Electrolytic Separation Factor for Hydrogen and Deuterium on Platinum Electrode

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The electrolytic separation factor (S factor) of hydrogen isotopes for platinum was measured by means of quantitative mass analysis. The S factor was 5.0 ± 0.2 at 298 K in sulfuric solution. The value was discussed on the basis of the transition state method. The temperature effect on the S factor was observed and the activation energy difference of 7.2 kJ/mol ($\Delta\epsilon = \epsilon_D - \epsilon_H$) was obtained. The origin of $\Delta\epsilon$ was discussed, and it was revealed that the hydrogen evolution process on Pt is assigned to a slow recombination mechanism. The present S factor measurements were done in the overvoltage region. In this region, it was recognized that the S factor is independent of the electrode current density. The S factor in the undervoltage region was discussed by taking account of electrochemical studies reported previously.

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I. Introduction

The study of mechanisms of interfacial reactions of a metal-hydrogen system is one of the important subjects in fundamentals and/or applications of the system. In a recent work, we have studied the interfacial reaction processes of metal-H and metal-D systems with an electrochemical method⁽¹⁾⁻⁽⁵⁾. From the measurement of electromotive force (EMF) of a $H_2|H^+$ electrolyte|Metal cell, the free energy of H for a metal was obtained. Measurements of the current in a short circuit of the cell and the recovery process of the EMF after breaking the short circuit have allowed us to evaluate activation energies of dynamical processes of hydrogen on a metal surface. These experimental results of interfacial reactions have been discussed on the basis of the adsorption energy of hydrogen and the work function of a metal⁽⁴⁾. The difference of hydrogen isotopes in their reaction properties has been interpreted on the basis of the mass difference⁽⁵⁾.

One of the useful applications of the isotope effect is the electrolytic separation of hydrogen isotopes. The separation factor (hereafter referred to as S factor) is defined by the isotopic abundance ratio in the gas phase to that in the liquid. For a hydrogen-deuterium system, the S value is

$$s = (h/d)_{\text{gas}} / (h/d)_{\text{liquid}}, \quad (1)$$

where h and d represent the number of hydrogen and deuterium atoms in the specified phase, respectively.

The S factor has been investigated by earlier workers⁽⁶⁾⁻⁽¹¹⁾. Horiuti and Okamoto⁽⁶⁾ measured the S value by means of micropycnometer for different metals with the same sulfuric solution at 298 K. They showed that metals are roughly divided into two groups according to the S value. The first group, Ni, Au, Ag, Cu and Pt, shows the

values of 6.7, 6.4, 6.0, 7.4 and 6.9, which are about 6 or more. The second group, Pb, Hg, and Sn, gives 3.0, 3.1 and 3.1, whose values are approximately equal to 3. Bell and Wolfenden⁽⁷⁾ reported the S value of 4.3 at 283 K and 3.8 at 373 K on a Ni electrode in alkaline solution. Walton and Wolfenden⁽⁸⁾ obtained 7 at 288 K and 5.9 at 368 K on Ni in acidic solution. Roy⁽⁹⁾ reported the temperature dependence of S factor on a mild steel in alkaline solution; the S values were 11.7, 9.6, 8.0 and 6.7 at 273.5 K, 295.5 K, 313 and 333 K, respectively. From the Arrhenius plots, the activation energy difference ($\Delta\epsilon = \epsilon_D - \epsilon_H$) of 7.02 kJ/mol was obtained. Tsionskii⁽¹⁰⁾ studied characteristics of the electrochemical desorption step at metal surfaces in a high hydrogen overvoltage region. He showed the electrode charge density dependence of the S factor of Hg and Ga. Recently, much attention has been directed to semiconductor materials. Baba *et al.*⁽¹¹⁾ investigated the mechanism of the hydrogen evolution process on metal-loaded semiconductor electrodes, where the metal deposition was made in order to overcome some disadvantages of semiconductor materials such as low activity, instability, etc. They observed the S value of 5.1 on Pt/TiO₂. The hydrogen evolution process on it was assigned to a slow recombination mechanism.

Theoretical evaluation of the S factor was carried out by Okamoto *et al.* with the transition state method⁽¹²⁾. Their results showed that the S value of Pt is 7.1. Recently, calculations have been achieved by the same lines of the above original methods. In Bockris and Srinivasan's calculations⁽¹³⁾, effects of variation of the metal-metal internuclear distance and the Coulombic exchange energy were taken into account, and tunneling correction was also applied to the S value. Calculated S values excluding or including tunneling effect are 5.4 or 5.8 on Ni, and 4.9 or 5.5 on Pt, respectively.

