and the discussions on the properties of the half-wave potential and others are presented. The experimental part will follow in other papers.

General Remarks

Many theories have been presented to interpret theoretically Tafel's equation,(12)

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

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-determin-

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(2) J. Tomes, *Collection Czechoslov. Chem. Communs.*, **9**, 150 (1937).

(3) J. Novak, ibid., **9**, 207 (1937).

(4) J. Heyrovsky, ibid., **9**, 271 (1937).

(5) J. Heyrovsky and D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, **7**, 198 (1935).

(6) For example, P. Delahay, *J. Phys. Colloid. Chem.*, **54**, 630 (1950).

(7) M. Kalousek, *Collection Czechoslov. Chem. Communs.*, **13**, 105 (1948).

(8) R. Brdicka, ibid., **12**, 522 (1947).

(9) R. Brdicka and K. Wiesner, ibid., **12**, 138 (1947); etc.

(10) J. J. Lingane and B. A. Loveridge, *J. Am. Chem. Soc.*, **72**, 438 (1950); H. Strehlov and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950); T. Kambara, M. Suzuki and I. Tachi, This Bulletin, **23**, 219 (1950); T. Kambara and I. Tachi, ibid., **23**, 225 (1950).

(11) N. Tanaka and R. Tamamushi, This Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, ibid., **22**, 227 (1949); **23**, 110 (1950); R. Tamamushi, ibid., **23**, 250 (1950); N. Tanaka, ibid., **23**, 253 (1950); R. Tamamushi and N. Tanaka, ibid., **24**, 127 (1951); N. Tanaka and R. Tamamushi, *Proc. I. International Polarographic Congress in Prague, Part I*, p. 468 (1951).

(12) J. Tafel, *Z. physikal. Chem.*, **50**, 641 (1905).

ing process. In the slow discharge theory(13) the rate-determining step is the discharge process of the hydrogen ion (1), while in the recombination theory(14) the process of the formation of the molecular hydrogen (2) is the slowest step.

$$
\text{A.}\quad \begin{cases} \mathrm{H^+} + e \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftharpoons}} \mathrm{H} & (1) \\ \mathrm{H} + \mathrm{H} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2} & (2) \end{cases}
$$

In the electrochemical theory of Horiuchi and others,(15) the following reduction process is assumed:

$$
\text{B.}\quad \begin{cases} \mathrm{H^+} + e \underset{\kappa_2 E_2}{\overset{\kappa_1 E_1}{\rightleftharpoons}} \mathrm{H}_a & (3) \\ \mathrm{H}_a + \mathrm{H^+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{H_2^+} & (4) \\ \mathrm{H_2^+} + e \underset{\kappa_4 E_4}{\overset{\kappa_3 E_3}{\rightleftharpoons}} \mathrm{H_2} & (5) \end{cases}
$$

H_a: the adsorbed hydrogen atom.

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

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 (2), molarization process (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. (Hereafter, forward means the direction from left to right of a chemical equation.) For example, if the rate constant of the forward process of (2) is larger than those of the diffusion process of the hydrogen atom from the electrode surface and the other processes, process (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, i.e., in a dynamic equilibrium. It is to be mentioned here that the electrode potential is used in the following discussion instead of the overvoltage.

The Mechanism A

(I) One Hydrogen Ion participates in Process (1).—Let us consider that the rate constants of the forward (reduction) and the reverse (oxidation) reactions of process (1) are represented by $\kappa_1 E_1$ and $\kappa_2 E_2$ and that those of recombination process (2) by k_1 and k_2, respectively. κ_1, κ_2, E_1 and E_2 are the abbreviations of $s\frac{kT}{h}e^{-\Delta F_1/RT}$, $s\frac{kT}{h}e^{-\Delta F_2/RT}$, $e^{-n\alpha VF/RT}$ and $e^{(1-\alpha)nVF/RT}$, respectively, where ΔF_1 and ΔF_2 are the free energies of activation of the forward and the reverse reactions of process (1), V the electrode potential referred to a certain reference electrode, α the fraction of the potential V which is operative between the initial and the activated states, n the number of electrons which participate in redox reaction (1), and s is a constant which depends on the nature of the electrode. Since the current flowing is represented by the difference of the two rates, i.e., the forwerd and the reverse, the cathodic current at the dropping mercury electrode can be written as follows:

$$
I = F(\kappa_1 E_1[A_{H^+}] - \kappa_2 E_2[A_H]) \qquad (6)
$$

$$
I = 2F(k_1'[A_H]^2 - k_2'[A_{H_2}]) \qquad (7)
$$

$$
k_1' \equiv \sigma k_1 \qquad k_2' \equiv \sigma k_2
$$

in which $[A_{H^+}]$, $[A_H]$ and $[A_{H_2}]$ are the activities of the hydrogen ion, the hydrogen atom and the hydrogen molecule at the electrode surface, respectively, and σ is a proportional constant.

The hydrogen ion at the electrode surface is supplied by the diffusion process of this ion from the bulk of the solution where the activity of the hydrogen ion remains constant. Moreover, it is assumed that the molecular hydrogen produced at the electrode will disappear from the electrode surface by diffusion. Taking into consideration these diffusion processes, the current flowing is represented by

$$
\begin{aligned} I &= FK_{H^+}([C_{H^+}]^\circ - [C_{H^+}]) \\ &= FK'_{H^+}([A_{H^+}]^\circ - [A_{H^+}]) \qquad (8) \end{aligned}
$$

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(13) M. Volmer and T. Erdey-Gruz, *Z. physikal. Chem.*, **150** A, 203 (1930); R. W. Gurney, *Proc. Roy. Soc.*, **134** A, 137 (1931); A. Frumkin, *Faraday Society Discussion*, No. 1, p. 57 (1947); etc.

(14) J. Tafel, loc. cit.; J. O'M. Bockris, *Faraday Society Discussion*, No. 1, p. 95 (1947); etc.

(15) G. Okamoto, J. Horiuchi and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936); etc.

$$\begin{aligned} K'_{H^+} &\equiv K_{H^+}/f_{H^+} \\ I &= 2FK_{H_2}([C_{H_2}]-[C_{H_2}]^\circ) \\ &= 2FK'_{H_2}([A_{H_2}]-[A_{H_2}]^\circ) \qquad (9) \\ K'_{H_2} &\equiv K_{H_2}/f_{H_2} \end{aligned}$$

where $[C_{H^+}]^\circ$, $[C_{H_2}]^\circ$, $[C_{H^+}]$ and $[C_{H_2}]$ are the concentrations of the hydrogen ion and the hydrogen molecule in the bulk of the solution and at the electrode surface, respectively, $[A_{H^+}]^\circ$ and $[A_{H_2}]^\circ$ the activities of the corresponding terms, and f_{H^+} and f_{H_2} are the activity coefficients of the hydrogen ion and the hydrogen molecule, respectively. We can ignore the existence of the migration current because of the presence of the excess of the supporting electrolyte in the polarographic studies.⁽¹⁶⁾

By assuming that all processes at the electrode surface including the diffusion processes are kept in a dynamic equilibrium, the current, I, can be expressed as the function of V, $[A_{H^+}]^\circ$ $[A_{H_2}]^\circ$ from Eqs. (6), (7), (8) and (9), i.e.:

$$\begin{aligned} I = F\kappa_1E_1&\left(\frac{FK'_{H^+}[A_{H^+}]^\circ-I}{FK'_{H^+}}\right) \\ &-F\kappa_2E_2\left(\frac{\Gamma}{2FK'_{H_2}}\left(2FK'_{H_2}[A_{H_2}]^\circ\right.\right. \\ &\left.\left.+\frac{K'_{H_2}}{k_2'}I+I\right)\right)^{1/2} \qquad (10) \end{aligned}$$

$$\Gamma \equiv k_2'/k_1'$$

This is the general equation for the current-voltage curve of the hydrogen ion discharge under mechanism (A).

