



Title	ANOMALOUS VALUE OF THE OBSERVED STOICHIOMETRIC NUMBER AND THE MECHANISM OF THE HYDROGEN ELECTRODE REACTION ON RHODIUM
Author(s)	MATSUSHIMA, Tatsuo; ENYO, Michio
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 18(1), 34-51
Issue Date	1970-04
Doc URL	<a href="http://hdl.handle.net/2115/24903">http://hdl.handle.net/2115/24903</a>
Type	bulletin (article)
File Information	18(1)_P34-51.pdf



[Instructions for use](#)

## ANOMALOUS VALUE OF THE OBSERVED STOICHIOMETRIC NUMBER AND THE MECHANISM OF THE HYDROGEN ELECTRODE REACTION ON RHODIUM

By

Tatsuo MATSUSHIMA<sup>\*</sup>) and Michio ENYO<sup>\*</sup>)

(Received January 31, 1970)

### Abstract

The stoichiometric number of the rate-determining step of the hydrogen electrode reaction (HER) on Rh was determined in solutions of various pH by measuring deuterium exchange reaction rate between hydrogen gas and water. The value was unity in solutions with pH of lower than 3 or higher than 12, but became extremely large in neutral solutions.

From the results and from pH and hydrogen pressure dependences of rates of the HER and the deuterium exchange reaction, the following conclusions are drawn; (1) the HER obeys the catalytic mechanism in the entire range of pH as long as the surface reaction is concerned and (2) the extremely large value of the stoichiometric number observed in neutral solutions results from that the deuterium exchange reaction by-passes the diffusion step of  $H^+$  or  $OH^-$  in solution near the electrode, which controls the overall rate of the HER there.

### Introduction

The importance of the stoichiometric number,  $\nu(r)$ , of the rate-determining step as one of the mechanistic parameters has been well realized.<sup>1,2)</sup> Several investigations have been carried out in this Laboratory<sup>3~5)</sup> on the  $\nu(r)$  of the hydrogen electrode reaction (HER),



where  $H^+$  is a hydrogen ion associated with a Brönsted base,  $H_2O$  or  $OH^-$ , and  $e$  is a metal electron. In those, however,  $\nu(r)$  was determined only with solutions in a limited range of pH, typical solutions being 1N  $H_2SO_4$  and 0.5N NaOH. The present work was initially designed to determine  $\nu(r)$  of HER on Rh in solutions of various pH, in order to investigate the mechanism in the entire range of pH. However, it has been soon disclosed that  $\nu_{ex}$ , the value of the stoichiometric number determined from deuterium exchange

---

<sup>\*</sup>) Research Institute for Catalysis, Hokkaido Univ., Sapporo, Japan.

*Stoichiometric number of hydrogen electrode reaction*

reaction rate, is unity only in solutions with pH lower than 3 and also higher than 12, but becomes extremely large in neutral solutions, thus exhibiting a phenomenon of the "infinite" stoichiometric number.<sup>6)</sup> The present work hence covers also the investigation in the latter solutions to clarify the correlation between this phenomenon and the mechanism of the HER.

### Experimental

At equilibrium potential of HER, we have,

$$i_0 = \nu(r) \frac{RT}{2F} \left( \frac{\partial i}{\partial \eta} \right)_{\eta=0} \quad (2)$$

where  $i_0$  is the exchange current density,  $i$  is the net current density (positive in the anodic direction),  $\eta$  is the "overpotential" defined as potential of the test electrode as referred to the isotopic mixed potential<sup>7)</sup> of the same electrode in the same environment and  $R$ ,  $T$  and  $F$  have their usual significance. The magnitude of the right-hand side of Eq. (2) except  $\nu(r)$  is determinable experimentally from polarization measurements, and hence we write as,

$$i_0 = \nu(r) \cdot I_{0(pol)} \quad (3)$$

where  $I_{0(pol)}$  is in practice obtained from the time average of the reaction admittance at the isotopic mixed potential as,

$$I_{0(pol)} = \frac{RT}{2F} \overline{\left( \frac{\partial i}{\partial \eta} \right)}_{\eta=0} \quad (4)$$

On the other hand, the exchange current density is obtained from a deuterium exchange reaction, provided that the isotope does not by-pass the HER. Under the condition that the atomic fraction of deuterium  $X^G$  in the gaseous hydrogen and its initial value  $X_0^G$  are both close to unity and that the deuterium separation factor of the HER in the direction of hydrogen ionization is not far separated from unity (actually found at  $1 \sim 2$ )<sup>8)</sup>,  $i_{0(ex)}$  is given approximately by the following equation without involving the isotope effect<sup>4)</sup>,

$$i_{0(ex)} = \frac{2nF}{At} (X_0^G - X^G) \quad (5)$$

where  $t$  is the reaction time,  $n$  is the total number of moles of the hydrogen gas and  $A$  is the surface area of the test electrode. The  $\nu_{ex}$  defined above is now given in terms of  $I_{0(pol)}$  and  $i_{0(ex)}$  as,

$$\nu_{ex} = i_{0(ex)} / I_{0(pol)} \quad (6)$$

The exchange reactions were carried out in a vacuum type reaction vessel<sup>4)</sup>

