On the Mechanism of the Reduction Process of the Hydrogen Ion at the Dropping Mercury Electrode. III. Experimental Part —The Half-wave Potential, Log-plot Analysis and the Reversibility of the Wave

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While the properties of the limiting current of the hydrogen wave have been discussed in Part II of the present study,(2) the experimental results and the discussion on the half-wave potential of the hydrogen wave, the reversibility of the reduction process of the hydrogen ion and the other properties of the wave are presented in this paper.

Experiments

Apparatus.—Most of the measurements concerning the electrode potential were carried out by the manually operated polarograph,(2) with which the electrode potential of the dropping mercury electrode (D.M.E.) referred to a certain reference electrode can be directly measured without any correction of the iR-drop.

To study the reversibility of the electrode reaction by Kalousek's methods,(3) a photo-recording polarograph with the special circuit for this method was used. By this apparatus all methods presented by Kalousek can be carried out with a simple operation, the details of which are omitted in the present paper.

The assembly of the electrode and the polarographic cell and the materials used were quite the same as described in Part II of the present study.(2)

The system of the dil. HCl in 0.1 N KCl solution was used throughout the following experiments, because, as shown in Part II, we can obtain a typical polarogram of the hydrogen ion in this system.

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(2) R. Tamamushi, This Bulletin **25**, 293 (1952).

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

Experimental Results

On the Half-wave Potential and the Log-plot

The Log-plot Analysis of the Reduction Wave—The log-plot, i.e. the relation between log $I/(I_1-I)$ and the electrode potential, V, is widely used to analyse the form of the current-voltage curve, where I is the current flowing at V and I_1 the limiting current. In the reduction wave of the hydrogen ion in 0.1 N KCl solution, this relation is not linear and an apparent deviation from a straight line appeared at the more negative potential region than the half-wave poteneial as shown in Fig. 1. It must be noted that this deviation is not clear when the concentration of the hydrogen ion is less than about 0.5 millimole/l. (Fig. 2). At present, it is not clear whether this tendency in the log-plot of the lower concentration of the hydrogen ion is an essential phenomenon or only due to the inaccuracy of the measurement.

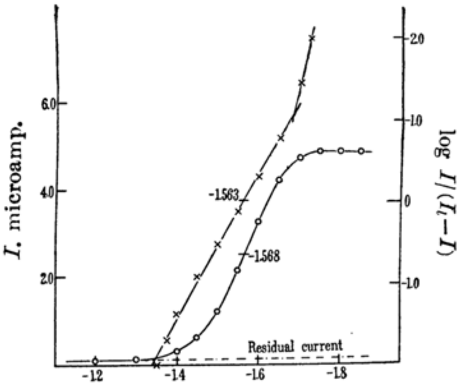

Fig. 1.—Polarogram of the hydrogen ion of dil. HCl in 0.1 N KCl solution and the log-plot analysis of the wave. $[C_H{}^+]^\circ=0.78$ millimole/l.

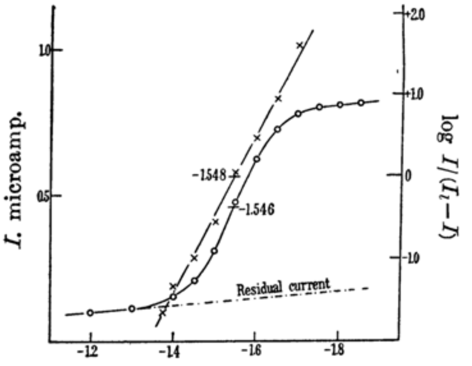

Fig. 2.—Polarogram of the hydrogen ion of dil. HCl in 0.1 N KCl solution and the log-plot analysis of the wave. $[C_H{}^+]^\circ=0.137$ millimole/l.

The Relation between the Half-wave Potential and the Concentration of the Hydrogen Ion.—It was found out by the experiment carried out in 0.1 N KCl-dil. HCl system that the half-wave potential, $V_{1/2}$, of the hydrogen wave changes with the change of the concentration of the hydrogen ion in the bulk of the solution, $[C_{H^+}]^\circ$, or I_1 over the concentration range of 0.039 to 1.95 millimole/l. As $[C_{H^+}]^\circ$ or I_1 became larger, $V_{1/2}$ shifted to be more negative. The experimental results are shown in Table 1 and Fig. 3. From these data we can obtain the following relation between $V_{1/2}$ and I_1 by the least square method:

$$V_{1/2}=-1.687-0.022 \log I_1 \qquad (1)$$

in which I_1 is represented in amp. and $V_{1/2}$ in volt.

