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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 10(2), 153-164
Issue Date	1962-10
Doc URL	http://hdl.handle.net/2115/24759
Type	bulletin (article)
File Information	10(2)_P153-164.pdf



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ON THE MECHANISM OF HYDROGEN ELECTRODE REACTION ON PLATINUM

By

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(Received Oct. 27, 1962)

Abstract

Exchange reaction between pure deuterium and light water, P_2O , on platinum catalyst was conducted in acidic solutions and in pure water under a strong stirring, and the resultant exchange between deuterium and water, and extent of equilibration $r \equiv [PD]/[PD]_{eq}$ were observed, where $[PD]$ is the concentration of PD in gas and $[PD]_{eq}$ that in the same gas brought to equilibrium of $P_2 + D_2 = 2 PD$.

The r must be zero or unity according as the intermediate of the hydrogen electrode reaction is in equilibrium either with water as in the case of catalytic and electrochemical mechanisms or with hydrogen gas as in the case of the slow discharge mechanism; this proposition is subject to the conditions that the exchange reaction is governed by the appropriate heterogeneous reaction on the catalyst's surface but not by any transport process and that the equilibration $P_2 + D_2 = 2 PD$ as well as the exchange reaction is effected solely by hydrogen electrode reaction but not by any other reaction, *e.g.* that of RIDEAL-ELEY mechanism, which concurrently results in the equilibration but not the exchange reaction by itself (called simply other reaction in what follows).

The apparent heat of activation of the exchange reaction showed that the rate is purely governed by the heterogeneous reaction on the catalyst under a certain condition. Under this condition r was found zero in acidic solutions, from which it follows that either the catalytic or the electrochemical mechanism, but not the slow discharge mechanism, is operative, with a predominant rate over that of the other reaction, if any. An appreciable pH effect upon the exchange rate observed excludes now the catalytic mechanism. The r was found on the other hand somewhere between zero and unity in pure water, which indicates either that the electrochemical mechanism is operative but not with predominant rate over that of the other reaction or that the intermediate of the hydrogen electrode reaction is not in equilibrium with water as in the case of the electrochemical or the catalytic mechanism. The electrochemical mechanism alone thus fits in with these experimental results on platinum at least in acidic solutions.

Introduction

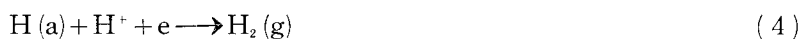
The mechanism of hydrogen electrode reaction on platinum is still in

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dispute. The overall reaction



may consist of various combinations of the following elementary reactions



where e is a metal electron, H^+ is proton associated with BRÖNSTED base B, H_2O or OH^- , and (a) and (g) indicate the adsorbed state and gaseous state, respectively. In earlier works, Frumkin¹⁾ and others^{2,3)} concluded the proton discharge mechanism (rate-determining (2) with $\text{B}=\text{H}_2\text{O}$ followed by rapid (3)). The water discharge mechanism (rate-determining (2) with $\text{B}=\text{OH}^-$ followed by rapid (3)) was suggested from a common value of pre-exponential factors of hydrogen electrode reaction rates on various metals by EYRING *et al.*⁴⁾, but the experimental fact was shown by HORIUTI *et al.*⁵⁾ not to evidence the mechanism. From studies on overpotential-current density relationship (TAFEL relation), BOCKRIS *et al.*^{6,7,8)} concluded the catalytic mechanism (rapid (2) followed by rate-determining (3)) except at extremely high overpotentials^{7,8)}, but SCHULDINER⁹⁾ suggested from studies on pH effect upon the TAFEL relations that this is true only near equilibrium but the mechanism changes to ion + atom mechanism (rapid (2) followed by rate-determining (4)) at moderately high overpotentials. The latter mechanism was originally suggested by HORIUTI and OKAMOTO¹⁰⁾ and HORIUTI, KEII and HIROTA¹¹⁾ have later amended it as hydrogen molecule-ion mechanism (rapid (5) followed by rate-determining (6)) on the ground of quantum mechanical calculations¹¹⁾ and on its basis accounted for the TAFEL relation^{11,12)}, the isotopic separation factor of deuterium¹¹⁾ and its dependence upon overpotentials on platinum electrode¹³⁾. Both the proton discharge and the water discharge mechanisms will be termed together the slow discharge mechanism hereafter in this paper. The last two mechanisms, *i. e.* ion + atom and hydrogen molecule-ion mechanisms will also be termed together the electrochemical mechanism, as they are hardly distinguishable kinetically and this name is frequently used in literatures for both the mechanisms; (4) will be included in (6) in accordance with this presentation in what follows.