T. MATSUSHIMA and M. ENYO

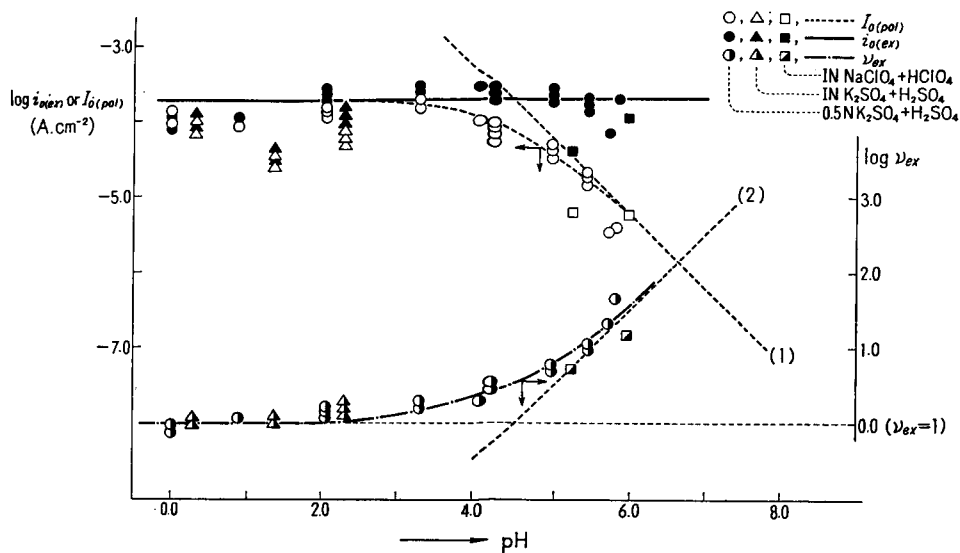


Fig. 1. pH-dependences of  $I_0(pol)$ ,  $i_0(ex)$  and  $\nu_{ex}$  in acidic region.  
 $P_{H_2} = 20 \pm 2$  cmHg at the working temperature, 12°C.

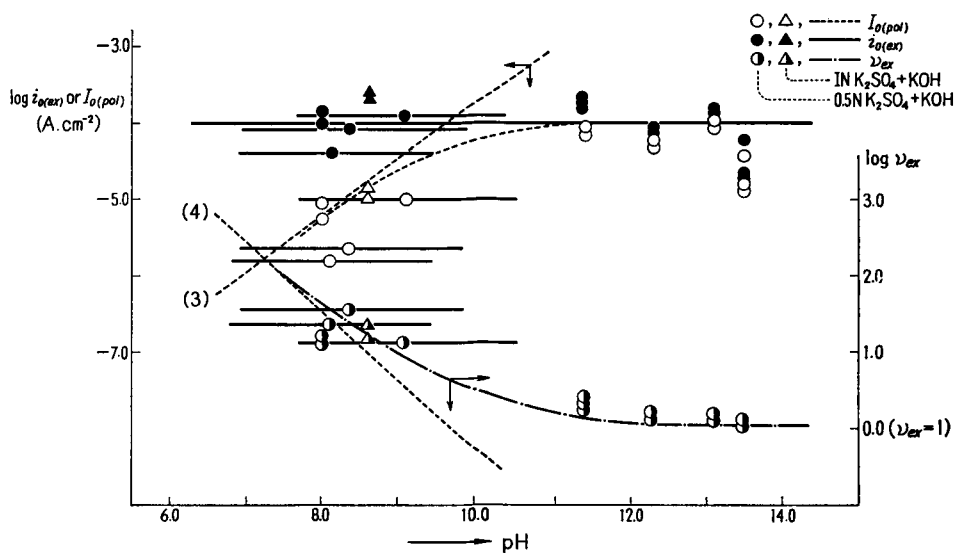


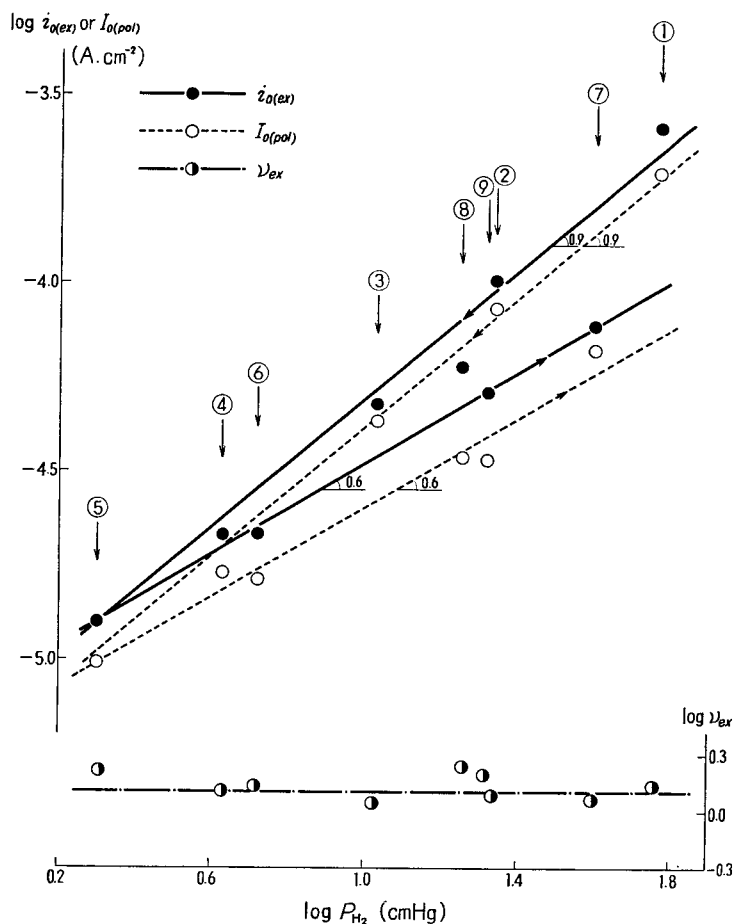
Fig. 2. pH-dependences of  $I_0(pol)$ ,  $i_0(ex)$  and  $\nu_{ex}$  in alkaline region.  
 $P_{H_2} = 20 \pm 2$  cmHg at the working temperature, 12°C. The horizontal bar indicates the inaccuracy associated with the pH value.

