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

By

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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 re-action 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.[1,2] Several investigations have been carried out in this Laboratory[3~5] on the $\nu(r)$ of the hydrogen electrode reaction (HER),

$$H_2 = 2H^+ + 2e \tag{1}$$

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 ν_{ex}, the value of the stoichiometric number determined from deuterium exchange

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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.[6] 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,

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

where i_0 is the exchange current density, i is the net current density (positive in the anodic direction), η is the "overpotential" defined as potential of the test electrode as referred to the isotopic mixed potential[7] 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,

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

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

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

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 $1\sim2$)[8], $i_{0(ex)}$ is given approximately by the following equation without involving the isotope effect[4],

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

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 ν_{ex} defined above is now given in terms of $I_{0(pol)}$ and $i_{0(ex)}$ as,

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

The exchange reactions were carried out in a vacuum type reaction vessel[4]

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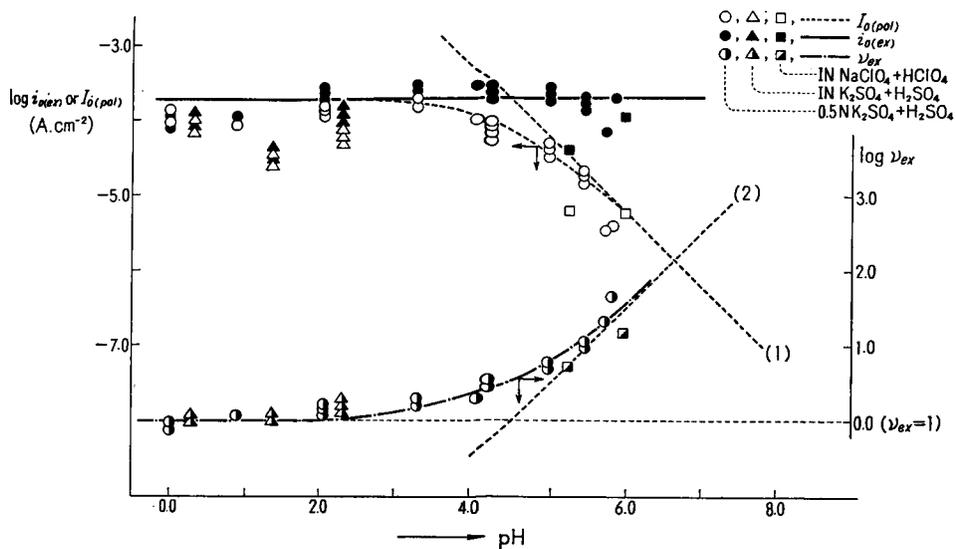
Fig. 1. pH-dependences of $I_{0(pol)}$, $i_{0(ex)}$ and ν_{ex} in acidic region. $P_{H_2} = 20 \pm 2$ cmHg at the working temperature, 12°C.
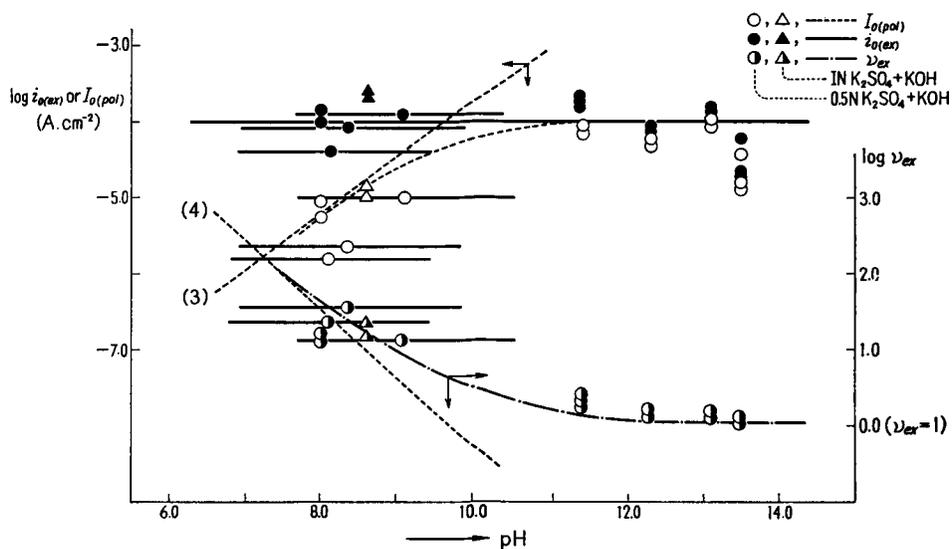