The slow discharge mechanism and the catalytic or the electrochemical mechanism are now discriminable by conducting an exchange reaction between

pure deuterium and light water in the presence of an electrode material as catalyst, provided that the heterogeneous reaction on the catalyst's surface itself governs the rate, and that the equilibration



where P is light hydrogen atom, is effected solely by the hydrogen electrode reaction but not by any other reaction *e.g.* the reaction of RIDEAL-ELEY mechanism¹⁰⁾ which concurrently results in the equilibration but not the exchange reaction by itself between hydrogen gas and water.

If the slow discharge mechanism is operative, the intermediate H(a) is in quasi-equilibrium with the gas phase, and hence hydrogen in gas must be in equilibrium of (7), and in consequence the quantity $[PD]^2/[P_2][D_2]$ must be the equilibrium constant K of (7) ($K=3.3$ at room temperature), or the quantity $\bar{\gamma} \equiv [PD]/[PD]_{eq}$ is unity, where $[PD]$ is the concentration of PD and $[PD]_{eq}$ that of the same gas brought to equilibrium of (7). If on the other hand either of the other two mechanisms, *i.e.* the catalytic and the electrochemical mechanisms is operative, the intermediate should be in quasi-equilibrium with solution through step (2), and provided the deuterium concentration in water is kept practically zero throughout the exchange reaction, *i.e.* the total number of moles of light water is sufficiently large as compared with that of deuterium gas, the intermediate consists of protium alone, hence P_2 alone is evolved by (3) or (6) in exchange for D_2 without forming PD; $\bar{\gamma}$ is in consequence kept at zero. The slow discharge mechanism is thus discriminated from the other two ones by conducting the exchange reaction between pure D_2 and P_2O , and by determining $\bar{\gamma}$ as reported below.

Experimental

Materials

Deuterium: Cylinder deuterium from STUART Oxygen Co. San Francisco (purity >99.5%) was purified by filtering through a palladium thimble heated at about 300°C. The thimble was carefully evacuated prior to the use to remove light hydrogen possibly occluded.

Water: Water was distilled from deionized water with addition of KOH and $KMnO_4$, and twice further under flow of air purified with KOH solution.

Platinum: Commercial net (0.1 mm diameter, 80 mesh, purity 99.99%) from TANAKA Noble Metal Co. Tokyo was used.

HCl: Special grade from JUNSEI Pure Chemicals Co. Tokyo was used.

Reaction Vessel

The reaction vessel with 8~12 breakable joints was constructed of borosilicate glass "Hario" of SHIBATA & Co. Tokyo, with platinum net fixed to wall by glass fusion as shown in Fig. 1.

Procedure

The reaction vessel was cleaned by filling it with hot chromic acid mixture at least overnight, washed several times with the water mentioned above, filled with it and kept at boiling temperature for more than 10 hr, renewing the water repeatedly in the mean time.

Water was discarded and the reaction vessel was fused to vacuum system without drying via a liquid nitrogen trap together with solution container (Fig. 1). The solution was preliminarily degassed by freezing—evacuation—melting cycle for at least four times, by means of a greaseless stop cock (C in Fig. 1) connected between the container and a liquid nitrogen trap. The reaction vessel was dried by evacuation, heated to 350°C for 2hr in the presence of 3~5 cmHg deuterium, and evacuated to 10^{-6} mmHg at 400°C for a few hr. The whole system was sealed off at constriction S_1 in Fig. 1, breakable joint B_1 opened, the solution distilled from about 60 to 10°C completely into the reaction vessel, frozen by liquid nitrogen and finally the solution container was removed by sealing off at S_2 . Purified D_2 was introduced through a liquid nitrogen trap and a breakable joint, the reaction vessel then warmed at first with hot water bath to avoid possible cracking by expansion of ice, then cooled to 0°C, pressure