*Stoichiometric number of hydrogen electrode reaction*

In order to investigate the cause of the anomalously large values of  $\nu_{ex}$ , further experiments were conducted on the effects of pressure and temperature. Results are presented below separately for three regions; A) pH=0~3, B) pH=3~7~12 and C) pH=12~14.

*D. Dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  upon total hydrogen pressure*  
*Region A*

Data obtained in solution of  $H_2SO_4$  with 0.5N  $K_2SO_4$  (pH=0.9) under the total hydrogen pressure  $P_{H_2}$  ranging from 1 to 60 cmHg are shown in Fig. 3. It is seen that  $i_{0(ex)}$  and  $I_{0(pol)}$  show similar dependences upon  $P_{H_2}$  and



**Fig. 3.** Pressure dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in 0.5N  $K_2SO_4 + H_2SO_4$  (pH=0.90). Numbers on the Figure indicate the sequence of the experiment.

T. MATSUSHIMA and M. ENYO

that  $\nu_{ex}$  is close to unity independent of  $P_{H_2}$ . The pressure dependences expressed by

$$\beta_{ex} = d \ln i_{0(ex)} / d \ln P_{H_2} \quad (7)$$

and

$$\beta_{pol} = d \ln I_{0(pol)} / d \ln P_{H_2} \quad (8)$$

are obtained as  $\beta_{ex} \simeq \beta_{pol} \simeq 0.9$  from measurements conducted in the direction of decreasing  $P_{H_2}$  and  $\beta_{ex} \simeq \beta_{pol} \simeq 0.6$  in the direction of increasing  $P_{H_2}$  (numbers on Fig 3 indicate the sequence of the measurements). The discrepancy between two data is due to decrease in the catalytic activity of the electrode with time, as shown in Fig. 4; in each run under a fixed value of  $P_{H_2}$ , the reaction admittance always decreased with time. This means that the  $\beta$ 's are over-estimated in the former direction and under-estimated in the latter direction. Figure 5 shows data in aqueous sulfuric acid (pH=0.9) without added neutral salt. The results,  $\beta_{ex} \simeq \beta_{pol} \simeq 0.9 \sim 0.7$  and  $\nu_{ex} = 1$ , are substantially the same

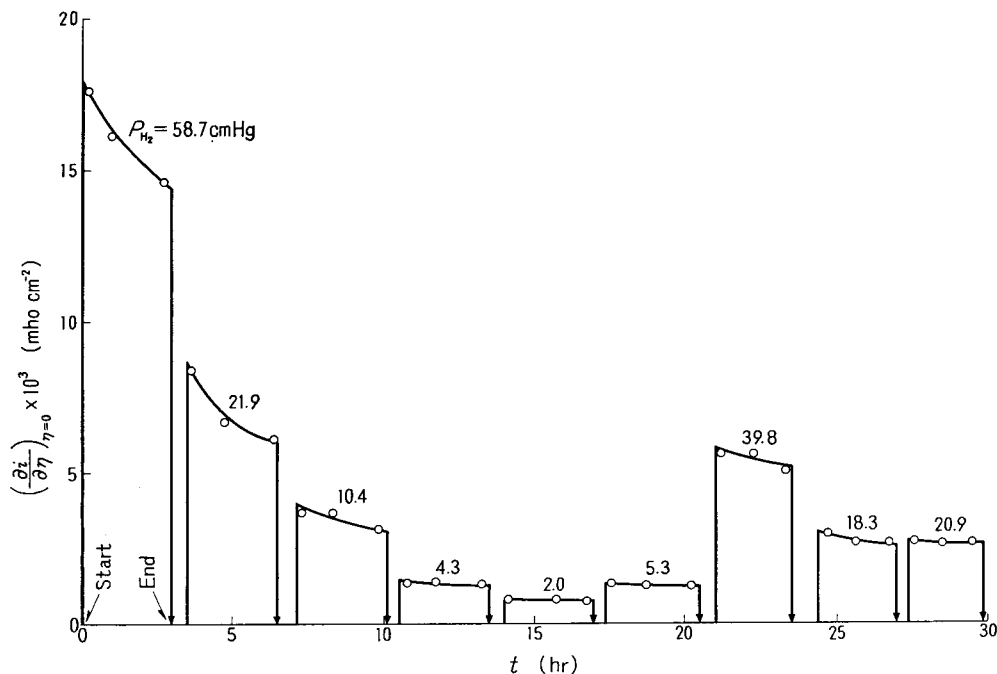
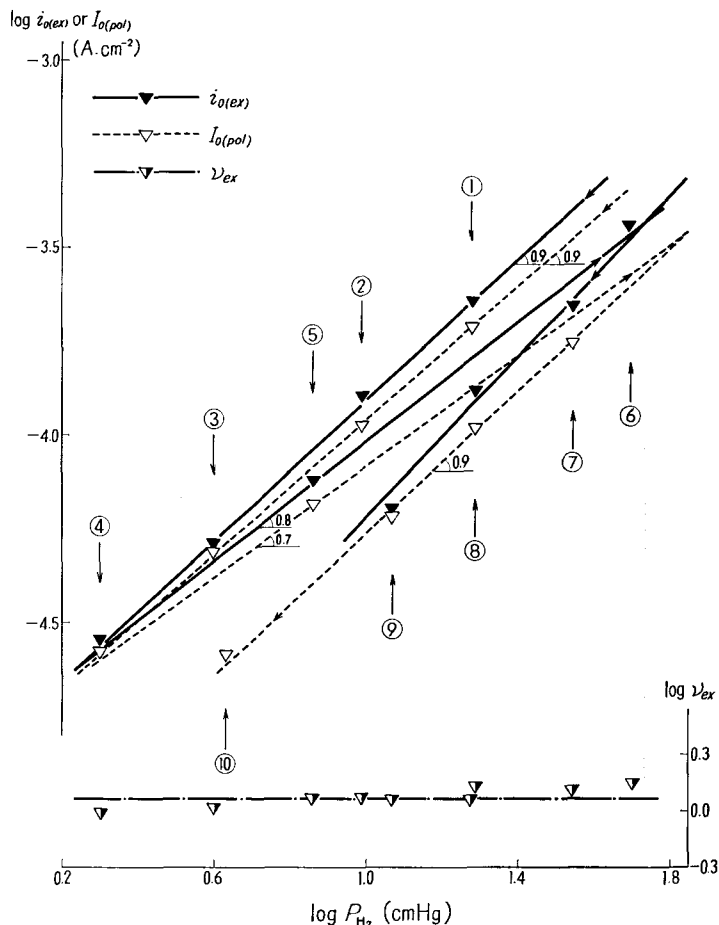