Fig. 2. pH-dependences of $I_{0(pol)}$, $i_{0(ex)}$ and ν_{ex} in alkaline region. $P_{H_2} = 20 \pm 2$ cmHg at the working temperature, 12°C. The horizontal bar indicates the inaccuracy associated with the pH value.

In order to investigate the cause of the anomalously large values of ν_{ex}, further experiments were conducted on the effects of pressure and temperature. Results are presented below separately for three regions; A) pH$=0\sim3$, B) pH$=3\sim7\sim12$ and C) pH$=12\sim14$.

D. *Dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{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
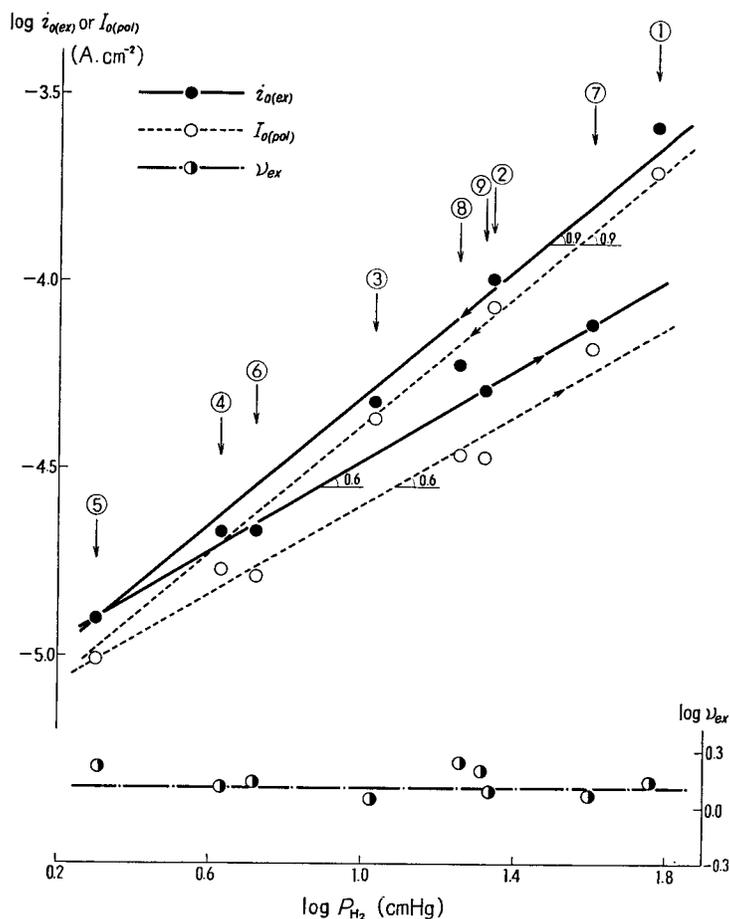

Fig. 3. Pressure dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in 0.5N $K_2SO_4 + H_2SO_4$ (pH$=0.90$). Numbers on the Figure indicate the sequence of the experiment.