This paper describes the electrolytic S factor of hydrogen isotopes on Pt in sulfuric solution, including the temperature and the electrode current density dependence of the S factor, which were measured by quantitative mass spectroscopy. The mechanism of the electrolytic evolution of hydrogen and its isotope on Pt will be discussed on the basis of the transition state method. Systematic measurements for a series of metals will be reported elsewhere.

II. Experimental Procedure

An apparatus used is shown in Fig. 1. The electrolytic cell as shown in Fig. 1(a) was made of Pyrex glass, and the vessel of the cathode was closed with a silicone rubber stopper. The electrolyte was a mixed solution of $\text{H}_2\text{O} + 50 \text{ mol/m}^3 \text{H}_2\text{SO}_4$ and $\text{D}_2\text{O} + 50 \text{ mol/m}^3 \text{D}_2\text{SO}_4$ solutions. The total capacity of the electrolyte was $3 \times 10^{-5} \text{ m}^3$. Purities of D_2O and D_2SO_4 were 99.75% and 99.5%, respectively. A Pt wire of 99.9% purity with 0.5 mm in diameter and 30 mm in length was used as the cathode (specimen) and the anode of the cell. The cell was placed in a thermostated bath controlled to $\pm 0.05 \text{ K}$ and the cell temperature was measured with a thermocouple. The electrolyte and liquid bath were continuously agitated by magnetic stirrers. The electrolytic current density was

$1.5 \times 10^4 \text{ A/m}^2$ at about 10 V. Figure 1(b) shows schematic representation of a mass analysis system. The gas handling system, made of Pyrex glass, had a capacity of $2.5 \times 10^{-4} \text{ m}^3$ and was plugged with a silicone rubber stopper. The gas handling vessel was connected to the capillary inlet port of a mass spectrometer (JEOL SX102A) by a stainless steel tube of 0.26 mm in inside diameter and 69 mm in length. The mass resolution was 1000 ($M/\Delta M$) in the present measurements. Ionization was done by an electron impact method. The ionizing voltage was 70 V and ionizing current was fixed at $300 \mu\text{A}$. The temperature of the ionizing chamber was kept at 553 K throughout the experiments. The gas handling vessel was evacuated to 2 Pa. The pressure of the vessel was monitored by a vacuum gauge. A sample gas was introduced into the vessel by using a pressure-lock gas syringe. The gas sampling from the electrolytic cell was done carefully under the same conditions at the cell temperature of 298 K.

III. Results

1. Sensitivity factor and fragment correction of the mass analysis

Standards of H_2 , D_2 and mixed $\text{H}_2 + \text{HD} + \text{D}_2$ gases of varying HD and D_2 contents were prepared by the electrolysis of water, heavy water and their mixtures. The sensitivity factor of the mass analysis had been determined as follows: (1) the ion sensitivity as a function of the amount of gas, (2) the ionizing voltage and current dependence of the sensitivity and (3) the chamber temperature dependence.

Ion counts, that is the peak intensity of $I(m/e=2)$, $I(3)$ and $I(4)$, were proportional to the amount of introduced gas, respectively, where m and e mean the mass and electric charge of the respective ions. However, the observed counts for a given amount of H_2 , HD and D_2 gas were not the same because the sensitivity depends on the kind of ions. The sensitivity factors were evaluated by the least square method of the ion counts data on the assumption that the gas population per unit-amount of sampling gas is constant. The evaluated relative sensitivity factors of HH^+ , HD^+ and DD^+ were 5.86, 1.20 and 1(unit), respectively. The calibrated ion counts is given by the relation of (sensitivity factor) $\times$ (observed count).

The ionization efficiency curve of the present system was measured as a function of the ionizing voltage. In our operating condition at 70 V, the value was stable. The ionizing current was proportional to the ion counts as is well known. The chamber temperature, which was often overlooked, was an important factor for the sensitivity. The total intensity at 453 K decreased to half the value at 553 K. The origin of the chamber temperature dependence remains unclear, although a suggestion was once made that the variation of the thermal kinetic energy of gases may be playing a role⁽¹⁴⁾. Accordingly, the ionizing voltage, current and the chamber temperature should be kept constant throughout the experiments.