Fig. 4. Pressure and time dependences of reaction admittance in 0.5N  $K_2SO_4 + H_2SO_4$  (pH=0.90). Values on the Figure give the total hydrogen pressure (in cmHg) at the working temperature, 12°C.

## Stoichiometric number of hydrogen electrode reaction



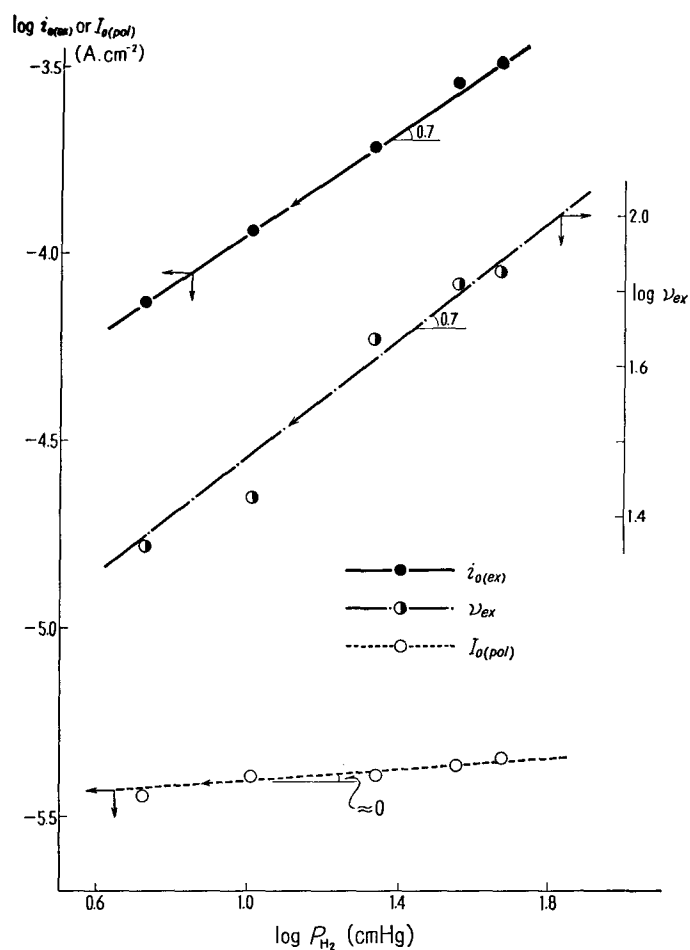
**Fig. 5.** Pressure dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in  $H_2SO_4$  (pH=0.90) without supporting electrolyte; (region A). Numbers on the Figure indicate the sequence of the experiment.

with those obtained in the presence of 0.5N  $K_2SO_4$  (Fig. 3), *viz.*, the alkali metal ions have no significant influence upon kinetics of the HER on Rh. (In the case of Pt electrode, influences of alkali metal ions upon  $\nu_{ex}$  and upon isotopic composition of hydrogen gas were observed).<sup>9)</sup>

### Region B

Figure 6 shows results obtained in the solution of pH=5.8 containing 0.5N  $K_2SO_4$ ;  $i_{0(ex)}$  is dependent upon  $P_{H_2}$  and the value  $\beta_{ex} \approx 0.7$  is of similar magnitude with both  $\beta_{ex}$  and  $\beta_{pol}$  observed in region A. In contrast with

