On the Mechanism of the Reduction Process of the Hydrogen Ion at the Dropping Mercury Electrode. II. Experimental Part — The Limiting Current of the Hydrogen Wave

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In the theoretical part of this work(2) the formulas for the current-voltage curve of the reduction wave of the hydrogen ion have been studied from the standpoint of the chemical kinetics and the theoretical considerations on the properties of the reduction wave have been presented. In this paper the experimental results and the discussion on the limiting current of the hydrogen ion are set down.(3)

Experimental

Apparatus:—A Heyrovsky-Shikata type photo-recording polarograph and a manually operating

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

(3) Recently, the discussion on the hydrogen wave was reported by J. Kůta in the Proceedings of the I. International Polarographic Congress in Prague, Part I, p. 852 (1951).

polarograph similar to that used by J. J. Lingane and I. M. Kolthoff(4) were used. An over-damped galvanometer was used to measure the polarographic current.

A specially designed all-glass polarographic cell as shown in Fig. 1 was used throughout this study to avoid the contamination from the rubber connection. The anode was a large area mercury pool connected with the cell-solution by the saturated KCl solution and a h-type sat. KCl-agar-bridge. The reference electrode for the measurement of the electrode potential of the D.M.E. was a normal calomel electrode connected with the cell-solution by 1N KCl solution and a h-type sat. KCl-agar-bridge. The part **be** of a h-type bridge was filled with a sat. KCl-agar and the cell-solution was sucked into 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 great extent. The liquid junction potential may be greatly reduced by the use of saturated KCl.

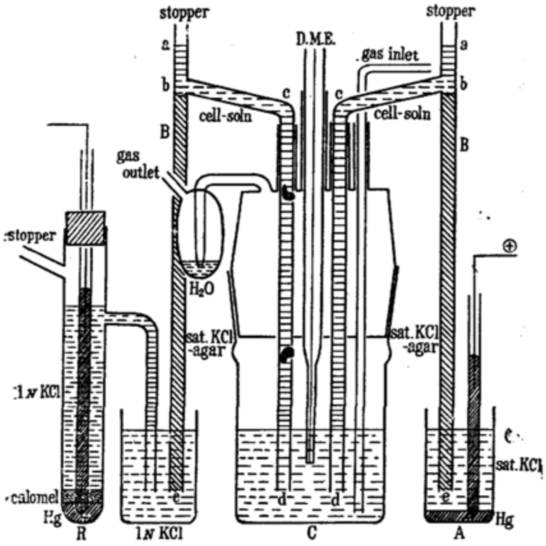

Fig. 1.—All-glass polarographic cell assembly: A: anode; B: h-type sat. KCl-agar-bridge; C, polarographic cell; R: reference electrode (N. C. E.).

The capillary constant, $m^{2/3}\,t^{1/6}$, of the dropping mercury electrode, which was used throughout the present experiment, was 1.028 mg.$^{2/3}$ sec.$^{-1/2}$ at the height of the mercury reservior of 53 cm. This value was determined in 0.1N KCl solution open to air without the applied potential.

The dissolved oxygen was removed from the cell-solution by bubbling pure hydrogen gas obtained by the electrolysis of a NaOH solution for about 40 minutes.

A water or a liquid-paraffin thermostat maintained at 25.0° was used throughout the experiments except when the effect of the temperature on the reduction wave of the hydrogen ion was examined.

Materials:—The pure mercury, which was distilled under vacuum after washing several times with dil. HNO_3 solution and dist. water, was used for the dropping mercury electrode. As a supporting electrolyte 0.1N KCl solution was used in the present study. The potassium chloride used was recrystallized from dist. water. Reagent grade HCl and Fixanal HCl were used to make a stock solution, the composition of which is 0.1N KCl–0.01N HCl. No maximum suppressor was used. The concentration of HCl in the original solution was determined by the acid-base titration.