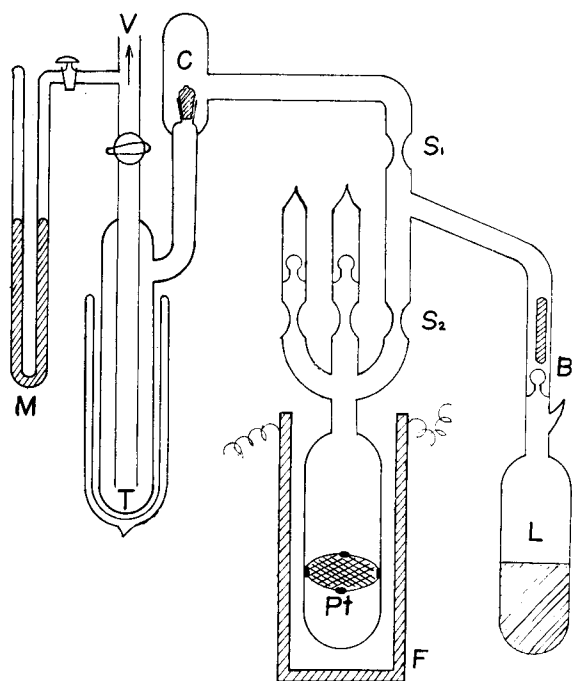


Fig. 1. Apparatus.

- | | |
|-------------------------|--------------------------------|
| B; Breakable joint | Pt; Platinum net |
| C; Greaseless stop cock | S; Constriction |
| F; Regulated furnace | T; Liquid nitrogen trap |
| L; Solution container | V; Connection to vacuum system |
| M; Manometer | |

On the Mechanism of Hydrogen Electrode Reaction on Platinum

of D_2 recorded, and the reaction vessel sealed off at constriction below the breakable joint used.

Reaction was conducted at various fixed temperatures by means of a container filled with water and provided with water jacket, through which thermostated water was circulated. The constant temperature container was shaken horizontally with the reaction vessel fixed in it in 30° slant position from horizontal. The shaking was usually 390 times per min, over 5 cm amplitude. After a recorded time the solution inside the reaction vessel was quickly frozen by liquid nitrogen, the reaction vessel fused to vacuum system, and the gas sampled through one of breakable joints. This procedure was repeated using other breakable joints in each series of experiment.

The reaction vessel usually contained about 20 cc of solution and 40~80 cc of gas. Reaction time was 0.5~3 hr in acidic solutions, or 20 hr in pure water, and reaction temperatures were over the range 0~50°C each kept constant within 0.1°C unless otherwise stated. Apparent surface area of the platinum catalyst was 30~60 cm^2 .

Analysis

Sample gases were analyzed by the thermal conductivity method of FARKAS and MELVILLE¹⁵). A mass-spectrometer specially designed to analyze hydrogen of mass number 2, 3 and 4 (HITACHI RMD-3) was also used in some occasions for reference purpose. Data from the two methods agreed within 1% in deuterium concentration, and 0.1 in τ -value. The solution was titrated after the experiment.

Results

Typical results of the exchange reactions at various temperatures on platinum catalyst in an acidic solution are listed in Table 1. The exchange reaction rate is given in terms of the exchange current density i_0 on the catalyst as calculated by the equation

TABLE 1 Values of τ and Exchange Reaction Rates at Various Temperatures

Solution: 0.30 N HCl. Shaking: 390/min. Apparent surface area of Pt: 37.5 cm^2

Expt. no.	P_{D_2} (cmHg at 0°C)	gas volume (cc)	Temp. (°C)	Time (min)	x (%)	τ	i_0 (mA/cm ²)	i_0^0 (mA/cm ²)
1	20.2	89	17.3	70	42	0.0	1.1 ₃	3.9 ₃
2	20.6	88	27.5±2	38	56	0.1	1.4 ₂	4.7 ₃
3	20.4	87	36.3	50	43	0.0	1.5 ₁	4.9 ₇
4	20.3	86	10.1	85	48	0.0	0.7 ₆	2.7 ₅
5	20.1	85	0.0	120	54	0.0	0.4 ₄	1.6 ₈
6	20.7	84	0.0	57	72	0.1	0.5 ₁	1.8 ₅
7	18.6	83	10.2	55	63	0.0	0.6 ₆	2.6 ₈