T. MATSUSHIMA and M. ENYO

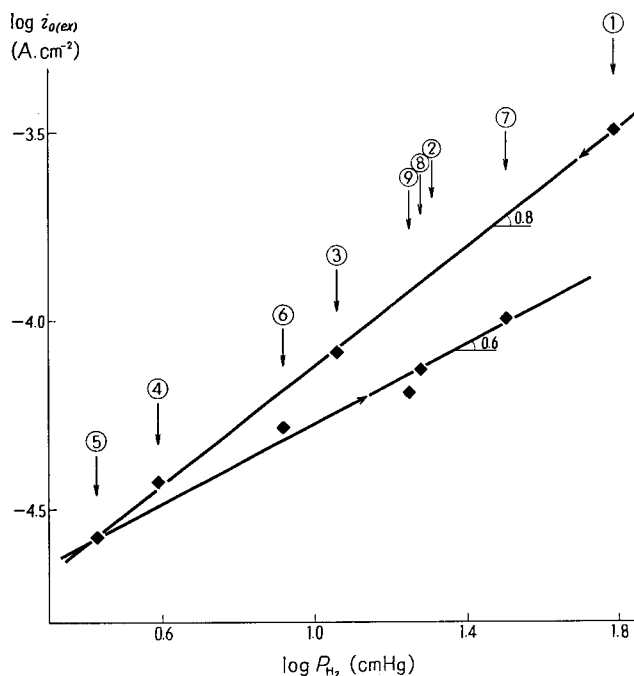


**Fig. 6.** Pressure dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in 0.5N  $K_2SO_4 + H_2SO_4$  (pH=5.8); (region B, acidic side).



*Stoichiometric number of hydrogen electrode reaction*

this,  $I_{0(pol)}$  is independent of  $P_{H_2}$ , or  $\beta_{pol} \simeq 0$ . Consequently,  $\nu_{ex}$  increases remarkably with  $P_{H_2}$ . Figure 7 shows results obtained in water with no electrolyte (pH=5.4). The result,  $\beta_{ex} \simeq 0.8 \sim 0.6$ , is close to that observed above at pH=5.8 in the presence of the neutral salt. No data were obtained on  $I_{0(pol)}$  and  $\nu_{ex}$  owing to poor conductance of the water.



**Fig. 7.** Pressure dependence of  $i_{0(ex)}$  in water containing no added electrolyte (pH=5.4); (region B, acidic side).

Figure 8 shows data obtained at pH=8.5;  $\beta_{ex}$  was roughly 0.8. The slight variation of  $I_{0(pol)}$  with  $P_{H_2}$  ( $\beta_{pol} \simeq 0.3 \sim 0$ ) is to be attributed to the decrease in the activity of the electrode with time. The activity decrease is clearly seen in Fig. 9; the reaction admittance is practically independent of  $P_{H_2}$  but decreases monotonously with the reaction time.

*Region C*

Results at pH=13.5 are shown in Fig. 10. The values,  $\beta_{ex} \simeq \beta_{pol} \simeq 0.6$ , are close to those observed in region A. Also,  $\nu_{ex}$  is close to unity and is independent of  $P_{H_2}$ .