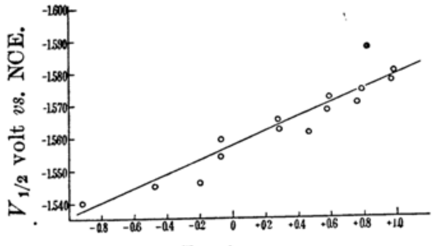

Fig. 3.—The relation between $V_{1/2}$ and log I_l.

The Effect of the Temperature on $V_{1/2}$.—The value of $V_{1/2}$ became more positive as the temperature, τ, of the cell-solution rose over the temperature range of 0 to 50° as shown in Table 2 and Fig. 4. From these data the absolute temperature coefficient of

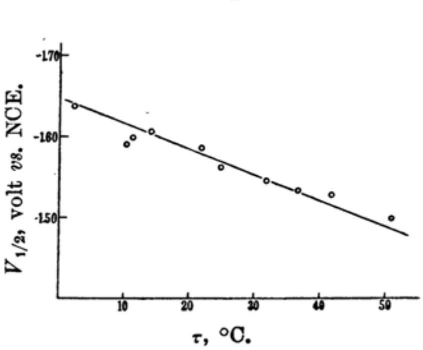

Fig. 4.—The effect of temperature on $V_{1/2}$. $[C_H{}^+]^\circ=0.78$ millimole/l.

$V_{1/2}$, $\Delta V_{1/2}/\Delta\tau$, was obtained to be about 0.003 volt per degree.

The Application of the Kalousek's Methods

In order to examine the reversibility of the electrode process of the hydrogen ion discharge at the D. M. E., the Kalousek's methods—K-I, K-II and K-III—were applied to the solution of 0.52 millimole/l. HCl in 0.1 N KCl solution, the results of which are illustrated in Figs. 5, 6, 7 and 8. The polarograms of the reduction of Pb^{2+} ion in the medinm of KOH solution are also presented in these figures as the typical examples of the application of the Kalousek's methods to a reversible electrode reaction.

It is said that no oxidation current due to the oxidation process of the reduction product of the hydrogen ion at the D. M. E. ever appears in any cases. On the other hand, the apparent oxidation currents appear in the case of the reduction of Pb^{2+} ion in KOH solution.

Discussion

It is shown in Figs. 5∼8 that no oxidation current appeared when the Kalousek's methods were applied to the reduction process of the hydrogen ion at the D. M. E. These results exclude the possibility of the existence of any electrochemically active hydrogen species at the surface of the electrode. If the reduction product can be easily oxidized at the potential region of the reduction wave and does not escape from the electrode surface instantaneously, the oxidation current should appear as in the case of Pb^{2+} ion, when the Kalousek's methods are applied. Under this circumstance, it is impossible to assume the reduction mechanism in which the redox process between H^+ and H is kept in a rapid equilibrium and the recombination process is the slowest step. It seems possible to conclude that probably the current-voltage curve of the hydrogen ion obtained in 0.1 N KCl solution at the D. M. E. is a kind of the activation-controlled type.

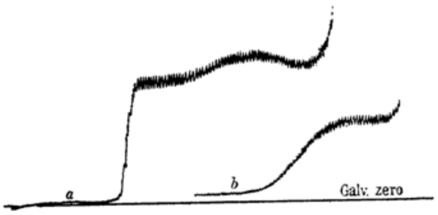

Fig. 5.—Polarograms of Pb^{2+} ion and H^+ ion: a, Pb^{2+} ion in KOH solution; b, 0.52 millimole HCl—0.1 N KCl.

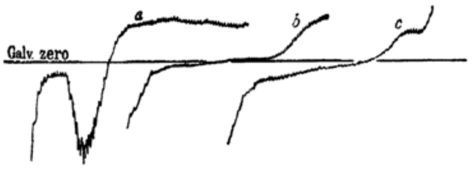

Fig. 6.—Application of the Kalousek's method K-I: a, Pb^{2+} ion in KOH solution, $\Delta V=$ 300 mV.; b, 0.52 millimole HCl—0.1 N KCl, $\Delta V=100$ mV.; c, the same solution as b, $\Delta V=300$ mV.