Experimental Results

A typical polarogram with a well-defined limiting current was obtained with the dil. solution of HCl in 0.1N KCl solution, which is due to the deposition of the hydrogen ion of HCl. The various properties of the limiting current, I_l, of the hydrogen ion,—i. e., the relation between I_l and the concentration of the hydrogen ion, $[C_{H^+}]^\circ$, in the bulk of the solution, the relation between I_l and the height of the mercury reservoir, p, the temperature coefficient of I_l, etc.—were studied in this medium.

The Relation between I_l and $[C_{H^+}]^\circ$.—This relation is represented by a straight line as shown in Fig. 2 over the concentration range of the hydrogen ion from 0.039 to 1.95 millimole per liter. It is obvious that the relation between I_l and $[C_{H^+}]^\circ$ is represented as follows:

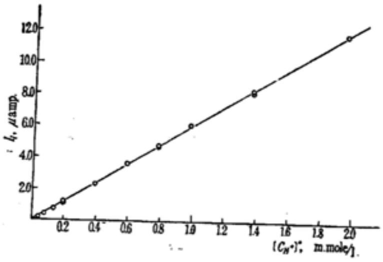

Fig. 2.—The relation between I_l and $[C_{H^+}]^\circ$ at 25°C.

$$I_l = a[C_{H^+}]^\circ \qquad (1)$$

$$a = 6.04 \text{ microamp./millimole/l.}$$

The value of a is calculated from the experimental data with the least square method.

The Temperature Coefficient of I_l.—The effect of the temperature of the cell-solution

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(4) J. J. Lingane and I. M. Kolthoff, *J. Am. Chem. Soc.*, **61**, 825 (1939).

Table 1

Temperature Coefficient of I_l.

Temp. τ, °C.	I_l, microamp.	$\mathrm{d}I_l/\mathrm{d}\tau$, microamp./°C.	$(1/I_l)(\mathrm{d}I_l/\mathrm{d}\tau)$, %	$\mathrm{d}\log I_l/\mathrm{d}\tau$, %
$[C_{H^+}]^\circ=0.78$ 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

on the limiting current was studied over the temperature range of 0 to 50°, the results of which are shown in Table 1 and Fig. 3. In Table 1, the term $[\mathrm{d}\log I_l/\mathrm{d}\tau]$ represents a tangent of the relation between $\log I_l$ and the temperature, τ, at any temperature, and this is called as the "relative temperature coefficient", while the term $\mathrm{d}I_l/\mathrm{d}\tau$ represents the "absolute temperature coefficient".

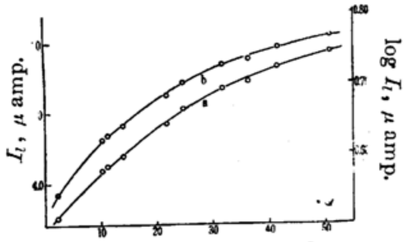

Fig. 3.—The effect of temperature on I_l: a, I_l vs. τ; b, $\log I_l$ vs. τ. $[C_{H^+}]^\circ=0.78$m. mole/l.

The Relation between I_l and p.—In order to examine whether the limiting current of the hydrogen ion under the present condition is controlled only by the diffusion process or not, the experiment on the relation between I_l and was carried out. As shown in Fig. 4, the relation between I_l and $\sqrt{p}$ is linear and represented by the following equation:

$$I_l=0.76\sqrt{p}+2.0 \text{ (microamp.)} \qquad (2)$$

The value of p is corrected with the back pressure, p_b, which is calculated by the following relation: (5)

$$p_b=\frac{7.73\times10^{-3}\sigma}{m^{1/3}t^{1/3}}=\frac{3.1}{m^{1/3}t^{1/3}} \text{ (cm.)} \qquad (3)$$

$$\sigma=400 \text{ dyne cm.}^{-1}$$

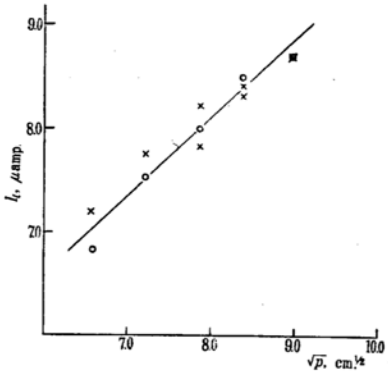

Fig. 4.—The relation between I_l and $\sqrt{p}$: ○, data obtained by the manual apparatus; ×, data obtained by the Heyrovsky-Shikata type polarograph.