T. MATSUSHIMA and M. ENYO

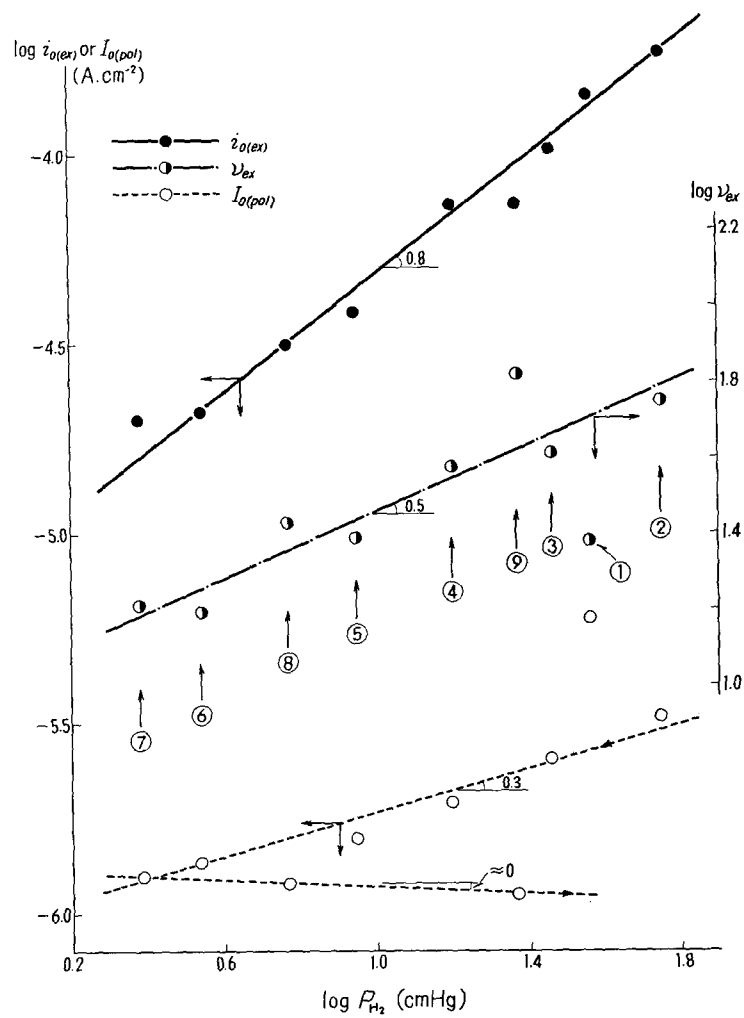
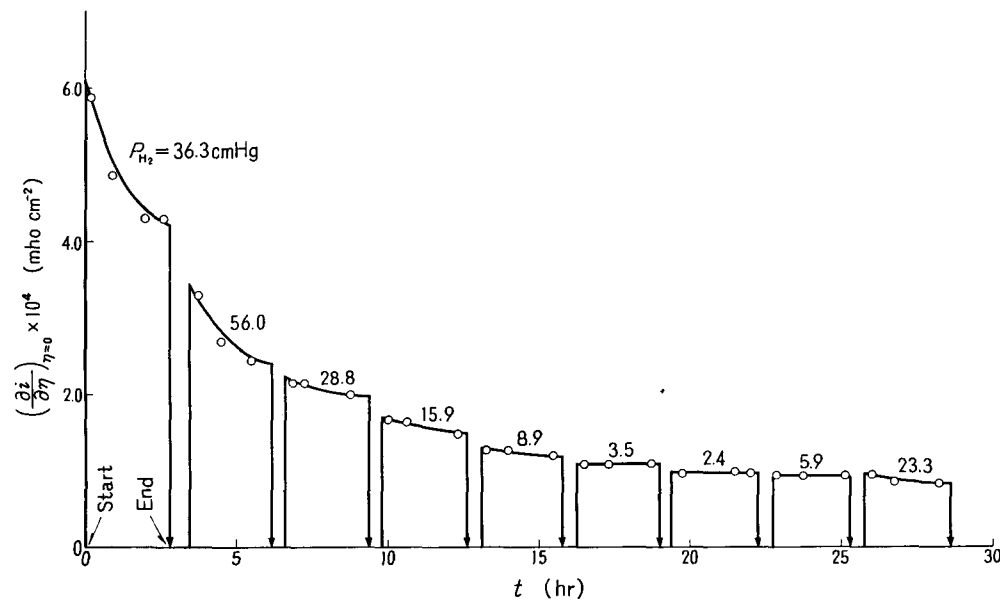


Fig. 8. Pressure dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in 0.5N  $K_2SO_4+KOH$  (pH=8.4); (region B, alkaline side).

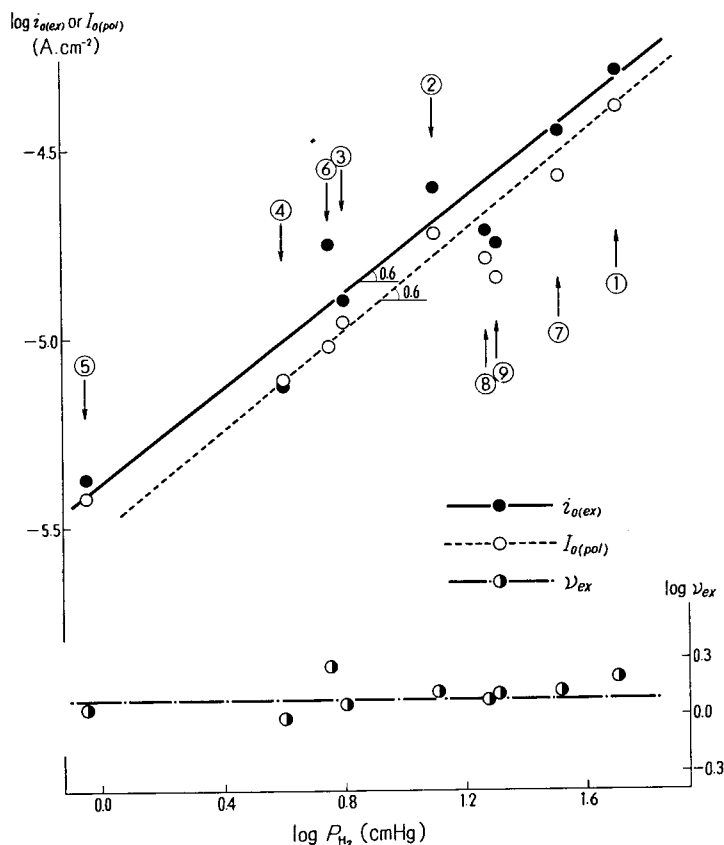


**Fig. 9.** Pressure and time dependences of reaction admittance in 0.5 N  $K_2SO_4 + KOH$  (pH=9.4); (region B, alkaline side).

