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ADSORPTION OF HYDROGEN ON A PLATINUM-GRAPHITE CATALYST

Part II. Measurements in the Electrochemical System by Electron Spin Resonance and Potential-Sweep Techniques

By

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Abstract

Adsorbed hydrogen on a platinum-graphite was investigated by electron spin resonance (ESR) and potential-sweep method, as functions of electrode potential, surface ratio of platinum to graphite, and temperature. The adsorption of hydrogen was found to reveal the change of the ESR signal. The change of the signal depends not only on the electrode potential but also on pH of the solution. At 0~0.15 V (RHE) the signal decreases with the increase of the potential only in acidic solution whereas at 0.2~0.4 V it decreases in both acidic and alkaline solutions. These ESR features of adsorbed hydrogens are discussed in comparison with results of potential-sweep measurement. Thus the adsorbed hydrogens are classified by ESR, their different responses to different ionization potentials, and heat of adsorption. The mechanism of hydrogen electrode reaction is also discussed on the basis of the above results.

Introduction

The adsorption of hydrogen on a platinum has been an important subject in the field of surface science, catalysis, and electrochemistry. Much attention has been paid to the adsorption not only in the gas-solid system but also in the electrochemical system. However, there seems not to be sufficient linkages among the results observed by different techniques under different conditions in different systems.

Part I¹⁾ dealt with the adsorption of hydrogen from gas phase on platinum-graphite catalyst (Pt/C), which can be used also in the electrochemical system. ESR measurements on Pt/C in the gas-solid system show that the

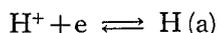
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adsorbed hydrogen increases the amount of conduction electrons in graphite of Pt/C and consequently stays in a positively polarized form. Present work reports the study of the adsorption of hydrogen on the same Pt/C in the electrochemical system where Pt/C serves as an electrode. Comparison of the results obtained on a common catalyst but in different systems will give a useful information which provides a deep understanding of the adsorption state of hydrogen.

The adsorption of hydrogen on a platinum electrode has been mainly studied by electrochemical methods (potential-sweep²⁾ or galvanostatic³⁾ method) in which the adsorption-desorption process of



is studied in terms of electric current, electric charge, and electrode potential. As a method in parallel with the electrochemical method (*in-situ* method), photo-reflectance,⁴⁾ surface conductance,⁵⁾ and ESR⁶⁾ are practically available for the study of the adsorption of hydrogen. We have chosen an ESR measurement which enables us to compare the results with those in the gas-solid system.¹⁾

The electrochemical behavior of the adsorbed hydrogen on a platinum-graphite (or charcoal) electrode has been studied by potential-sweep method^{7,8)} and is reported to be identical to the feature on a pure platinum electrode.⁷⁾

Adsorbed hydrogens on a platinum electrode have been characterized by two to four adsorption states depending on experimental circumstances, *e.g.*, kind and concentration of electrolyte, temperature, pretreatment of electrode, etc. Particularly an anion even in the solutions of same pH gives a considerable effect on the feature of the adsorbed hydrogen.⁹⁾ The behavior of the adsorbed hydrogen is also different in acidic and alkaline solutions.^{9,10)} These facts assist in elucidation of properties of the adsorbed hydrogen and ultimately in understanding of its reactivity in the hydrogen electrode reaction and also an electrochemical hydrogenation of organic substances.

Experimental

1. Catalyst.

Platinum-graphite (Pt/C) powder catalyst was prepared from graphite and various amounts of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$, where the graphite (Union Carbide SP-1) had a surface area of 2.0 m²/g and $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ was prepared by the Grube-Beischer method.¹¹⁾ The graphite is immersed into $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$ nitric acid solution, dried at 80°C with stirring, and heated at 300°C for 2 hrs in air. The Pt/C catalyst thus prepared was further processed so as to serve

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as an electrode (see below).