where σ is the surface tension of mercury in the electrolyte solution, m the weight of mercury in mg. flowing from the capillary per second, and t the drop-time of one drop in second. If the experimental value, $m^{1/3}t^{1/3}=1.50$, is used, p_b is equal to 2.1 cm. It is apparent from Eq. (3) that p_b is independent of p, because $m^{1/3}t^{1/3}$ is independent of p. It is to be noted here that, when the value of p is changed from about 40 cm. to about 80 cm., the term $t\times p$ is kept nearly constant as shown in Table 2.

Table 2

p, cm.	t, sec.	$p\times t$
80.1	2.98	238
70.2	3.40	238
61.6	4.06	250
51.9	4.56	236
43.4	5.54	240

The Relation between the Diffusion-current Constant and t.—If we assume that the limiting current of the hydrogen ion is

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(5) I. M. Kolthoff and J. J. Lingane, "Polarography", Interscience Pub. Inc., New York, N. Y., 1946, p. 67.

equal to the diffusion current, I_d, it is possible to obtain the relation between the diffusion-current constant, $I_d/m^{2/3}t^{1/6}$, and t from the experiment which was carried out to investigate the relation, I_l vs. $\sqrt{p}$. The value of m at each drop-time, t, can be calculated by assuming the following equation:

$$m = \text{const.} \times p \qquad (4)$$

The value of the constant in Eq. (4) was obtained by inserting the experimental data, $m=0.708$ mg./sec. at $p=52.0$ cm., into this equation.

The result obtained is shown in Fig. 5. It can be said that the diffusion-current constant is not independent of t, but it increases almost linearly with the increase of t over the range of t from 3 to 6 seconds. The diffusion-current constant also is not independent of the term, $m^{-1/3}t^{1/6}$, as shown in Fig. 6.

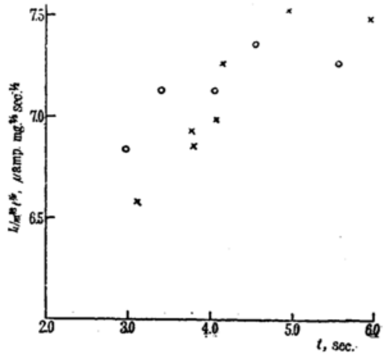

Fig. 5.—The relation between the diffusion current constant and t.

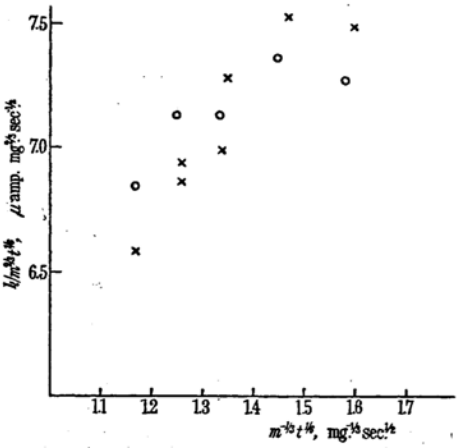

Fig. 6.—The relation between the diffusion current constant and $m^{-1/3}t^{1/6}$.