T. MATSUSHIMA and M. ENYO

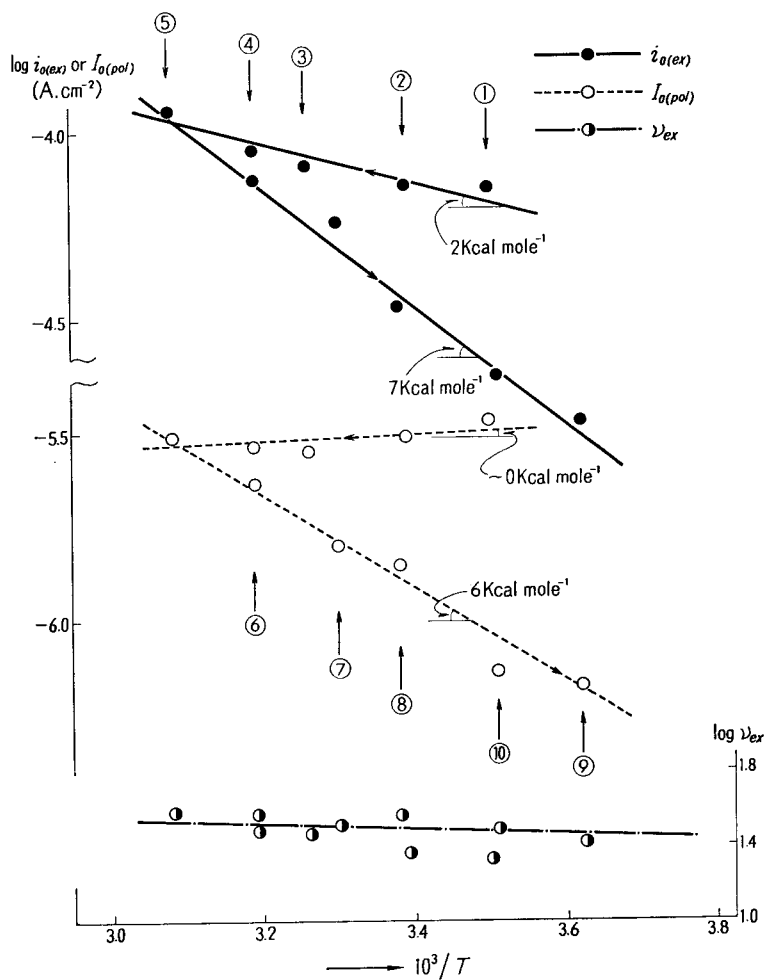
*E. Temperature dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$*

Figure 11 summarizes the temperature dependences observed at pH=5.7 (region B);  $\nu_{ex}$  is practically independent of temperature. Both  $i_{0(ex)}$  and  $I_{0(pol)}$  are temperature-dependent, but no accurate data were obtained owing to significant changes in the catalytic activity; rough values of the activation energy with respect to  $i_{0(ex)}$  and to  $I_{0(pol)}$  evaluated as the mean of the values obtained with rising and lowering temperature are 4.5 and 3 Kcal mole<sup>-1</sup>, respectively.



**Fig. 10.** Pressure dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in 0.5N  $K_2SO_4+KOH$  (pH=13.5); (region C). Numbers on the Figure indicate the sequence of the experiment.

## Stoichiometric number of hydrogen electrode reaction



**Fig. 11.** Temperature dependences of  $i_{0(ex)}$ ,  $I_{0(pol)}$  and  $\nu_{ex}$  in 0.5N  $\text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  (pH = 4.7),  $P_{\text{H}_2} = 20 \pm 2 \text{ cmHg}$ ; (region B). Numbers on the Figure indicate the sequence of the experiment.

## Discussion

Results are summarized in Table 2; the value  $\infty$  of  $\nu_{ex}$  represents that  $\nu_{ex}$  is much larger than the theoretically expected value<sup>4)</sup> of  $\nu(r)$ , 1 or 2, and  $\gamma_{ex}$  and  $\gamma_{pol}$  represent the pH-dependences of  $i_{0(ex)}$  and  $I_{0(pol)}$ , defined respectively as

T. MATSUSHIMA and M. ENYO

TABLE 2. Results on the HER and the deuterium exchange reaction on Rh

( $\beta$  and  $\gamma$  are hydrogen pressure and pH-dependences of  $i_{0(ex)}$  or  $I_{0(pol)}$ , respectively).

Region (pH)	A (0~3)	B (3~7~12)	C (12~14)
$\nu_{ex}$	1	$\infty$	1
$\beta_{ex}$	0.9~0.6	0.8~0.6	0.6
$\beta_{pol}$	0.9~0.6	0	0.6
$\gamma_{ex}$	0	0	0
$\gamma_{pol}$	0	$\sim 1$ (acidic side) $\sim -1$ (alkaline side)	0

$$\gamma_{ex} \equiv -d \log i_{0(ex)} / d \text{ pH} \quad (9)$$

and

$$\gamma_{pol} \equiv -d \log I_{0(pol)} / d \text{ pH} . \quad (10)$$

In region A, the HER on Rh was previously reported<sup>4)</sup> to obey the catalytic mechanism,



where H(a) is a hydrogen adatom on the electrode surface. The results in region A (Table 2),  $\nu_{ex}=1$ ,  $\gamma_{ex} \simeq \gamma_{pol} \simeq 0$ , are in agreement with previous data and are consistent with the catalytic mechanism but not with other mechanisms such as the slow-discharge and the electrochemical.<sup>4)</sup> The new data,  $\beta_{ex} \simeq \beta_{pol} \simeq 0.9 \sim 0.6$ , are also consistent with this mechanism according to the following consideration:  $\beta$  is expressed as<sup>10,11)</sup>,

$$\beta \equiv \frac{d \ln i_0}{d \ln P_{\text{H}_2}} = \left( \frac{\partial \ln i_+}{\partial \ln P_{\text{H}_2}} \right)_{\varphi} - \frac{RT}{2F} \left( \frac{\partial \ln i_+}{\partial \varphi} \right)_{P_{\text{H}_2}} \quad (11)$$

where  $\varphi$  is the electrode potential as referred to the potential in the bulk of the solution and  $i_+$  is the unidirectional rate in the direction of hydrogen ionization. The last term of this equation except the factor 2 is nothing but the forward Tafel constant ( $RT/F$ ) ( $d \ln i_+ / d \eta$ ), and its value on Rh is  $0.6 \sim 0.4$  at  $\eta=0$ .<sup>9)</sup> Hence, from the above value of  $\beta$ , the first term in the right-hand side, *viz.*, the reaction order of the forward unidirectional rate with respect to hydrogen, is calculated to be  $1.2 \sim 0.8$ , or close to unity which is the value expected for the catalytic mechanism.