$$i_0 = \frac{Fn}{ANt} \ln \frac{x_0}{x} \quad , \quad (8)$$

where A is surface area of the catalyst, F Faraday, N Avogadro number, n the total number of hydrogen atoms in gas phase, x_0 the initial deuterium content in atomic fraction in the gas phase and x that at time t . i_0^0 is the exchange current density obtained by extrapolating i_0 to the atmospheric pressure in accord with the observed proportionality between i_0 and the initial pressure P_{D_2} of D_2 as shown in Fig. 2. ARRHENIUS plot of the results listed in Table 1 is shown in Fig. 3.

The $\log i_0^0 - 1/T$ line consists of two portions (Fig. 3). Above about 17°C , slope of the line gives apparent heat of activation, ΔH^* , defined by

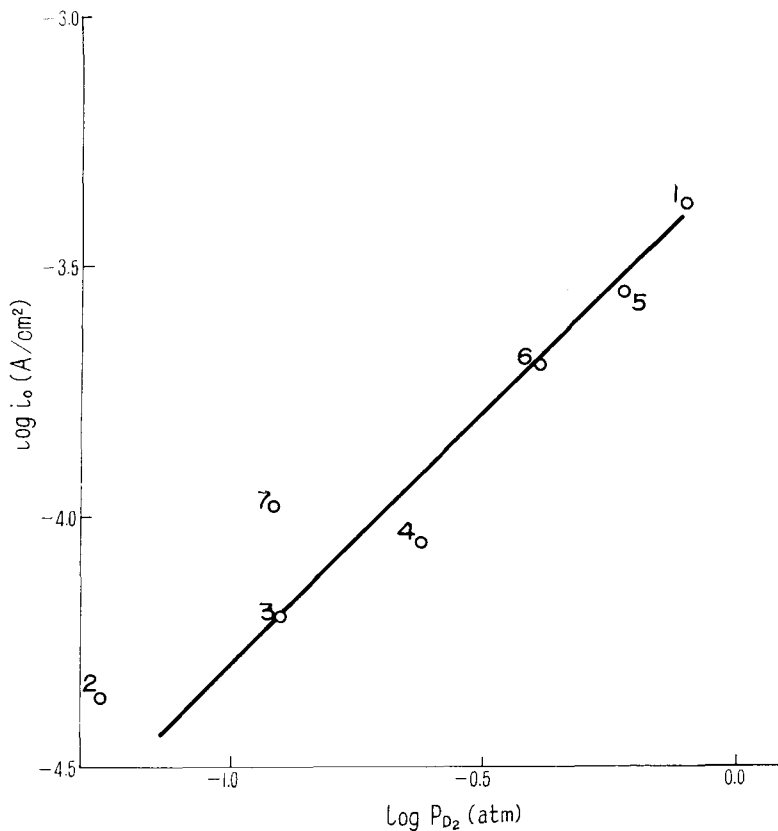


Fig. 2. Pressure dependence of exchange reaction rate.

Reaction temperature; 0°C , Solution; 10^{-3} N HCl, Shaking; 390/min. Numbers indicate order of experiment.