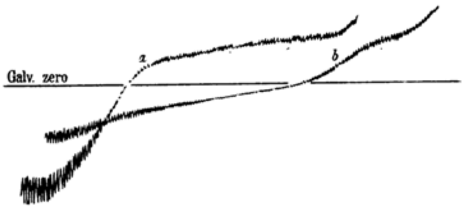

Fig. 7.—Application of the Kalousek's method K-II: a, Pb^{2+} ion in KOH solution, $V_{aux.}=-0.8$ volt; b, 0.52 millimole HCl—0.1 N KCl, $V_{aux.}=-1.9$ volts.

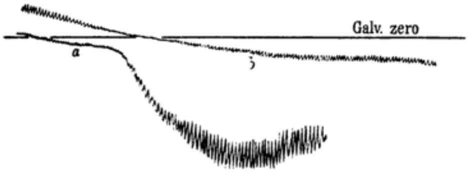

Fig. 8.—Application of the Kalousek's method K-III: a, Pb^{2+} ion in KOH solution, $V_{aux.}=0$; b, 0.52 millimole HCl—0.1 N KCl, $V_{aux.}=-0.6$ volt.

This conclusion is also confirmed by the relatively large temperature coefficient of the half-wave potential, namely about 0.003 volt per degree, because the temperature coefficient of $V_{1/2}$ expected from the diffusion-controlled type is much smaller than the value mentioned above.(4)

In this paper, the activation-controlled type means the process in which the rate constant of the forward reaction of the redox process is much smaller than that of the diffusion process at the potential region, where the forward rate is nearly equal to the reverse one, and the reverse rate of the redox reaction is negligibly small at the electrode potential where the reduction wave appears. On the other hand, we define the process as the diffusion-controlled type when the rate constant

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(4) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Pub. Inc., New York, N. Y., 1946, p. 153.

of the forward or the reverse reaction of the redox process is much larger than that of the diffusion at the electrode potential where the forward rate is nearly equal to the reverse one. As for the details about these points, the previous papers should be referred.⁽⁵⁾

Now, let us consider the relation between the half-wave potential and the limiting current of the hydrogen ion. It was found out that $V_{1/2}$ tends to be more negative as the limiting current increases as shown by Eq. (1). This result does not agree with those of the previous authors, i.e., J. Tomes⁽⁶⁾ reported that the half-wave potential of the hydrogen ion of the diluted solution of HCl in 1 N LiCl or $CaCl_2$ solution becomes to be more positive with the increase of the diffusion current, I_d, according to the relation $\Delta V_{1/2}/\Delta \log I_d = 0.028$ volt, and, quite recently, it was mentioned by J. Kůta⁽⁷⁾ that the half-wave potential of the hydrogen ion in the system, HCl or H_2SO_4 in 0.1 N solution of the supporting electrolyte (KCl, KBr, K_2SO_4 and $BaCl_2$), is independent of the concentration of the acid.

Furthermore, as for the log-plot of the current-voltage curve Kůta stated that this relation is a straight line whose tangent is nearly equal to $2RT/F$, while the present author observed the apparent deviation from a straight line, as shown in Fig. 1 over a certain range of the concentration of the hydrogen ion. 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, because he found experimentally 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 $V_{3/4}$ represent the electrode potentials where $I=1/4\ I_d$ and $I=3/4\ I_d$, respectively. J. Kůta attributed this discrepancy between his results and those of J. Tomes to the possibility of the existence of the maximum of the second kind in 1 N solution of the supporting electrolyte. At any rate, further investigations on the current-voltage curve of the hydrogen ion in the solution of various supporting electrolytes are necessary to make clear these points.