The results in region C are practically the same with those in region



Step (I) is the dissociation of hydrogen molecule to hydrogen adatoms and this plays the role of the common rate-determining step for the deuterium exchange reaction and the HER in regions A and C. Step (II) is the ionization of  $H(a)$  to  $H^+(S)$  (a proton in the neighbourhood of the electrode), which is rapid in the whole range of pH. Step (III) is the diffusion of  $H^+(S)$  to  $H^+(B)$  (a proton in the bulk of the solution), which is far more rapid than step (I) in regions A and C but becomes slower than step (I) in region B owing to low concentration of  $H^+$  or  $OH^-$  and hence determines the overall rate of the HER. Step (IV) is the reaction between proton and a Brönsted base, which is probably very rapid<sup>14)</sup>;  $D^+$  (deuterium ion produced by step (II)) is hence transformed rapidly into PDO. Step (V) is the diffusion of  $H_2O(S)$  (water molecule near the electrode) towards bulk of the solution, which must be very rapid because of the high concentration of  $H_2O$ , 55 mole  $l^{-1}$ . Thus, the route of the deuterium exchange reaction is constructed of steps  $(I) \leftrightarrow (II) \leftrightarrow (IV) \leftrightarrow (V)$ , in which step (I) is rate-determining in the whole pH-range. The route of the HER is constructed of steps  $(I) \leftrightarrow (II) \leftrightarrow (III)$ , in which step (I) is rate-determining in regions A and C and step (III) in region B. As a result,  $\nu_{ex}$  becomes large in neutral solutions.

The HER on Rh hence obeys the catalytic mechanism in the whole range of pH if one refers only to the surface processes (*viz.*, excepting the diffusion step of reactant or product in the solution phase). Incidentally, it is to be stressed that the experimental determination of pH-dependence of HER from polarization measurements is not secured in the neutral region, irrespective of presence or absence of a supporting electrolyte.

The result  $\nu_{ex} = \infty$  in region B provides an example of the "infinite" stoichiometric number<sup>6)</sup> predicted for the case that the isotopic exchange takes place without passing through the rate-determining step of the overall reaction.

In the present system composed of pure deuterium and light water, we expect, on the basis of the above conclusion of the catalytic mechanism being operative, formation of  $P_2$  alone by the exchange reaction<sup>15)</sup>, that is, the value of the quantity,  $(X_{PD} - X_{PD,0})/X_{PD,eq}$ , should be zero, where  $X_{PD}$  is the mole fraction of PD in the hydrogen gas sample after the exchange,  $X_{PD,eq}$  is the value when the same gas is equilibrated with respect to the isotopic equilibration reaction,  $P_2 + D_2 = 2 PD$ , and  $X_{PD,0}$  is that before the exchange reaction. However, the experimental results were 0.3~0.8, in disagreement with this figure. Such a significant degree of formation of PD was considered previously<sup>15)</sup> to be due to concurrent occurrence of a side reaction which independently equilibrates hydrogen isotopes. Further works are, however, required to ascertain this assumption and to clarify its mechanism.



*Stoichiometric number of hydrogen electrode reaction*

### References

- 1) J. O'M. BOCKRIS, *Modern Aspects of Electrochemistry*, Vol. 1, J. O'M. BOCKRIS ed., Butterworths, London, 1954, p. 180.
- 2) J. HORIUTI and T. NAKAMURA, *Advances in Catalysis*, **17**, 1 (1967).
- 3) M. ENYO and T. YOKOYAMA, *This Journal*, **13**, 222 (1965).
- 4) T. MATSUSHIMA and M. ENYO, *ibid.*, **17**, 14 (1969).
- 5) T. MATSUSHIMA, T. YOKOYAMA and M. ENYO, *ibid.*, **17**, 165 (1969).
- 6) A. MATSUDA and J. HORIUTI, *ibid.*, **10**, (1962).
- 7) M. ENYO and T. YOKOYAMA, *Electrochim. Acta*, **12**, 1631 (1967).
- 8) M. ENYO and T. YOKOYAMA, *ibid.*, **12**, 1641 (1967).
- 9) T. MATSUSHIMA, unpublished data.
- 10) K. J. VETTER, *Elektrochemische Kinetik*, Verlag Chemie, GMBH (1961).
- 11) M. ENYO and T. YOKOYAMA, to be published.
- 12) R. PARSONS, *Handbook of Electrochemical Constants*, Butterworths, London, 1959, p. 79.
- 13) D. GLIETENBERG, A. KUTSCHKER and M. V. STACKELBERG, *Ber. Bunsenges. Physik. Chem.*, **72**, 562 (1968).
- 14) M. EIGEN and L. D. MAEYER, *Z. Elektrochem.*, **59**, 986 (1955).
- 15) M. ENYO, *This Journal*, **15**, 1 (1967).