Discussion

There are several kinds of limiting currents in polarography, i. e., the diffusion current, the kinetic current,(6) the adsorption current(7) and the combination of these currents. The diffusion current, I_d, is represented as follows according to Ilkovic equation (6) or revised Ilkovic equation (7):(8)

$$I_d=605\, nCD^{1/2}m^{2/3}t^{1/6} \qquad (6)$$

$$I_d=605\, nCD^{1/2}m^{2/3}t^{1/6}\left(1+\frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right) \qquad (7)$$

where n is the number of the electrons which participate in the redox reaction, C the concentration of the oxidant or the reductant in millimole per liter, D the diffusion coefficient of the corresponding substance in the medium under investigation in cm.^{2} per second, m the weight of mercury flowing from the D. M. E. per second in mg., and t the drop-time in second. In Eq. (7) A is a constant and equal to 39 or 17 according to Lingane-Loveridge and Kambara-Tachi or Strehlov-Stackelberg, respectively.

It is well known that the kinetic current is independent of the height of the mercury reservior, p,(6) and the diffusion current is proportional to the square root of p as readily shown from the Ilkovic equation. Revised Ilkovic equation (7) requires that the relation between I_l and p is represented as follows:

$$I_l=a_0+a_1\sqrt{p} \qquad (8)$$

where a_0 and a_1 are constants. This relation is quite the same as Eq. (2) obtained from the experiment.

By means of Eq. (7) the constant term, a_0, in Eq. (8) can be written as follows:

$$a_0=605\, nADCm^{1/3}t^{1/3}$$

If we use the following numerical values obtained under the present experimental conditions,

$m=0.708$ mg./sec., $t=4.56$ sec.
$D_{H^+}=8.0\times10^{-5}$cm.^{2}/sec., $C=1.30$ millimole/l.

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(6) R. Brdicka and K. Wiesner, *Collection Czechoslov. Chem. Communs.*, **12**, 138 (1947); J. Koutecky and R. Brdicka, ibid., **12**, 337 (1947).

(7) R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 522 (1947).

(8) 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).

the constant, a_0, is equal to 3.6 microamp. or 1.6 microamp. according to $A=39$ or $A=17$, respectively. In this calculation it is assumed that n equals one. The value of D_{H^+}—the diffusion coefficient of the hydrogen ion in 0.1 N KCl solution—will be discussed later. The experimental value, $a_0=2.0$ microamp., is in fairly good agreement with the theoretical value mentioned above.

Furthermore, the experimental result, that the diffusion-current constant is not independent of t or $m^{-1/3}t^{1/6}$ as shown in Figs. 5 and 6, suggests that it is more appropriate to use Eq. (7) for the diffusion current of the hydrogen ion rather than Eq. (6). From the slope of the relation between the diffusion-current constant and the term, $m^{-1/3}t^{1/6}$, we can obtain the value of A in Eq. (7). If the value of 8.0×10^{-5} cm.²/sec. is used for D_{H^+} in 0.1 N KCl solution, A is calculated to be equal to about 35, and this value is quite reasonable.

From these results it seems probable to consider that the limiting current of the hydrogen ion in 0.1 N KCl solution is the diffusion current which is represented by Eq. (7).

This conclusion is also confirmed by the temperature coefficient of I_l. If the limiting current of the hydrogen ion is controlled by some other processes different from the diffusion process, *e. g.*, if I_l is equal to the kinetic current, the temperature coefficient of I_l will be much larger than those in Table 1. When it is assumed 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 temperature coefficient of the diffusion current can be calculated as follows from the Ilkovic equation:⁽⁹⁾

$$\left[\frac{1}{I_d}\frac{\mathrm{d}I_d}{\mathrm{d}T}\right]_{298}=0.0053+\left[\frac{1}{2\lambda^\circ}\frac{\mathrm{d}\lambda^\circ}{\mathrm{d}T}\right]_{298}.^{(10)} \tag{9}$$

According to B. B. Owen and F. H. Sweeton,⁽¹¹⁾ the temperature coefficient of λ° of the hydrogen ion at 25° is equal to 0.015, so we can obtain from Eq. (9) the temperature coefficient of I_l of the hydrogen ion as follows:

$$\left[\frac{1}{I_d}\frac{\mathrm{d}I_d}{\mathrm{d}T}\right]_{298}\doteqdot 0.013. \tag{10}$$