When we consider the results mentioned above, it seems possible to assume the following probable mechanism for the deposition process of the hydrogen ion of the dil. HCl in 0.1 N KCl solution, at the D.M.E.:

$$H^+(\text{surface}) \rightleftharpoons H^+(\text{adsorbed}), \text{ adsorption}$$
$$H^+(\text{adsorbed}) \rightleftharpoons H(\text{surface}), \text{ oxidation-reduction}$$

This means that only the hydrogen ion adsorbed on the electrode surface can be neutralized at the electrode and that the produced hydrogen atom will disappear from the electrode surface by a certain process, e.g., the recombination process giving the hydrogen molecule. It is assumed that there exists an adsorption equilibrium of the Freundlich adsorption isotherm type between H^+ (surface) and H^+ (adsorbed) and that the reduction-oxidation process proceeds under the condition of the activation-controlled type. As in the preceding paper (Part I),⁽⁸⁾ let us call this mechanism the "slow discharge mechanism of the adsorbed hydrogen ion." If we consider that the whole process is kept in a dynamic equilibrium, the equations for the current-voltage curve and for the half-wave potential can be represented as follows, according to the derivation carried out in Part I:

$$V = const. - \frac{RT}{\alpha' F}\log\frac{I}{I_l - I} + \frac{RT}{\alpha' F}(\nu - 1) \times \log(I_l - I) \tag{2}$$

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

$$I_1 = FK'_{H^+}[A_{H^+}]^\circ = FK_{H^+}[C_{H^+}]^\circ \tag{3}$$

and

$$V_{1/2} = \text{const}'. + \frac{RT}{\alpha' F}(\nu - 1)\log I_l \tag{4}$$

$$const'. = \frac{RT}{\alpha' F}\left(-\frac{\Delta F_1}{RT} + \log\gamma + \log s + \log\frac{kT}{h} + \log F - \nu\log(FK'_{H^+}) - (\nu - 1)\log 2\right) \tag{4'}$$

in which K_{H^+} and K'_{H^+} are the constants concerning the diffusion process of the hydrogen ion, $[A_{H^+}]^\circ$ the activity of the hydrogen ion in the bulk of the solution, F the Faraday constant, and s a proportional constant which

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(5) N. Tanaka and R. Tamamushi, This Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, ibid., **22**, 227 (1949).

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

(7) J. Kůta, *Proc. I. International Polarographic Congress in Prague, Part* I, p. 852 (1951).

(8) R. Tamamushi, This Bulletin, **25**, 287 (1952).

can be represented as follows as an approximation[9]:

$$s \cong q \cdot \mu \cdot 10^{-3} \qquad (5)$$

μ: the thickness of the reaction layer at the electrode surface in cm.

q: the surface area of the dropping mercury electrode in cm^2.

α' is also a proportional constant concerning the distribution of the electrode potential at the vicinity of the electrode surface. The terms ν and γ are constants in the equation for the adsorption equilibrium between H$^+$ and H$_a{}^+$,

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

where $[A_{Ha}{}^+]$ and $[A_H{}^+]$ mean the equilibrium activities of the hydrogen ion adsorbed on the electrode and at the electrode surface (solution side), respectively, and V_a is the electrical potential difference between the adsorbed state and the solution side.

As ν is generally less than unity, it is quite obvious from Eq. (4) that the half-wave potential shifts to more negative potential as the limiting current increases and this is in accordance with the experimental results obtained by the present author. Moreover, the same tendency in the log-plot analysis of the current-voltage curve, which showed a deviation from a straight line, can be expected from Eq. (2).

The values of the constants, α' and ν, can be obtained from the experimental data on the current-voltage curve by the following method: Eq. (2) is rewritten as follows:

$$-V = a_0 + a_1 A + a_2 B \qquad (6)$$

$$A \equiv \frac{RT}{F}\log\frac{I}{I_l - I}, \quad B \equiv \frac{RT}{F}\log(I_l - I)$$

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

The values of a_1 and a_2 are obtained by the application of the least square method. It is natural that these values change with the change of the unit of the current as well as the change of the value of the reference electrode to which the electrode potential is referred, if the least square method is applied to Eq. (6). To avoid this effect due to the change of the unit, the least square method was applied to the following equation instead of Eq. (6):

$$\begin{aligned} \Delta V_i &= a_1 \Delta A_i + a_2 \Delta B_i \qquad (7) \\ \Delta V_i &= -V_{i+1} - (-V_i) \\ \Delta A_i &= A_{i+1} - A_i \\ \Delta B_i &= B_{i+1} - B_i \end{aligned}$$

From the normal equations of Eq. (7), the next relations are derived:

$$a_1 \sum_i (\Delta A_i)^2 + a_2 \sum_i (\Delta A_i \Delta B_i) - \sum_i (\Delta V_i \Delta A_i) = 0$$

$$a_1 \sum_i (\Delta A_i \Delta B_i) + a_2 \sum_i (\Delta B_i)^2 - \sum_i (\Delta V_i \Delta B_i) = 0$$

from which we can easily calculate α' and ν.