The amount of platinum on the catalyst was expressed by a ratio of platinum to graphite at the surface, S_{Pt} , which was calculated under the assumption that all of the introduced platinum atoms remain on the surface of the catalyst. $S_{Pt}=0$ represents pure graphite with or without the treatment by nitric acid solution.¹⁾

(a) **ESR measurement.** The Pt/C powder catalyst was mounted on a Teflon sheet of 0.1 mm in thickness at the pressure of 400 kg/cm². The sheet was then hammered onto platinum gauze (0.5 × 3 cm), where the Teflon and gauze had been proved in advance to give no ESR signal. Electrical contact was taken through the platinum gauze.

(b) **Potential-sweep measurement.** The Pt/C powder catalyst was pressed at 400 kg/cm² into a pellet, which served as a test electrode. Apparent area and density of the pellet were respectively 1.5 cm² and 1.9 g/cm³, where the density of graphite is 2.3 g/cm³.¹²⁾ Electrical contact was simply taken by hanging the pellet on a hook of gold-plated platinum. The current of the hook was small enough to be neglected.

2. Cells.

(a) **ESR measurement.** The cell is schematically shown in Fig. 1 where T is the test electrode of Pt/C, R reference, C counter, and A auxiliary electrodes, respectively. R, C, and A electrodes are platinized platinum electrodes. A flat portion of the cell which was placed in an ESR cavity was very thin, *i. e.*, 0.5 mm in inner thickness, 1 cm in width, and 5 cm in length.

(b) **Potential-sweep measurement.** An H-type cell was used; one of the compartments accommodates the test and counter electrodes, and the other compartment contains the reference electrode. The reference and counter electrodes are platinized platinum electrodes.

3. Solutions.

Aqueous solutions of 0.5 M H₂SO₄ and 1 M NaOH were employed for potential-sweep measurement, and 0.5 M H₂SO₄, 1 M

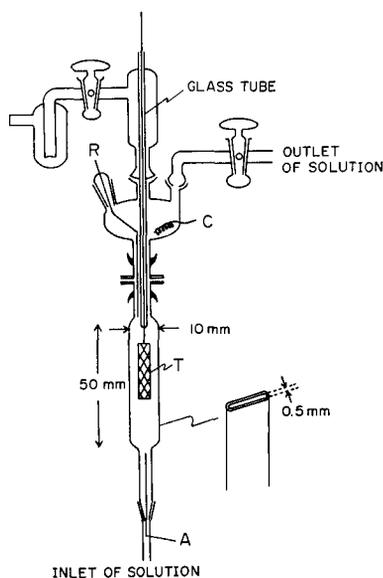


Fig. 1. Schematic diagram of the electrolytic cell for ESR measurement.

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HClO₄, 1 M HClO₄+10⁻³M KBr, and 2M NaOH were for ESR measurement. Specific resistances of 0.5 M H₂SO₄ and 2 M NaOH are respectively ca. 5 and 4 ohm·cm at room temperature.¹³⁾ The solutions were saturated with hydrogen gas.

4. Measurements.

Electrode potential was measured against the reversible hydrogen electrode (RHE) in the same solution.

Pretreatment of anodic activation of the test electrode was carried out by applying two to three times the potential sequence of 1.2 V for 30 sec and then 0 V for 30 sec.

(a) **ESR measurement.** The ESR spectrometer was X-band Varian E-4. Solution saturated with hydrogen gas was introduced into the cell by circulating⁶⁾ or pumping the solution. The measurement was done at room temperature.

(b) **Potential-sweep measurement.** A triangular potential pulse was applied to the electrode through a potentiostat. The current was recorded as IR drop directly by a recorder or by a paper tape for computer calculation. Every measurement was carried out after aging the electrode for 1 min at 0 V.

The potential range swept was from 0 to 1.2 V. The limit of 1.2 V was due to the oxidation of graphite at $V > 1.2$ V. During the measurement the flow of hydrogen gas was interrupted so as to make the ionization current of hydrogen gas small.