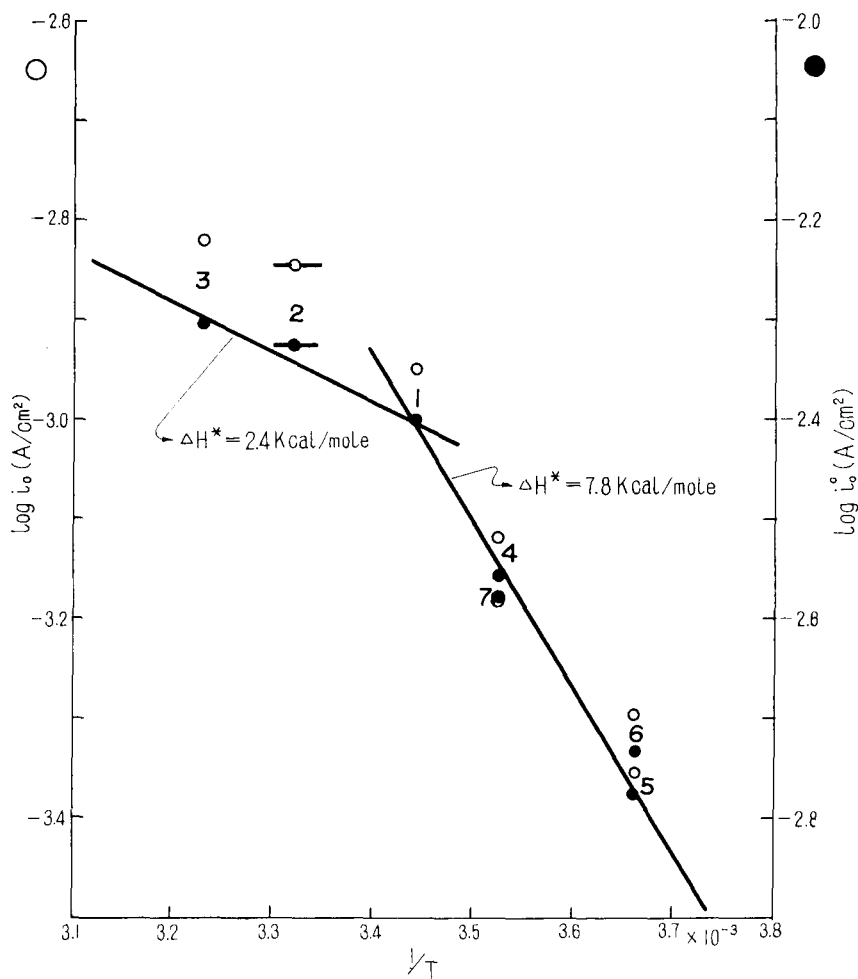


Fig. 3. ARRHENIUS plot of exchange reaction rate.

Solution; 0.30 N HCl, Shaking; 390/min, ○; $\log i_0$ (A/cm²), ●; $\log i_0^0$ (A/cm²).

$$\Delta H^* = -R d \ln i_0^0 / d(1/T) \quad (9)$$

of ca. 2.4 kcal/mole, while below this it gives ca. 8 kcal/mole. As seen in Table 1, γ was always zero within the experimental errors (± 0.1). Results obtained in pure water is given in Table 2, where γ fluctuates between 0.1 and 0.6.

Reproducibility of the exchange rate is rather poor, and systematic shift of the line was frequently observed in the ARRHENIUS plot. The reproducibility of $\log i_0 - \log P_{D_2}$ plot at 0°C was usually better (Fig. 2) than that of other

TABLE 2 Values of τ and Exchange Reaction Rate in Pure Water
Shaking: 220/min

Expt. no.	Surface area (cm ²)	gas volume (cc)	P_{D_2} (mmHg at 0°C)	Temp. (°C)	Time (hr)	x (%)	τ	i_0 (mA/cm ²)	i_0° (mA/cm ²)
1	56	58	23	26 ± 0.5	27.2	25.5	0.42	0.037	0.11 ₂
2	40	51	35	0.0	2	94.2	0.45	0.042	0.09 ₁
3	40	35	31	22.5	24	32	0.14	0.041	0.09 ₂
4	40	49	30	22.5	15	46	0.46	0.060	0.14 ₁
5	60	40	23	22.5	19	9	0.59	0.061	0.18 ₇