In the typical mass spectrometer, fragmentations were

Fig. 1 (a) Schematic drawing of the electrolytic cell. (b) Schematic drawing of mass analysis system.

observed as metastable peaks⁽¹⁴⁾. For instance, the peak intensity of $I(1=H^+)$ comes from the reaction of $HH+e \rightarrow H^++H$ or that of $HD+e \rightarrow H^++D$. The $I(5=HDD^+)$ mainly arises from the following scheme.

or

These fragment corrections were statistically evaluated by using the intensity correlation curves. In the case of the above example, the derived relations were $I(1) \approx 0.06 \times I(2) + 0.03 \times I(3)$ and $I(5) \approx 10^{-8} \times I(2)I(4) + 10^{-8} \times I(3)I(3)$. By using the relations, metastable peaks were divided into H and D parts.

2. Separation factor

As mentioned above, the S factor is defined by eq. (1). The ratio of $(h/d)_{\text{gas}}$ was evaluated from the mass spectra by using the above sensitivity and fragment corrections. The ratio of $(h/d)_{\text{liquid}}$ was determined by the mixing ratio of H_2O and D_2O solution. Figure 2 shows the $(h/d)_{\text{liquid}}$ dependence of S factor at 298 K. The results suggest that the S factor is independent of the $(h/d)_{\text{liquid}}$. The electrolytic S value of the hydrogen isotopes on Pt was obtained as 5.0 ± 0.2 at 298 K in sulfuric solution.

Figure 3 shows an example of the temperature dependence of the S factor observed for an $H_2O(82.6 \text{ mol}\%) + D_2O(17.4 \text{ mol}\%)$ mixed electrolyte. The solid line in the figure is fitted by the following functional form;

$$s = s_0 \exp(\Delta\epsilon/k_B T), \quad (2)$$

and the best fit line gave $\Delta\epsilon = 7.2 \text{ kJ/mol}$ and $s_0 = 0.28$.

Fig. 2 The $(h/d)_{\text{liquid}}$ dependence of the S factor at 298 K. The solid line is the best-fit line.

Fig. 3 A typical temperature dependence of the S factor on a logarithmic scale as a function of $1/T$. The electrolyte was an $H_2O(82.6 \text{ mol}\%) + D_2O(17.4 \text{ mol}\%)$ mixed solution. The solid line is the best-fit line.

Fig. 4 (a) The electrode current density dependence of the S factor. An $H_2O(68.5 \text{ mol}\%) + D_2O(31.5 \text{ mol}\%)$ mixed electrolyte was used at 298 K. (b) The I - V curve of the electrolysis.

The S factor obtained by using an $H_2O(68.5 \text{ mol}\%) + D_2O(31.5 \text{ mol}\%)$ mixed electrolyte at 298 K is shown in Fig. 4(a) as a function of electrode current density. Figure 4(b) is the I - V curve of electrolysis.

IV. Discussion

Before analysing the present experimental results, a

short review of theoretical calculations of the S factor will be made.

Values of the S factor depend on the hydrogen electrode reaction on a metal surface. Okamoto *et al.*⁽¹²⁾ proposed that the catalytic mechanism is the rate determining step of hydrogen evolution on the first group of metals giving high S values (5~6 or more), whereas on the second group (≈ 3) the electrochemical mechanism plays a role⁽⁶⁾. Bockris and Srinivasan⁽¹³⁾ considered three mechanisms in their theoretical calculation of the S factor: The S values of 3~4 are assigned to the slow discharge mechanism⁽¹⁵⁾, the values of 8~9 to the slow electrochemical desorption mechanism⁽¹⁶⁾, and those of 5~6 to the slow recombination mechanism⁽¹³⁾. These mechanisms of the rate determining processes are expressed by the following reaction equations:

- (a) Slow Discharge Mechanism

$$\text{H}_3\text{O}^+ + e_{\text{from M}}^- \rightarrow \text{H}_{\text{ad}} + \text{H}_2\text{O}$$
- (b) Slow Electrochemical Desorption Mechanism (3)

$$\text{H}_{\text{ad}} + \text{H}_3\text{O}^+ + e_{\text{from M}}^- \rightarrow \text{H}_2\text{O} + \text{H}_2$$
- (c) Slow Recombination Mechanism
 (equivalent to the catalytic one)

$$2\text{H}_{\text{ad}} \rightarrow \text{H}_2,$$

where the symbol M denotes a metal atom and subscript H_{ad} denotes an adsorbed H atom.

The earlier calculation of the S factor was done by Okamoto *et al.*⁽¹²⁾. The calculated systems are composed of free hydrogen molecules, an electrode, metal electrons and a solution. Considering an electrode with m hydrogen molecules bound by Van der Waals forces and n chemisorbed atoms, the state sum of the electrode (m, n) was evaluated by using vibrational frequencies on various kinds of adsorption sites on a surface. The rate of the reaction ($m, n+2 \rightarrow m, n + \text{H}_2$), and that of the reversed reaction ($m, n + \text{H}_2 \rightarrow m, n+2$) were expressed in terms of the state sum and the transmission coefficient κ . The ratio of κ was equated to that of Wigner's correction $\{1 - (h\nu^*/k_B T)^2/24\}$ ⁽¹⁷⁾, where ν^* means the vibrational frequency in the activated state of chemisorbed hydrogen atoms. They evaluated the ν^* value on Pt surface and obtained the S value of 7.1 for Pt at 298 K.