Results

1. ESR measurements.

The Pt/C powder catalyst gives an anisotropic ESR signal of conduction carriers;¹⁾ g_{\parallel} and g_{\perp} are obtained as g values being parallel and perpendicular to the c -axis of graphite, respectively. When the Teflon sheet with Pt/C was placed in parallel to the magnetic field of the ESR spectrometer, ESR signal was isotropic and the observed g value was nearly equal to the value of a free electron, g_e .*) This is identical to that of charcoal.⁶⁾ Thus the Pt/C powder tends to align its crystal structure on the Teflon sheet so that c -axis of the powder is in perpendicular to the sheet. The observed g corresponds to g_{\perp} .¹⁾ The width of the ESR signal was not affected by the

*) It was not allowed in the flat cell to observe ESR signal in a position perpendicular to the magnetic field. However, the sheet in a tube cell gave the anisotropic signal which being dependent on the direction of the sheet to the magnetic field.

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electrode potential and hence we will describe the signal intensity in terms of the signal height. The ESR measurement was limited in a potential range of $V \geq 0$ V (*vs.* RHE) because of the bubble evolution of hydrogen at $V < 0$. The flat portion of the cell (Fig. 1) was so thin that a potential distribution in the cell might not be homogeneous. Such a possibility was examined by observing the potential of the test electrode referred to the auxiliary electrode A (V_A) and that to the reference electrode R (V_R). For example, V_R and V_A are respectively 75 and 68 mV at a current of $i=0.02$ mA in 0.5 M H_2SO_4 . The difference is small and will not affect our following discussion though we use V_R .

It is important to note that, irrespective of the solution, the ESR signal of pure graphite, *i.e.*, Pt/C at $S_{Pt}=0$, was found not to change with the change of electrode potential.

(a) **In acidic solution.** Figure 2 shows the change of ESR signal intensity of the catalysts with different S_{Pt} as a function of potential in acidic solutions. Curves in Fig. 2 are characterized into three parts in a potential region where hydrogen adsorbs. The intensity decreases with the increase of potential at $0 < V < 0.1 \sim 0.15$ V, stays nearly unchanged at $0.1 \sim 0.15 < V < 0.2 \sim 0.25$ V, and again decreases at $0.2 \sim 0.25 < V < 0.4$ V. A similar change, the decrease of the intensity with the increase of potential, was observed by Bonnemay, Lamy, and Malaterre⁶ in somewhat narrower potential region of $0 < V < 0.2$ V in sulfuric acid solution.

(b) **In alkaline solution.** Figure 3 shows the signal intensity in 2 M NaOH as a function of potential. The intensity is nearly constant at potentials of $0 < V < 0.15$ V in contrast to the case of acidic solutions and decreases with potential at $0.15 < V < 0.3 \sim 0.4$ V.

2. Potential-sweep measurements.

In this case, the adsorption and

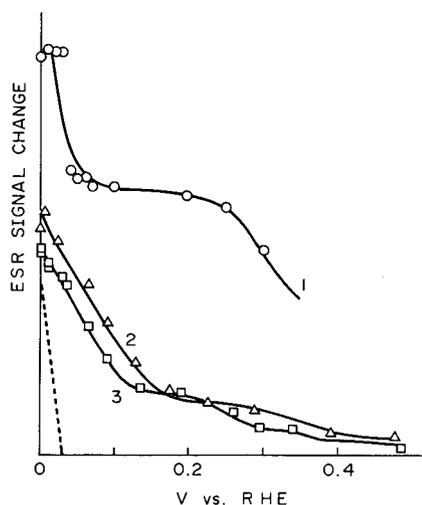


Fig. 2. Change of ESR signal intensity against electrode potential in acidic solutions.

Curve 1 at $S_{Pt}=0.074$ in 0.5 M H_2SO_4 ,
2 at $S_{Pt}=0.5$ in 1 M $HClO_4$, and
3 at $S_{Pt}=0.5$ in 1 M $HClO_4+10^{-3}$
M KBr.