Let us consider the meaning of the constant term, a_0, in Eq. (6) more closely. As shown in Eq. (2'), this constant term involves the free energy of activation of the forward process of the redox reaction, ΔF_1, and the constant γ of the equation of the adsorption equilibrium. According to the theoretical derivation of the Freundlich adsorption isotherm,[10] γ and ν can be represented as follows:

$$\gamma = \exp\left(\frac{f'(T)}{RT} + \frac{1}{i} - 1\right) \qquad (8)$$

$$\nu = \frac{1}{i} \qquad (9)$$

where i is a constant in the equation of state for the adsorbed layer, namely, $FA = iRT$, in which F is the surface pressure and A the surface area. $f'(T)$ is a function of the temperature and can be considered to be equal to the free energy of adsorption, $-\Delta F_a$ (Fig. 1 in Part I). If we ignore the term $\frac{1}{i} - 1$ against $f'(T)/RT$, Eq. (8) is reduced to

$$\gamma = \exp(-\Delta F_a / RT) \qquad (8')$$

From Eps. (2') and (8') the following equation for the constant, a_0, is obtained:

$$a_0 = -\frac{\overrightarrow{\Delta F}}{\alpha' F} - \frac{\nu RT}{\alpha' F}\log(FK'_H) + \frac{RT}{\alpha' F}\log F + \frac{RT}{\alpha' F}\log s + \frac{RT}{\alpha' F}\log\frac{kT}{h} \qquad (10)$$

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

where $\overrightarrow{\Delta F}$ is the difference of the free energy

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[9] R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947).

[10] B. Tamamushi, This Bulletin, **9**, 363 (1934).

between the activated state of the redox process, $H^+(\text{adsorbed}) \rightleftarrows H(\text{surface})$, and the solution side, S, in Fig. 1 of Part I, and can be considered as the free energy of activation of the overall discharge process of the hydrogen ion, $H^+(\text{solution}) \rightarrow H(\text{surface})$. If we assume that FK'_{H^+} is nearly equal to FK_{H^+}, the terms α', ν and FK'_{H^+} in Eq. (10) can be obtained from the experimental data. The constant, s, which is represented by Eq. (5), is also calculated from the experimental results by using the following expression for the mean surface area of the dropping mercury electrode:

$$q = \frac{3}{5} \times 0.85 \times m^{2/3} t^{2/3} \quad (\text{cm.}^2) \qquad (11)$$

in which m is the weight of mercury in gram flowing from the capillary per second and t the drop-time of one drop in second. In the present calculation the thickness of the reaction layer at the electrode surface, μ, is assumed to be approximately equal to 10^{-7} cm. according to R. Brdicka.$^{(9)}$ When we use these values and $kT/h = 6 \times 10^{12}$, $\overrightarrow{\Delta F}$ can be calculated from the constant, a_0, obtained from Eq. (6). In this case, the current is expressed in amperes and the value of the electrode potential referred to a normal calomel electrode is employed.

The numerical values of α', ν and $\overrightarrow{\Delta F}$ obtained from each current-voltage curve are shown in Tables 1 and 2. The values of α' are in the range of 0.4 to 0.6, however, those of ν diverge over the range of 0.4 to 1.0. When 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 the solution, these diverging values of ν seem to be rather reasonable. The fairly good constancy of the values of $\overrightarrow{\Delta F}$, which were obtained under the various conditions, can be considered as one of the experimental results which prove the correctness of the present discussion on the discharge process of the 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 Eqs. (4) and (4′). If we assume the value of either one of α' and ν, the other is automatically determined, because the relation, $(\nu-1)/\alpha'$, can be obtained from Eq. (4). According to Eq. (1) we get the following relation between α' and ν:

$$\frac{\nu-1}{\alpha'} = -0.37$$

If we assume that α' is nearly equal to 0.5, the value of $\overrightarrow{\Delta F}$ is calculated to be equal to about 29.8 kcal./mol. by this method, which is in good agreement with the values mentioned in Tables 1 and 2.