(a) Activation-controlled Case.—In this case it is assumed that κ_1E_1 is much smaller than K'_{H^+} and that the current flowing is negligibly small at the electrode potential, where κ_1E_1 is nearly equal to $\kappa_2E_2\Gamma^{1/2}$. When the electrode potential becomes more negative, κ_1E_1 becomes larger and $\kappa_2E_2\Gamma^{1/2}$ tends to be zero. In this potential region the current, which is accompanied by the reduction process, appears.⁽¹¹⁾ Under this condition the second term of the right-hand side of Eq. (10) can be neglected in comparison with the first term and the reduction current can be represented by

$$I = F\kappa_1E_1\frac{FK'_{H^+}[A_{H^+}]^\circ-I}{FK'_{H^+}} \qquad (11)$$

$$I_l = FK'_{H^+}[A_{H^+}]^\circ \qquad (12)$$

where I_l means the limiting current.

This relation is quite the same as that for the reduction of the simple (or hydrated) metal ion in the activation-controlled case.⁽¹¹⁾ It is readily shown that the relation between $\log I/(I_l-I)$ and V—so-called "log-plot"—is a straight line whose tangent is equal to $RT/\alpha F$ and that the half-wave potential, $V_{1/2}$, is independent of the limiting current. Moreover, Eq. (12) shows that the limiting current is controlled by the diffusion process and is equal to the diffusion current.

(b) Diffusion-controlled Case.—As mentioned in the previous papers⁽¹¹⁾ it is assumed, in the diffusion-controlled case, that κ_1E_1 and $\kappa_2E_2\Gamma^{1/2}$ are much larger than K'_{H^+}, K'_{H_2} or k'_2 at the electrode potential where κ_1E_1 is nearly equal to $\kappa_2E_2\Gamma^{1/2}$. In this potential region Eq. (10) can be reduced to

$$\begin{aligned} \left(\frac{\kappa_2E_2}{\kappa_1E_1}\right)^2 &= \frac{2}{F}\,\frac{K'_{H_2}}{(K'_{H^+})^2}\,\frac{1}{\Gamma} \\ &\times\frac{(FK'_{H^+}[A_{H^+}]^\circ-I)^2}{2FK'_{H_2}[A_{H_2}]^\circ+\dfrac{K'_{H_2}}{k'_2}I+I} \qquad (13) \end{aligned}$$

because the term $1/\kappa_1E_1$ can be neglected in comparison with the other terms in Eq. (10). When the activity of the hydrogen molecule in the bulk of the solution is equal to zero, the following equation for the reduction wave can be obtained from Eq. (13) by introducing the relation, $I_l = FK'_{H^+}[A_{H^+}]^\circ$, i.e.:

$$V = \text{const.} - \frac{RT}{F}\log\frac{I}{(I_l-I)^2} \qquad (14)$$

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

$$V_{1/2} = \text{const.} + \frac{RT}{F}\log I_l \qquad (15)$$

Eq. (15) 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.

(II) Two Hydrogen Ions participate in Process 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 (2), i.e.:

$$2\mathrm{H}^+ + 2\mathrm{e} \rightleftharpoons 2\mathrm{H} \qquad (2')$$

According to this process the current flowing is represented by

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(16) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Pub. Inc., New York, N. Y., 1946, p. 83.

$$I=2F(\kappa_1E_1[A_{H^+}]^2-\kappa_2E_2[A_H]^2) \quad (16)$$

By the use of Eq. (16) instead of Eq. (6), the general equation for the current-voltage curve can be easily obtained by the same method as mentioned before:

$$I=2F\kappa_1E_1\left(\frac{FK'_{H^+}[A_{H_+}]^\circ-I}{FK'_{H^+}}\right)^2-2F\kappa_2E_2 \times\left(\frac{I}{2FK'_{H_2}}\left(2FK'_{H_2}[A_{H_2}]^\circ+\frac{K'_{H_2}}{k_2'}I+I\right)\right) \quad (17)$$