The dotted line represents a change of ESR signal in the gas-solid system. The ordinate represents relative intensity in arbitrary units different for each curve.

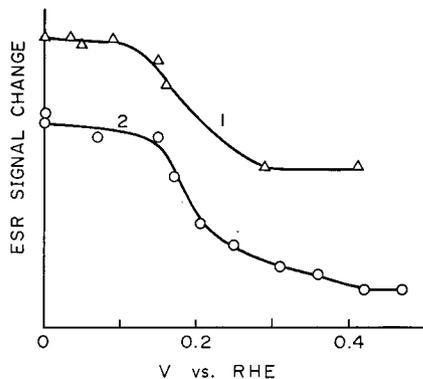


Fig. 3. Change of ESR signal intensity against electrode potential in 2 M NaOH.

Curve 1 at $S_{Pt}=0.25$ and 2 at $S_{Pt}=0.5$.

The ordinate represents relative intensity in arbitrary units different for each curve.

desorption processes of hydrogen on a pure platinum electrode are followed as cathodic and anodic currents in the potential region between 0 and 0.45 V.

(a) **In acidic solutions.** Figures 4 and 5 show typical current-potential ($i-V$) curves at sweep rates of 2.5 and 10 mV/sec for Pt/C electrodes of $S_{Pt}=0\sim 1.0$ in 0.5 M H_2SO_4 , where the ionization current of hydrogen gas dissolved in the solution has been subtracted.

As seen from Fig. 4, the electrode of $S_{Pt}=0$ does not give any peak in the hydrogen region of $0 < V < 0.45$ V but the electrodes of $S_{Pt} > 0$ do give peaks associated with the adsorbed hydrogen on platinum of Pt/C. In Fig. 5 the hump of anodic current at $V > 0.8$ V and the cathodic peak at $V=0.75$ V due to the formation and the desorption of adsorbed oxygen, respectively, increase

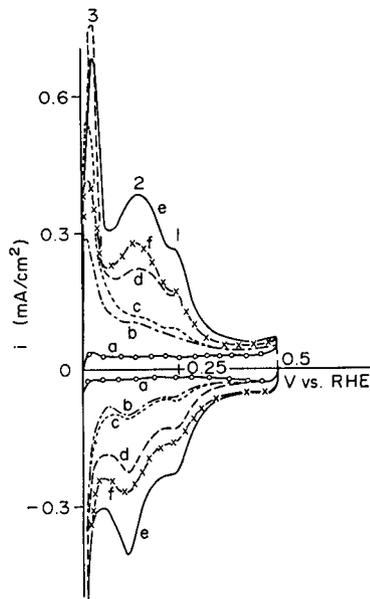


Fig. 4. Current-potential curves at a sweep rate of 2.5 mV/sec for various S_{Pt} in 0.5 M H_2SO_4 at room temperature.

Curve a at $S_{Pt}=0$; b, 0.074; c, 0.11; d, 0.25; e, 0.5; f, 1.0.

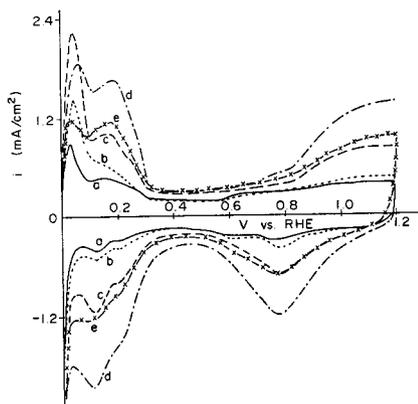


Fig. 5. Current-potential curves at sweep rate of 10 mV/sec for various S_{Pt} in 0.5 M H_2SO_4 at room temperature.

Curve a at $S_{Pt}=0.074$; b, 0.11; c, 0.25; d, 0.5; e, 1.0.