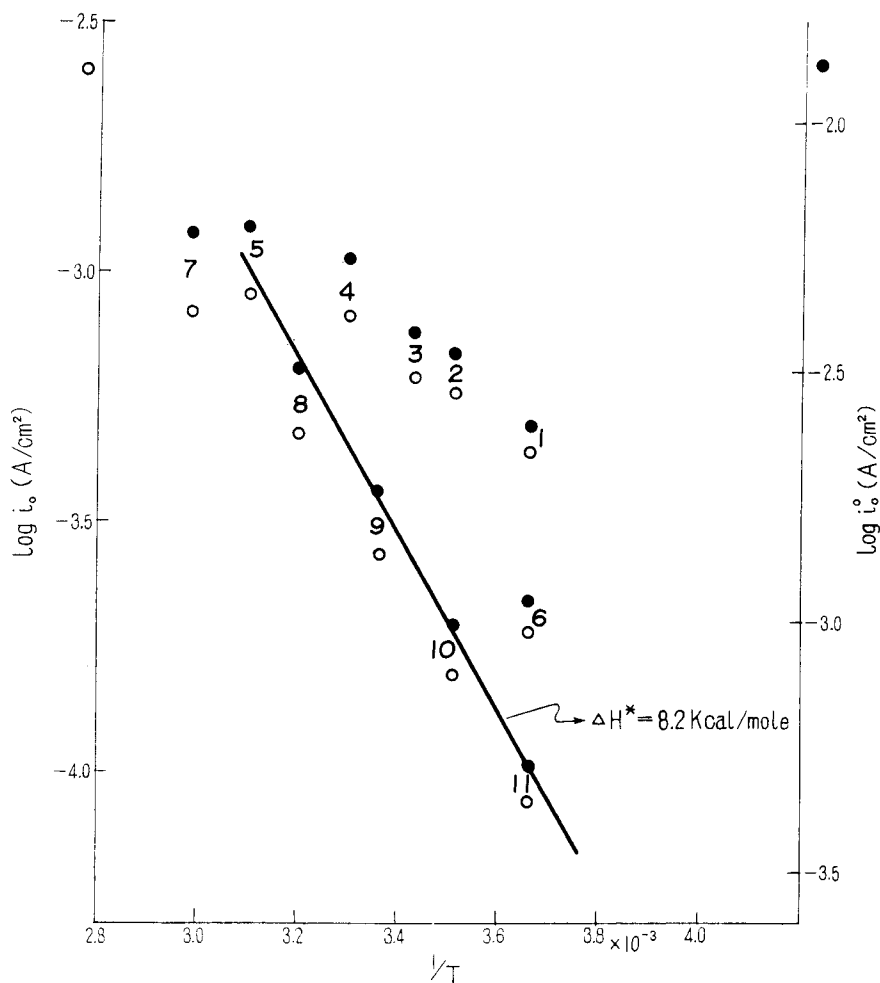


Fig. 4. ARRHENIUS plot of exchange reaction rate.
Solution; 0.1 N HCl, Shaking; 390/min, O; $\text{log } i_0 \text{ (A/cm}^2\text{)}$, ●; $\text{log } i_0^\circ \text{ (A/cm}^2\text{)}$.

experiments conducted at higher temperatures. Systematic decrease in the exchange rate in some results of poor reproducibility (see Fig. 4) stimulated the present authors to try to depoison the solution before use with, in presence of 40 cmHg hydrogen gas, platinum black prepared by usual method of reducing H_2PtCl_6 with formaldehyde¹⁶⁾ or of thermally decomposing H_2PtCl_6 , but they were without significant success. The data in Table 1 are of relatively good reproducibility as shown in Fig. 3. Nevertheless, other results of poor reproducibility as exemplified in Fig. 4 show essentially similar features to that of Fig. 3, supporting Fig. 3 as relevant to the basic character.

The exchange reaction rate depends significantly on pH of the solution, as seen from comparisons of i_0 -values in Table 1 (0.30 N HCl) and in Table 2 (pure water). Some experiments were tried to obtain somewhat clearer pictures of the pH effect by replacing the solution without exposing the solution and the catalyst to air during one series of experiment, but they were so far unsuccessful due to poor reproducibility. Experiments on this line are still in progress.

In hope to increase the diffusion rate of hydrogen molecule in the solution, shakings at higher rates (*ca.* 500/min) were tried, but the exchange rates at high temperatures were rather decreased, indicating that the shaking is the most effective near the rate here employed.