(a) Activation-controlled Case.—In this case the following relations for the reduction wave are derived from Eq. (17):

$$\kappa_1E_1=\frac{F(K'_{H^+})^2I}{2(I_l-I)^2}$$

or

$$V=\text{const.}-\frac{RT}{\alpha F}\log\frac{I}{(I_l-I)^2} \quad (18)$$

and

$$I_1=FK'_{H^+}[A_{H^+}]^\circ$$

It is quite obvious in this case that the limiting current is determined by the diffusion process and that the half-wave potential becomes more positive as I_l increases.

(b) Diffusion-controlled Case.—By the same treatment as mentioned in **(I)**-(**b**), the equation of the current-voltage curve under the present condition can be obtained, the results of which are quite similar to Eqs. (13), (14) and (15).

Electrochemical Mechanism

According to the electrochemical theory, the reduction mechanism of the hydrogen ion is represented by process (B). In this case, besides Eqs. (8) and (9) due to the diffusion processes, the current flowing can be written as follows:

$$I=F(\kappa_1E_1[A_{H^+}]^\circ-\kappa_2E_2[A_{Ha}]) \quad (19)$$

$$I=F(k_1'[A_{Ha}][A_{H^+}]-k_2'[A_{H_2^+}])$$

$$k_1'\equiv\sigma k_1 \quad k_2'\equiv\sigma k_2 \quad (20)$$

$$I=F(\kappa_3E_3[A_{H_2^+}]-\kappa_4E_4[A_{H_2}]) \quad (21)$$

$$\kappa_3E_3\equiv s\frac{kT}{h}e^{-\Delta F_3/RT}e^{-\beta VF/RT}$$

$$\kappa_4E_4\equiv s\frac{kT}{h}e^{-\Delta F_4/RT}e^{(1-\beta)VF/RT}$$

ΔF_3 and ΔF_4 are the free energies of activation of the forward and the reverse processes of (5), respectively, and β has the same meaning as α.

(I) Rate-determining Step is Process (5).—If we assume that process (5) is the slowest step of processes (3), (4) and (5) in the potential region where the reduction wave appears and that these processes are in a dynamic equilibrium at the electrode surface, the relation (22) for the current-voltage curve can be derived from Eqs. (8), (9), (19), (20) and (21): By taking into account the condition of the activation-controlled case, the second term of the right-hand side of Eq. (22) can be neglected in the potential region of the reduction wave, because κ_4E_4 is nearly equal to zero under this condition, and Eq. (22) can be reduced to Eq. (23). Furthermore, it seems reasonable to assume that κ_1E_2/κ_1E_1 is very small in this potential region and that I is much larger than $K'_{H^+}I$. By this assumption Eq. (23) can be simplified as follows:

$$I=\kappa_3E_3\frac{1}{(K'_{H^+})^2}\frac{(FK'_{H^+}[A_{H^+}]^\circ-I)^2}{FI\dfrac{\kappa_2E_2}{\kappa_1E_1}} \quad (24)$$

When the electrode potential is sufficiently negative and I/κ_3E_3 is negligibly small, the limiting current which is controlled by the diffusion process appears and it is represented by Eq. (12). From these equations the following formulas for the current-voltage curve and the half-wave potential are derived, i.e.:

$$V=\text{const.}-\frac{RT}{(1+\beta)F}\log\frac{I}{(I_l-I)^2} \quad (25)$$

and

$$V_{1/2}=\text{const.}+\frac{RT}{(1+\beta)F}\log I_l \quad (26)$$

$$I=F\left\{\kappa_3E_3\frac{k_1'\kappa_1E_1[(FK'_{H^+}[A_{H^+}]^\circ-I)^2-K'_{H^+}I(FK'_{H^+}[A_{H^+}]^\circ-I)]-F(K'_{H^+})^2\kappa_2E_2I}{F^2k_2'(K'_{H^+})^2\kappa_2E_2} -\kappa_4E_4\frac{2FK'_{H_2}[A_{H_2}]^\circ+I}{2FK'_{H_2}}\right\} \quad (22)$$