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monotonically with S_{Pt} . The anodic peaks at a sweep rate of 10 mV/sec (Fig. 5) at $0 < V < 0.4$ V are broad in comparison with those of Fig. 4. Curves at 5 mV/sec are almost identical to those at 2.5 mV/sec in their characteristics. At sweep rates higher than 10 mV/sec, the peaks become more broad and blunt. This means that the adsorption or desorption process of adsorbed hydrogen on Pt/C can not follow the potential change in a reversible way at sweep rate ≥ 10 mV/sec. Thus the $i-V$ curves taken at 2.5 mV/sec are treated in the following analyses. It will be mentioned, however, that the total charges associated with the desorption or adsorption of adsorbed hydrogen are not influenced by the sweep rate.

No additional peak on the Pt/C catalyst is observed in comparison with $i-V$ curves on a pure platinum electrode²⁾ but the peak height clearly depends on S_{Pt} . In the hydrogen region, the height of peaks 1 and 2 (Fig. 4) increases with the increase of S_{Pt} at $0 < S_{Pt} \leq 0.5$, whereas peak 3 behaves differently. The height of peaks at $S_{Pt}=1.0$ is rather exceptional and decreases down to the height corresponding to that between $S_{Pt}=0.25$ and 0.5. In the oxygen region of Fig. 5, the dependence of the height of the cathodic peak on S_{Pt} is identical to that of the height of peaks 1 and 2 in hydrogen region.

The roughness factor of the electrode was estimated as follows. The current in the double layer region of $i-V$ curve consists of the charging current of double layer and the ionization current.¹⁴⁾ The latter current is due to the ionization of hydrogen dissolved in the solution and is estimated from the steady current at a constant anodic polarization; 4.8×10^{-2} mA/cm² at $V \geq 50$ mV, irrespective of S_{Pt} . The charging current of double layer obtained by subtracting the ionization current from the current at 0.45 V in Fig. 4, shows a tendency to increase with the increase of S_{Pt} . This will be due to a current associated with the desorption of adsorbed hydrogen which still remains at 0.45 V on the electrode at the present sweep rate. Thus we choose the current at $S_{Pt}=0$ as the charging current of the double layer. With the assumption that the double layer capacity is indifferent to materials of electrode, platinum, graphite, and Pt/C, the value of $48 \mu\text{F}/\text{cm}^2$, observed on a smooth platinum by our separate experiment, gives rise to a roughness factor of 240 for Pt/C electrode.

In Table 1, the amounts of the adsorbed hydrogen at 50 mV, Q_i^H , and of the adsorbed oxygen, Q^O , at $V=1.2$ V at room temperature are given for different S_{Pt} . The ratio of Q_i^H/Q^O is almost independent of S_{Pt} . If oxygen is allowed to adsorb only on platinum but not on graphite, the constancy of the ratio indicates that Q_i^H is a quantity of adsorbed hydrogen on platinum.

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TABLE 1 Q and θ_{Pt} values against S_{Pt}

Solution	S_{Pt}	0.074	0.11	0.25	0.5	1.0
0.5 M H ₂ SO ₄	Q^H (m coul/cm ²)	4.5	6.6	13.5	25.8	16.2
	Q^O (m coul/cm ²)	3.8	5.2	12.3	21.0	13.8
	Q^H/Q^O	1.28	1.27	1.10	1.23	1.17
	θ_{Pt}	0.09	0.13	0.27	0.52	0.32
1 M NaOH	θ_{Pt}	0.06	0.09	0.24	0.28	0.15

Q^O is evaluated from cathodic desorption of adsorbed oxygen at 1.2 V, where the surface is not fully covered by oxygen so that $Q^H/Q^O > 0.5$.¹⁴⁾

The total charge at 50 mV on pure platinum electrode represents a monolayer quantity.⁹⁾ Taking that platinum of Pt/C at $V=50$ mV is also covered with hydrogen at a monolayer, we evaluated the ratio of platinum to graphite on the surface of Pt/C, θ_{Pt} , from Q^H and the roughness factor of 240, as given in Table 1. It is interesting that θ_{Pt} is the same as S_{Pt} at $S_{Pt} \leq 0.5$. At $S_{Pt}=1.0$, however, only 30% of introduced platinum remains on the surface of Pt/C.