The result obtained from Eq. (7) differs from that of the Ilkovic equation only by the additional correction term,

$$\begin{aligned}&\frac{\mathrm{d}\log(1+AD^{1/2}m^{-1/3}t^{1/6})}{\mathrm{d}T}\\&=\frac{AD^{1/2}m^{-1/3}t^{1/6}}{1+AD^{1/2}m^{-1/3}t^{1/6}}\left\{\frac{1}{2}\left(\frac{1}{\lambda^\circ}\frac{\mathrm{d}\lambda^\circ}{\mathrm{d}T}\right.\right.\\&\left.\left.+\frac{1}{T}\right)+\frac{1}{6t}\frac{\mathrm{d}t}{\mathrm{d}T}-\frac{1}{3m}\frac{\mathrm{d}m}{\mathrm{d}T}\right\}\\&\doteqdot\frac{AD^{1/2}m^{-1/3}t^{1/6}}{1+AD^{1/2}m^{-1/3}t^{1/6}}\left\{\frac{1}{2}\left(\frac{1}{\lambda^\circ}\frac{\mathrm{d}\lambda^\circ}{\mathrm{d}T}\right.\right.\\&\left.\left.+\frac{1}{T}\right)-\frac{1}{3m}\frac{\mathrm{d}m}{\mathrm{d}T}\right\},\end{aligned}$$

where $\dfrac{1}{6t}\dfrac{\mathrm{d}t}{\mathrm{d}T}$ is neglected. By considering this correction term the temperature coefficient of I_d at 25° becomes to be 0.015, when $A=39$ and $\left[\dfrac{1}{m}\dfrac{\mathrm{d}m}{\mathrm{d}T}\right]_{298}\doteqdot 0.0037$ are used.

These results derived from Eqs. (7) and (6) are in comparatively good agreement with the experimental value, about 0.010, at 25°.

Under these circumstances, if we use Eq. (1) and Eq. (6) or (7), the values of n in Eqs. (6) and (7) are obtained as follows:

$n=1.09$ (The Ilkovic equation)
$n=0.72$ (The revised equation, $A=39$)
$n=0.89$ (Tht revised equation, $A=17$).

In the calculation of n the diffusion coefficient of the hydrogen ion in 0.1 N KCl solution was assumed to be equal to 8.0×10^{-5} cm.²/sec. These results prove the assumption that n is equal to one in the reduction process of the hydrogen ion at the D. M. E.

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 Eq. (6) or (7), i. e.,

$D_{H^+}=9.5\times10^{-5}$ cm.²/sec. (Eq. (6))
$D_{H^+}=4.8\times10^{-5}$ 〃 (Eq. (7), $A=39$)
$D_{H^+}=6.6\times10^{-5}$ 〃 (Eq. (7), $A=17$).

To calculate the value of D_{H^+} from Eq. (7), the following relation was used:

$$D^{1/2}=\frac{-a_2+\sqrt{a_2^2+4a_1a_0}}{2a_1}$$
$$a_0=I_d/C$$
$$a_1=605\,Am^{1/3}t^{1/3}$$
$$a_2=605\,m^{2/3}t^{1/6}.$$

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(9) I. M. Kolthoff and J. J Lingane, "Polarography", Interscience Pub. Inc., New York, N. Y., 1946 p. 74.

(10) 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°, $(\mathrm{d}I_l/\mathrm{d}T)_{298}$, by I_l at 25° (Table 1, column 4).

(11) B. B. Owen and F. H. Sweeton, *J. Am. Chem. Soc.*, **63**, 2811 (1941).