Table 1

The Effect of the Concentration of the Hydrogen Ion on the Reduction Wave

$[C_{H^+}]^\circ$, millimole/l.	I_l, microamp.	$V_{1/2}$, volt vs. NCE.	α'	ν	$\overrightarrow{\Delta F}$, cal.
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

Table 2

The Effect of Temperature on the Reduction Wave of the Hydrogen Ion

Temp. τ, °C.	I_l, microamp.	$V_{1/2}$, volt. vs. NCE	α'	ν	$\overrightarrow{\Delta F}$, cal.
$[C_{H^+}]^\circ = 0.78$ 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
$[C_{H^+}]^\circ = 1.95$ 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 (?)

At the end of this discussion a brief consideration about the effect of the height of the mercury reservior, p, on the half-wave potential, $V_{1/2}$, is set down. In 1937, J. Novak$^{(11)}$

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(11) J. Novak, *Collection Czechoslov. Chem. Communs.*, **9**, 207 (1937).

reported that the double increase of p causes a shift of $V_{1/2}$ to a more negative potential by 13 millivolts, while quite recently J. Kůta⁽⁷⁾ found that this shift is equal to 18 millivolts. This change of $V_{1/2}$ with the change of p can be expected from Eqs. (4) and (4′). In these equations the terms, $\log I_l$ and $\log(FK'_{H^+})$, which are approximately equal to $\log(FK_{H^+})$, are the functions of p. The term, $\log s$, is independent of p, because it is proportional to $m^{2/3}t^{2/3}$ which is independent of p. As pointed out in Part II of this work,⁽²⁾ the limiting current of the hydrogen ion in the present case is equal to the diffusion current, I_d, and, according to the Ilkovic equation, it is represented by the relation:

$$I_d = FK_{H^+}[C_{H^+}]^\circ = Kp^{1/2}[C_{H^+}]^\circ \qquad (12)$$

where K means a constant independent of p. If the revised Ilkovic equation⁽¹²⁾ is used instead of the Ilkovic equation, an additive constant term independeut of p appears in Eq. (12), but we can ignore this constant term as an approximation in the present discussion. By means of these relations, the following relation between $V_{1/2}$ and p can be derived:

$$V_{1/2} \fallingdotseq \text{const.}(p) - \frac{RT}{2\alpha' F}\log p \qquad (13)$$

in which const.(p) is a constant independent of p. As α' is generally equal to 0.4–0.6, it is said from Eq. (13) that $V_{1/2}$ shifts to more negative potential by about 18 millivolts with the double increase of p in accordance with Kůta's experemental results. In this discussion it is assumed that α' and ν are independent of p.

As described above it is obvious that all the result on the current-voltage curve of the hydrogen ion, which was obtained in the present experiment, can be satisfactorily interpreted by assuming the neutralization of the adsorbed hydrogen ion under the condition of the activation-controlled process. Under these circumstances it can be concluded that the discharge process of the hydrogen ion of the dilute hydrochloric acid in 0.1 N KCl solution may proceed according to the "slow discharge mechanism of the adsorbed hydrogen ion."

Summary

Various properties of the current-voltage curve of the reduction wave of the hydrogen ion were studied in the system of the dil. HCl in 0.1 N KCl solution.

It was found out that the log-plot of the reduction wave is not linear and that the half-wave potential shifts to be more negative with the increase of the limiting current.

The temperature coefficient of the half-wave potential was obtained to be about 3 millivolts per degree over the temperature range of 0 to 50°. This value of the temperature coefficient is much larger than the value which is expected when the reduction process of the hydrogen ion proceeds under the condition of the diffusion-controlled type.

The Kalousek's methods were applied to the hydrogen wave in order to test the reversibility of the reduction process and it was shown that this process is one of the irreversible type.

These experimental results were satisfactorily explained by assuming the reduction process of the hydrogen ion as follows: First, the hydrogen ion is adsorbed on the surface of the D. M. E., and, next, the adsorbed hydrogen ion is neutralized to the hydrogen atom under the condition of the activation-controlled process. In this case it was assumed that the equilibrium state represented by the Freundlich adsorption isotherm exists between the hydrogen ion in the neighborhood of the electrode surface and the adsorbed hydrogen ion in the adsorbed layer.

The value of the free energy of activation of the overall discharge process of the hydrogen ion was calculated.

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