In most of the previous works, the observation in the potential region of peak 3 has been avoided because in this region the ionization current is potential-dependent. However, on the electrode with a high roughness factor the surface reaction exceeds to a large extent the hydrogen ionization reaction whose current is controlled by the geometrical area of the electrode. Thus the relative contribution of the ionization current to peak 3 of Fig. 4 becomes smaller as expected from the roughness factor of 240. In fact, the steady current of hydrogen ionization was observed independent of S_{Pt} but peak 3 strongly depends on S_{Pt} as seen in Figs. 4 and 5. Peak 3 is larger than the calculated value of ionization current^{*)} of hydrogen gas in the solution which surrounds the electrode. The solution saturated with hydrogen gas may occupy the pore of the electrode which being 17% in the volume. The amount of electricity necessary to ionize the hydrogen gas in the pore is estimated as 4.5×10^{-4} coul. from the solubility of hydrogen gas.¹⁵⁾ However, this is negligibly small compared with the amount of the electricity of peak 3, 1.4×10^{-2} coul. at $S_{Pt}=0.074$. Thus peak 3 is considered to be associated with the process of adsorbed hydrogen. Figure 4 shows that the dependence of peak 3 on S_{Pt} is different from that of peaks 1 and 2.

*) The ionization current is diffusion-controlled and the diffusion peak current should be proportional to the square root of sweep rate but peak 3 was almost proportional to the sweep rate.

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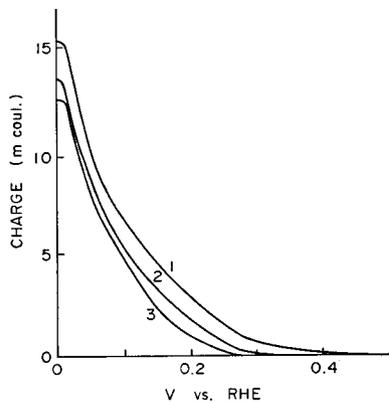


Fig. 6. Charge Q^H against electrode potential at $S_{Pt}=0.11$ in 0.5M H_2SO_4 at various temperatures.

Curve 1 at 20°C, 2 at 30°C, and 3 at 40°C. Sweep rate was 2.5 mV/sec.

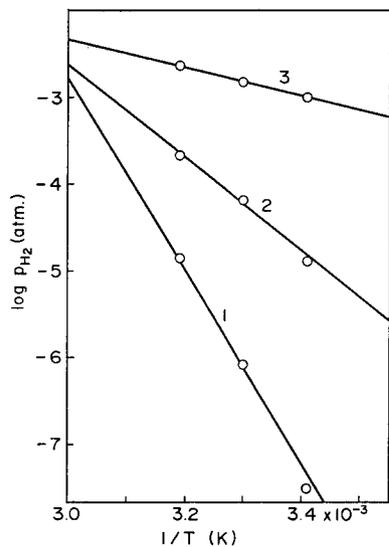


Fig. 7. $\log p_{H_2}$ against $1/T$. Values were obtained from Fig. 6.

Curve 1 at $\theta=0.25$, 2, 0.5; 3, 0.75.