$$I=F\kappa_3E_3\frac{\dfrac{1}{(K'_{H^+})^2}[(FK'_{H^+}[A_{H^+}]^\circ-I)(FK'_{H^+}[A_{H^+}]^\circ-I-K'_{H^+}I)]-F\dfrac{1}{k_1'}\dfrac{\kappa_2E_2}{\kappa_1E_1}I}{F^2\dfrac{k_2'}{k_1'}\dfrac{\kappa_2E_2}{\kappa_1E_1}} \quad (23)$$

These results are qualitatively similar to those obtained from Eqs. (14) and (15).

(II) Rate-determining Step is Process (3).—Let us consider that the rate constant, $\kappa_2 E_2$, of the reverse reaction of process (3) 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 (4) and (5) are sufficiently large. In this case the adsorbed hydrogen atom, H_a, produced in process (3) will instantaneously react with H^+ and an electron and give a molecular hydrogen. Under this condition the reduction current can be represented as follows:

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

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

This result is quite the same as that of the reduction of the simple metal ion in the activation-controlled case.(11) As far as the reduction process is concerned, processes (4) and (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 current-voltage curve.

The Mechanism in which the Adsorption Process of the Hydrogen Ion is taken into Consideration

Let us assume that only the hydrogen ions adsorbed on the electrode surface can be neutralized. This assumption seems probable 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.(17) 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 adsorption state, A, and the other is between the adsorption state and the electrode side, E. (Fig. 1). As suggested by P. van Rysselberghe, the hydrogen atom produced by the neutralization process will exist in various forms, e. g., adsorbed state H_a, free hydrogen atom, and so on.(18) Moreover, there may be various processes which will take place after the neutralization of the hydrogen ion, e. g., the recombination of the hydrogen atoms, the combination reaction of the hydrogen atom and the hydrogen ion, etc. At any rate, if it is assumed that the rate constant of the oxidation reaction, i. e., the reverse process from E to A, is negligibly small in comparison with that of the neutralization process from A to E in the potential region of the reduction wave, the equation for the reduction wave is not influenced by the processes which follow the neutralization reaction. In the following, only the results derived from this assumption are set down. For convenience' sake, let us call this mechanism "the slow discharge mechanism of the adsorbed hydrogen ion".

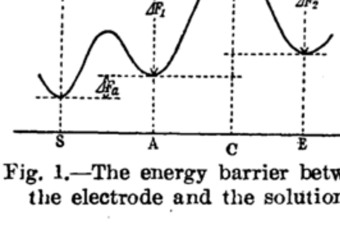

Fig. 1.—The energy barrier between the electrode and the solution.

Under these conditions the overall electrode process of the discharge of the hydrogen ion is represented as follows:

$$H^+(\text{bulk of the solution}) \xrightarrow{\text{diffusion}} H^+(\text{surface})$$

$$H^+(\text{surface}) \overset{\text{adsorption}}{\rightleftharpoons} H^+(\text{adsorbed})$$

$$H^+(\text{adsorbed}) \underset{\kappa_2 E_2' \text{ oxidation}}{\overset{\kappa_1 E_1' \text{ reduction}}{\rightleftharpoons}} H\ (\text{surface})$$

$H\ (\text{surface}) \longrightarrow$ disappears from the electrode surface by some processes

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

$$I = F K'_{H^+}([A_{H^+}]^\circ - [A_{H^+}]) \qquad (8)$$

$$I = F(\kappa_1 E_1' [A_{Ha^+}] - \kappa_2 E_2' [A_H]) \qquad (27)$$

$$\kappa_1 E_1' \equiv s \frac{kT}{h} e^{-\Delta F_1/RT} e^{-V_1 F/RT},$$

$$\kappa_2 E_2' \equiv s \frac{kT}{h} e^{-\Delta F_2/RT} e^{V_2 F/RT}$$

where ΔF_1 and ΔF_2 are the free energies of activation of the reduction-oxidation 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. 1). $[A_{Ha^+}]$ is the activity of the hydrogen ion adsorbed on the electrode

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(17) J. Weiss, *Faraday Society Discussion*, No. 1, p. 135 (1947).