Discussion

Diffusion of Hydrogen Molecule in Solution

In Fig. 3, the ARRHENIUS plot exhibits two lines intersecting at about 17°C. At higher temperatures, the slope gives the apparent heat of activation, ΔH^* , of *ca.* 2.4 kcal/mole, and here the exchange reaction rate is of the order of 1 mA/cm² at about 20 cmHg of deuterium pressure. These two values indicate as shown below that the reaction rate is controlled by diffusion of hydrogen molecule in the solution. The value of ΔH^* agrees well with that obtained (2.9 ± 0.2 kcal/mole) from literature values¹⁷⁾ of diffusion coefficients of hydrogen in water at various temperatures. The above exchange rate is reduced to *ca.* 0.4 mA/cm² at one atmospheric deuterium pressure in unstirred solution according to the proportional relationship between the exchange rate and deuterium pressure, and assuming that the diffusion layer is reduced to one tenth in thickness¹⁸⁾ by the shaking. This value is consistent with the diffusion rate of hydrogen molecule in aqueous solutions under one atmospheric hydrogen pressure reported by BREITER¹⁹⁾ (0.58 mA/cm² in slightly stirred solution). The diffusion control of the rate at higher temperatures thus concluded is now in harmony with the fact that the systematic decay of the exchange rate (Fig. 4) decreases with increase of temperature. Below this temperature, however, the

slope gives *ca.* 8 kcal/mole for ΔH^* , from which it is concluded that the exchange rate is no longer controlled by the diffusion process in this region. This value of ΔH^* is comparable with the literature value²⁰⁾ on the hydrogen electrode reaction on platinum in acidic solutions (10.5 ± 1 kcal/mole). Possibility of rate-determining diffusion of hydrogen ion or water molecule is excluded, since γ -value must then be unity instead of zero as observed. The systematic decrease in the exchange reaction rate by more than five times during one series of experiment at low temperatures (Fig. 4) speaks further against any diffusion process governing the rate. It is thus concluded from the result $\gamma=0$ that the slow discharge mechanism is not operative on platinum catalyst in acidic solutions at least at temperatures below 17°C.

Results Obtained in Pure Water

The γ -value in pure water lies between 0.1 and 0.6. This is possible in either of the two cases below; (A) the rate of conversion of the initial state $2H^+ + 2e$ into the intermediate and that of the latter into the final state H_2 are of comparable order of magnitude, or in other words, the intermediate is not completely in exchange equilibrium neither with $2H^+ + 2e$ nor with H_2 , (B) either of the catalytic and the electrochemical mechanisms is operative but associated with concurrent reactions *e.g.* that proposed by RIDEAL and ELEY¹⁴⁾



which promotes equilibration (7). Similar values of γ were also obtained with nickel catalyst in neutral solutions²¹⁾, which will be dealt with in the later paper²¹⁾.

pH Dependence and Possible Mechanism

From the above argument on γ , the slow discharge mechanism is excluded under the specified condition on platinum electrode in acidic solutions. Valid alternative of the other two mechanisms, *i.e.* the catalytic and the electrochemical, is now decided on the basis of the observed pH dependence as follows.

The rate of the forward uni-directional rate of step (3) which is the rate-determining step of the catalytic mechanism, is a sole function of coverage θ_H of electrode surface with $H(a)$ at constant temperature, but not of pH because of electric neutrality of $H(a)$. The backward unidirectional rate of (3) is now another sole function of θ_H at constant temperature and constant hydrogen partial pressure in gas. Hence, neglecting the isotopic difference, there should not be any pH effect upon the exchange rate if the catalytic mechanism is operative.

For the electrochemical mechanism, however, HORIUTI, MATSUDA and two of the present authors have shown²²⁾ on the basis of the theory of hydrogen

electrode reaction developed by HORIUTI and MATSUDA²³⁾ that the uni-directional rate at constant overpotential should depend on pH. The isotopic exchange rate which traces the uni-directional rate should hence vary with pH as observed.

The pH effect observed in the present experiment was rather fluctuating, but i_0 -values in 0.30 N HCl (Table 1) and in pure water (Table 2) differ at least by the order of 10. Similar pH dependence of the hydrogen electrode reaction rate on platinum have also been reported^{19,12,24,25)}. It is concluded from the above results on γ , ΔH^* and pH effect that only the mechanism applicable to platinum electrode under equilibrium condition in acidic solutions is the electrochemical mechanism. The same mechanism fits in sufficiently with the experimental results in pure water, if not necessarily, admitting the concurrence of such reaction as that of RIDEAL-ELEY mechanism, which gives rise to equilibration of (7).

Acknowledgment

The authors' sincere gratitudes are due to Prof. J. HORIUTI for his suggestions and many encouragements throughout this work. They would also like to express their thanks to Miss. A. TSUMURA for her mass-spectrometric analysis in several occasions.

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