TABLE 2 Heat of adsorption of hydrogen at $S_{Pt}=0.11$ at various coverages

θ	0.25	0.5	0.75
ΔH_{ads} (kcal/mol)	26	12	4

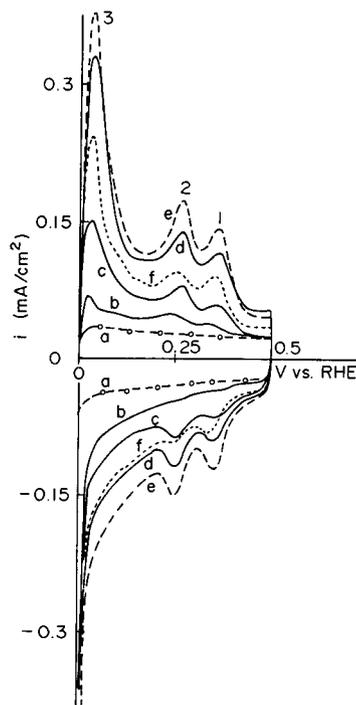


Fig. 8. Current-potential curves at sweep rate of 2.5 mV/sec for various S_{Pt} in 1 M NaOH at room temperature.

Curve a at $S_{Pt}=0$; b, 0.074; c, 0.11; d, 0.25; e, 0.5; f, 1.0.

Figure 6 shows the amount of charge Q^H against electrode potential at 20, 30, and 40°C on Pt/C of $S_{Pt}=0.11$, where Q^H was evaluated by integration of $i-V$ curves. In order to estimate the coverage of hydrogen at respective temperatures, we assume that the amount of the adsorbed hydrogen at 50 mV represents the monolayer quantity.⁹⁾

The heat of adsorption, ΔH_{ads} , is evaluated as follows. The Nernst equation allows us to estimate the pressure of hydrogen gas, p_{H_2} , which gives an electrode potential, V , by $V=RT/2F \cdot \ln [(a_{H^+})^2/p_{H_2}]$, where a_{H^+} is the activity of proton in the solution. Thus we can obtain ΔH_{ads} as a function of the coverage of hydrogen, θ , from $(\partial \ln p_{H_2}/\partial T)_\theta = \Delta H_{ads}/RT^2$. The plot of $\log p_{H_2}$ vs. $1/T$ is given in Fig. 7, where partial pressures of water of 0.023, 0.042, and 0.073 atm. at 20, 30, and 40°C, respectively,¹⁰⁾ are taken into account. Values of ΔH_{ads} are given in Table 2.

The steady ionization current increased with the increase of temperature; 0.074, 0.091, and 0.133 mA at 20, 30, and 40°C, respectively, but peak 3 showed an opposite tendency that its peak current decreased with the increase of temperature. This again suggests that peak 3 is not associated with the diffusion.

(b) In alkaline solution. Figure 8 shows $i-V$ curves at a sweep rate of 2.5 mV/sec at different S_{Pt} in 1 M NaOH. The qualitative feature of the curves is in good agreement with the results of Breiter and Kennel;⁹⁾ no additional peak to that of a pure platinum electrode was observed. The dependence of the current on S_{Pt} is also similar to that in acidic solution; the ionization current of hydrogen and charging current of double layer hold the same tendency with those in acidic solution. The coverage θ_{Pt} is equal to S_{Pt} at $S_{Pt} \leq 0.25$. There is a difference of θ_{Pt} at $S_{Pt} \geq 0.5$ in sulfuric acid and sodium hydroxide solutions, which is left for further investigation.

Discussion

The peak 3 in 0.5 M H_2SO_4 is sharp with the half width of *ca.* 0.05 V whereas that in 1 M NaOH has the half width of *ca.* 0.1 V, twice as wide as that in 0.5 M H_2SO_4 (Figs. 4 and 8). This suggests that at potentials $V < 0.1$ V (*vs.* RHE) the adsorbed hydrogen in acidic solution is different in its feature from that in alkaline solution. This was confirmed by ESR measurement (Figs. 2 and 3); at potentials $V < 0.1$ V in acidic solutions the ESR signal decreases with the increase of the potential, but not in alkaline solution. The ESR signal in the gas-solid system is quoted with a dotted line in Fig. 2 where the hydrogen pressure is represented by the electrode potential (see the Nernst equation). The signal change in the gas-solid system has been