(18) P. v. Rysselberghe, *J. Chem. Phys.*, **17**, 1226 (1949).

Table 1

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

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.

surface. According to the assumption mentioned above we can neglect the second term of the right-hand side of Eq. (27) in the potential region of the reduction wave and, therefore, Eq. (27) can be reduced to the following as an approximation:

$$I = F\kappa_1 E_1'[A_{Ha}{}^+] \tag{28}$$

Now, let us assume that the adsorption equilibrium of the Freundlich adsorption isotherm type is kept between the adsorbed ion and the ion in the solution side. It is shown that the Freundlich adsorption isotherm is more satisfactorily applied to the adsorption phenomena in solution than the Langmuir isotherm.(19) 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

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

$$\nu \leqq 1$$

where γ and ν are the constants of adsorption.

From Eqs. (8), (28) and (29) the equation for the current-voltage curve can be obtained as follows:

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

by which it is easily shown that at a sufficiently negative potential the limiting current, which is controlled by the diffusion process and represented by Eq. (12) cited before, appears. If the relation between the electrode potential, V, and the terms, V_1, V_2 and V_a,

$$V = V_1 + V_2 + V_a,\ V_1 + V_a = \alpha' V^{(20)}$$

and Eq. (12) are introduced, the following formula is obtained by rearranging Eq. (30),

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(19) J. N. Brönsted, "Physical Chemistry", William Heinemann Ltd., London, 1937, p. 355.

(20) α' is a proportional constant and is related to α by the following equation: $\alpha' \doteqdot \alpha\{(V-V_a)/V\} + (V_r/V)$, because α can be represented by $V_1/(V_1+V_2)$ in the present case. It is obvious that when V_a is very small α' becomes equal to α.

$$V = \text{const.} - \frac{RT}{\alpha' F}\log\frac{I}{I_l - I} + \frac{RT}{\alpha' F}(\nu - 1)\log(I_l - I) \qquad (31)$$

in which,

$$\text{const.} = \frac{RT}{\alpha' F}\left(-\frac{\Delta F_1}{RT} + \log\gamma + \log s + \log\frac{kT}{h} + \log F - \nu\log(F K'_{H^+})\right)$$

It is quite clear that the relation between V and $\log I/(I_l - I)$ is by no means linear in this case. By using the definition for the half-wave potential, $I = I_l/2$, we can get the relation between $V_{1/2}$ and I_l as follows:

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

in which,

$$\text{const'.} = \frac{RT}{\alpha' F}\left(-\frac{\Delta F_1}{RT} + \log\gamma + \log s + \log\frac{kT}{h} + \log F - \nu\log(F K'_{H^+}) - (\nu - 1)\log 2\right)$$

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

All results on the properties of the current-voltage curve of the hydrogen ion, which are obtained under the various reduction mechanisms, are summarized in Table 1.

Summary

The formulas for the current-voltage curve of the reduction wave of the hydrogen ion under the various mechanisms of the overall deposition process were derived from the standpoint of chemical kinetics. The results on the various properties of the current-voltage curve, — the relation between the half-wave potential and the concentration of the hydrogen ion in the bulk of the solution, the property of the limiting current, and the log-plot analysis of the current-voltage curve—are presented.

It is assumed throughout the present discussion that the processes at the electrode surface, including the diffusion process, are kept in a stationary state, i. e., in a dynamic equilibrium. This assumption seems to be reasonable when the stationary and reproducible current-voltage curve is obtained at the dropping mercury electrode.

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