Other terms neglected in the above calculations of the S factor were evaluated by Bockris and Srinivasan⁽¹³⁾ including; (1) the effect of variations of the metal-metal inter-nuclear distance, (2) the effect of the Coulombic exchange energy ratio and (3) the tunneling corrections. They found a rather small contribution of (1) and (2) to the S value. Calculated S values for Pt with and without including tunneling effects were 5.5 and 4.9, respectively. Main discrepancy from the earlier calculation, 4.9 and 7.1 (Okamoto *et al.*), is due to the evaluation of the Pt-Pt distance of 0.277 nm and 0.392 nm (Okamoto *et al.*) on the surface. In a bulky condition, the lattice constant of Pt is 0.3924 nm and the Pt-Pt first neighbour distance is 0.2775 nm ($=\sqrt{2}/2 \times 0.3924$).

In the present study, the S value on Pt was determined as 5.0 ± 0.2 at 298 K in sulfuric solution. It agrees very

well with the theoretical result without including tunneling effects. It seems to be reasonable in a present temperature region. The tunneling effect is known to be generally important in the diffusion of hydrogen in metals, for instance. The effect, however, can only be detected in a low temperature region⁽¹⁸⁾⁽¹⁹⁾. For hydrogen in Pd, diffusion coefficient is known to be well represented by a single straight line on the Arrhenius plot in a temperature region of 213 to 1273 K. Similarly, the tunneling effect is expected to play a role in other processes at low temperatures. In our measurement, the effect could not be clear because of the narrow temperature region of 273 to 353 K.

The fact that the S factor is independent of the ratio of $(h/d)_{\text{liquid}}$ indicates that its value is determined by electrode species as shown in Fig. 2. As a general rule, S factor depends on the equilibrium constants of K_{H} of the process $\text{H}^+(\text{liquid}) + e^- \leftrightarrow \text{H}_{\text{ad}}$ and that of K_{D} of the process $\text{D}^+(\text{liquid}) + e^- \leftrightarrow \text{D}_{\text{ad}}$ ⁽²⁰⁾. The ratio of the terms is thought to be constant in a normal mixed solution. It will be important in a special case such as the photo-assisted decomposition. Baba *et al.* have reported the S factor of 5.3 ± 0.1 for Pt/TiO₂ on photocatalyst⁽¹¹⁾.

The temperature dependence of the S factor as shown in Fig. 3 gave the $\Delta\varepsilon = 7.2$ kJ/mol. By the definition of the S factor, the activation energy difference $\Delta\varepsilon$ is equal to the $\varepsilon_{\text{D}} - \varepsilon_{\text{H}}$, that is, $\exp(\Delta\varepsilon/k_B T) = \exp(-\varepsilon_{\text{H}}/k_B T) / \exp(-\varepsilon_{\text{D}}/k_B T)$. In the equation, ε_{H} and ε_{D} are the activation energies for the rate determining process of the electrode reaction in the H₂O and D₂O solutions, respectively. In our previous work, we obtained the chemisorption energy difference, $\Delta\mu_{\text{D}} - \Delta\mu_{\text{H}} (=9.6$ kJ/mol), of D and H on Pt by electrochemical studies. Comparing these two values, we concluded that H_{ad} in eq. 3(c) is in the chemisorbed state.

As pointed out by Bockris and Srinivasan⁽¹³⁾, S values for a slow recombination and slow molecular hydrogen diffusion mechanism are not distinctly separated. The S factor for a slow molecular hydrogen diffusion mechanism is given by $s_d = k_{\text{D}}(m_{\text{D}}/m_{\text{H}})^{1/2}$, where k_{D} is the equilibrium constant for reaction $\text{HD} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{HDO}$. The m_{H} and m_{D} mean the reduced mass of H₂ and HD, respectively. With $k_{\text{D}} = 3.8$, s_d is calculated as 4.5. On the other hand, from the temperature dependence of k_{D} ⁽²¹⁾, we can evaluate the $\Delta\varepsilon$ of s_d as 3.9 kJ/mol. Therefore, our experimental results of $s = 5.0$ and $\Delta\varepsilon = 7.2$ kJ/mol point to a slow recombination mechanism for Pt. This means that the temperature coefficient of the S factors is useful in distinguishing between these two mechanisms.