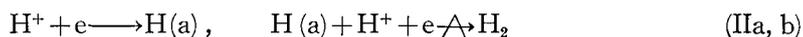
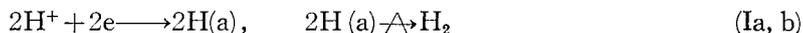
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concluded to be due to the adsorbed hydrogen which is in a molecular form with a partly polarized positive charge and forms a multi-adsorption layer.⁹ The dotted line in Fig. 2 suggests that the change of the signal in the gas-solid system finishes within a potential range of $0 < V < 0.04 \sim 0.05$ V. However, in the electrochemical system the change occurs at $0 < V < 0.4$ V in acidic solution and no change at $V < 0.1$ V in alkaline solution. These facts suggest that in acidic solution the positively polarized adsorbed hydrogen molecule is more stabilized than in the gas phase, but in alkaline solution it does not exist at $V < 0.1$ V. This trend is inferred from a qualitative consideration that the positively polarized adsorbed hydrogen molecule cannot exist stable in alkaline solution because of the presence of a large amount of OH^- in solution side.

At potential of $V > 0.05$ V in the hydrogen region two major peaks have been commonly observed in the potential-sweep measurement.⁹ The adsorbed hydrogens of the major peaks, *e. g.*, at 0.15 and 0.28 V in sulfuric acid solution, have been phenomenologically called as weakly and strongly adsorbed hydrogens, respectively. According to the results from *in situ* measurements of photo-reflectance⁴⁾ and surface conductance,⁵⁾ the strong one adsorbs in a positively polarized manner. In our results of ESR, the decrease of the signal was observed with the increase of potential at $V > 0.2$ V where the strongly adsorbed hydrogen desorbs, in both acidic and alkaline solutions. Following the discussion in Part I we infer that, in this potential region, hydrogen adsorbs in positively polarized form as a result of transferring partly an electron to graphite. Thus with the increase of adsorbed hydrogen, ESR signal of graphite increases. This conforms the results of Refs. (4) and (5). Little change of the signal observed at $0.1 < V < 0.2$ V, where the weakly adsorbed hydrogen is present, will be considered to be due to its neutral character or its partly polarized negative charge¹⁷⁾ which compensates the positive charge of the other adsorbed hydrogen, resulting in the apparent neutrality.

The adsorption of hydrogen on platinum electrode occurs over a potential range of $0 \sim 0.45$ V; the free energy of the adsorption for hydrogen varies by 2×0.45 eV (21 kcal/mol) as a two-electron transfer reaction. The heat of the adsorption in Table 2 changes by 22 kcal from $\theta = 0.25$ to 0.75. As the adsorbed hydrogen is considered to be an intermediate of the hydrogen electrode reaction on a platinum electrode, the above large difference of the adsorption energy will affect the reactivity of the adsorbed hydrogen. Since the hydrogen evolution reaction (HER) as the backward reaction of hydrogen ionization reaction appreciably starts at $V = 0.05$ V the adsorbed hydrogen

with a large heat of adsorption at $V > 0.05$ V seems not to be practically participating in HER. This is supported by the kinetic analysis of HER by means of the deuterium tracer technique;¹⁸⁾ the coverage of the adsorbed hydrogen which is reactive at $V=0$ is smaller than unity. The reaction mechanism of HER on platinum has been widely discussed; two main schemes, (I) and (II), are mostly considered,



where step (II, b) is also expressed as¹⁹⁾



and $\xrightarrow{\Delta}$ represents the rate-determining step and (a) the adsorbed state. Step (II, b') is taken as the rate-determining step of HER near a reversible potential on the platinum electrode.¹⁹⁾ Bagotzky, Kanevsky, and Palanker⁸⁾ reported that the rate of HER decreases with the increase of pH in acidic solution but independent of pH in neutral and alkaline solutions. They summarized that scheme (II) governs HER in acidic solution but scheme (I) does in neutral and alkaline solutions.

The present work also supports their consideration and we have concluded that at $V < 0.1$ V, positively polarized hydrogen in a molecular form is present in acidic solution.

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