The diffusion coefficient of the hydrogen ion, D_{H^+}, in 0.1 N KCl solution, which was employed in the above calculations concerning the limiting current, was computed by the Onsager's limiting law for the diffusion coefficient.(12) As the concentration of the diffusing ion is generally very small in comparision with that of the supporting electrolyte whose composition is sensibly constant in the polarographic measurements, the diffusion coefficient of the hydrogen ion under the present condition can be represented as follows according to this law:

$$D_{H^+}=\frac{\lambda^\circ{}_{H^+}RT}{|Z_{H^+}|F^2}\times 10^{-7}-\frac{\lambda^\circ{}_{H^+}|Z_{H^+}|v^2\mathcal{E}}{3D}$$

$$\times 10^{-9}\sqrt{\frac{4\pi}{1000DRT}}\left(1-\sqrt{\mathrm{d}(\omega_{H^+})}\right)\sqrt{\Gamma}$$

$$\mathrm{d}(\omega_{H^+})=\left(\frac{|Z_{H^+}|}{|Z_{K^+}|+|Z_{Cl^-}|}\right)$$

$$\times\left(\frac{|Z_{K^+}|\lambda^\circ{}_{K^+}}{|Z_{H^+}|\lambda^\circ{}_{K^+}+|Z_{K^+}|\lambda^\circ{}_{H^+}}\right.$$

$$\left.+\frac{|Z_{Cl^-}|\lambda^\circ{}_{Cl^-}}{|Z_{H^+}|\lambda^\circ{}_{Cl^-}+|Z_{Cl^-}|\lambda^\circ{}_{H^+}}\right)$$

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

$$\doteqdot C_{K^+}Z^2{}_{K^+}+C_{Cl^-}Z^2{}_{Cl^-}$$

where λ° is the ionic conductance of the corresponding ion, Z the valency, C the concentration in mole per liter, R the gas constant per mole, T the absolute temperature, F the Faraday constant, D the dielectric constant, v the velocity of light, and $\mathcal{E}$ the electric charge. In the present calculation the following numerical values were used.

$$\lambda^\circ{}_{H^+}=349.8,\quad \lambda^\circ{}_{K^+}=73.52,\quad \lambda^\circ{}_{Cl^-}=76.34$$

$$Z_{H^+}=Z_{K^+}=Z_{Cl^-}=1,\quad C_{K^+}=C_{Cl^-}=0.1$$

$$R=8.314\times 10^7,\quad T=298,\quad F=96500$$

$$D=78.55,\quad v=3.0\times 10^{10},\quad \mathcal{E}=4.80\times 10^{-10}.$$

Although the agreement between the theoretical predictions of the Onsager's limiting law and the experimental results is not exact and is only reasonably satisfactory as stated by L. J. Gosting and H. S. Harned,(12) it seems to be more appropriate to use this limiting law rather than the Nernst equation for the diffusion coefficient of the individual ion in the polarographic study. A systematic investigation may be necessary to answer the question: "By which theoretical relation can the diffusion coefficient under the condition of the polarographic study be most adequately computed?"

According to the discussion carried out in the present paper, it can be concluded that the limiting current of the hydrogen ion in the system of dil. HCl in 0.1N KCl solution is controlled by the diffusion process of the hydrogen ion and it is represented by the revised Ilkovic equation. Under these conditions we can apply the theoretical results on the current-voltage curve obtained in the theoretical part(2) of the present study to the actual hydrogen wave, because each mechanism, which was assumed for the reduction process of the hydrogen ion in the theoretical part, requires the limiting current controlled by the diffusion process.

Summary

The properties of the limiting current of the reduction wave of the hydrogen ion were studied in the system of dil. HCl in 0.1 N KCl solution.

The relation between the limiting current and the concentration of the hydrogen ion in the bulk of the solution was linear, and the experimental relation between the limiting current and the height of the mercury reservior was interpreted by the revised Ilkovic equation.

It was shown that the temperature coefficient of the limiting current is nearly equal to 1.0 % at 25° which is in agreement with the theoretical value computed from the revised Ilkovic equation.

From these results it was concluded that the limiting current of the hydrogen ion obtained under the present condition is controlled by the diffusion process of the hydrogen ion.

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(12) Louis J. Gosting and Herbert S. Harned, *J. Am. Chem. Soc.*, **73**, 159 (1951).