The present S factor measurements were done in the overvoltage region. In this region, the electrode charge density dependence of the S factor was not recognized as was shown in Fig. 4. Fullenwider⁽²²⁾ proposed a method for the S factor measurements in the undervoltage region by use of the bi-electrode technique in conjunction with mass analysis. In the previous paper⁽⁵⁾, the electrode reaction in the undervoltage region was studied by the EMF method by measuring the steady current in a short circuit

of the cell. The rate determining process of the steady current is the release process of H_2 molecules. The activation energy difference of the process was measured as $U_D - U_H \approx 0$ kJ/mol for Pt. This suggests that the S factor in the undervoltage region will be ≈ 1 .

V. Conclusion

The electrolytic separation factor (S factor) of hydrogen isotopes on Pt was measured by means of mass analysis. In our experiment, a method for the evaluation of the sensitivity and fragment factors was proposed for the quantitative mass analysis. We pointed out that the chamber temperature, which was often overlooked, was an important factor for the sensitivity.

The S factor was obtained as 5.0 ± 0.2 for Pt at 298 K in sulfuric solution. The value agrees very well with the theoretical result of Bockris and Srinivasan⁽¹³⁾ without including tunneling effects. From the temperature dependence of the S factor, the activation energy difference $\Delta\epsilon = \epsilon_D - \epsilon_H$ was obtained as 7.2 kJ/mol. The origin of this activation energy difference was discussed and it was suggested that the hydrogen evolution process on Pt could be assigned to a slow recombination mechanism. The temperature coefficient of the S factors should prove useful in distinguishing between a recombination and molecular hydrogen diffusion mechanism. Our experimental results revealed the slow recombination mechanism for Pt electrode. The present S factor measurements done in the overvoltage region show that the S factor is independent of the electrode current density. The feature of the S factor in the undervoltage region was discussed by taking account of the experimental results obtained previously with electrochemical method.

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REFERENCES

- (1) S. Harada: J. Phys. Soc. Jpn., **54** (1985), 430.
- (2) S. Harada and S. Tamaki: J. Phys. Soc. Jpn., **54** (1985), 1642.
- (3) S. Harada: Trans. JIM, **29** (1988), 939.
- (4) S. Harada: J. Phys. Soc. Jpn., **58** (1989), 2200.
- (5) S. Harada: Mater. Trans., JIM, **34** (1993), 753.
- (6) J. Noriuti and G. Okamoto: Sci. Papers Inst. Phys. Research Tokyo, **28** (1936), 231.
- (7) R. P. Bell and J. N. Wolfenden: Nature, **133** (1934), 25.
- (8) H. F. Walton and J. H. Wolfenden: Trans. Faraday Soc., **34** (1938), 436.
- (9) L. P. Roy: Can. J. Chem., **40** (1960), 1452.
- (10) V. M. Tsionskii: Sov. electrochem. (USA), **21** (1985), 1534.
- (11) R. Baba, S. Nakabayashi, A. Fujishima and K. Honda: J. Phys. Chem., **89** (1985), 1902.
- (12) G. Okamoto, J. Horiuti and K. Hirota: Sci. Papers Inst. Phys. Research (Tokyo), **29** (1936), 223.
- (13) J. O'M. Bockris and S. Srinivasan: J. Electrochem. Soc., **111** (1964), 858.
- (14) R. Tuchiya: "Buturi Bunsekihou (Physical Analytical Technique)", ed. by The Physical Society of Japan, Asakura, Tokyo, (1964), p. 323.
- (15) J. O'M. Bockris and S. Srinivasan: J. Electrochem. Soc., **111** (1964), 844.
- (16) J. O'M. Bockris and S. Srinivasan: J. Electrochem. Soc., **111** (1964), 853.
- (17) E. Wigner: Z. Phys. Chem., **B19** (1932), 203.
- (18) J. Völkl and G. Alefeld: Topics in Applied Physics, Vol. 28 Hydrogen in Metals Vol. 1, ed. by G. Alefeld and J. Völkl, Springer, Berlin, (1978).
- (19) Y. Fukai: The Metal-Hydrogen System, Springer, Berlin, (1993).
- (20) K. Watanabe, K. Ichimura, N. Inoue and I. Matsuura: J. Phys. Chem., **90** (1986), 866.
- (21) W. F. Libby: J. Chem. Phys., **11** (1943), 101.
- (22) M. A. Fullenwider: J. Electrochem. Soc., **126** (1979), 2045.