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

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

and

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

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 β'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
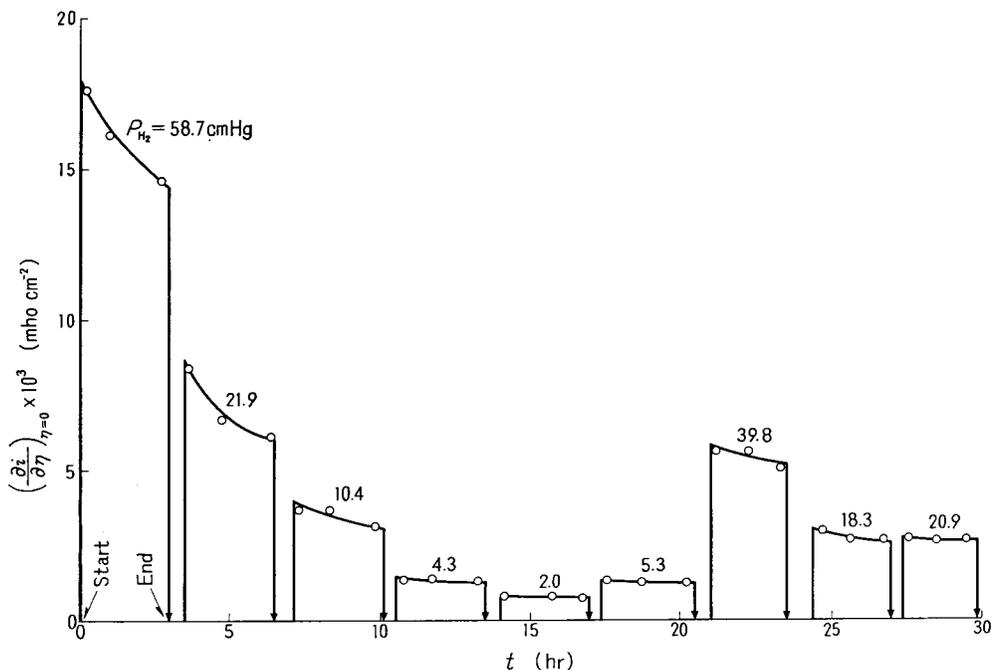

Fig. 4. Pressure and time dependences of reaction admittance in 0.5 N $K_2SO_4 + H_2SO_4$ (pH$=0.90$). Values on the Figure give the total hydrogen pressure (in cmHg) at the working temperature, 12°C.
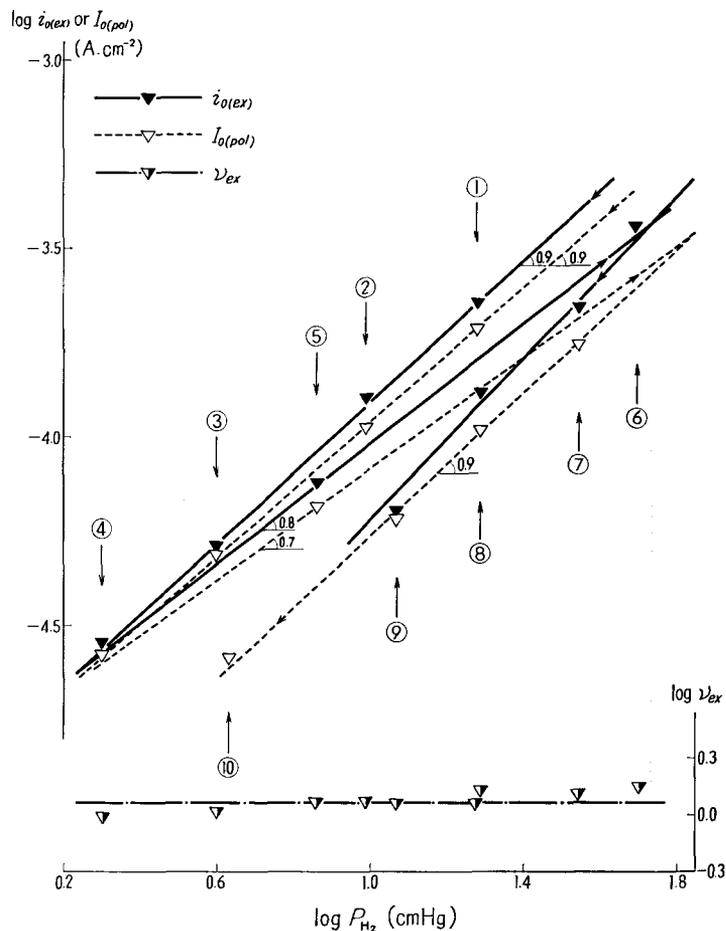
Fig. 5. Pressure dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in
H$_2$SO$_4$ (pH = 0.90) without supporting electrolyte;
(region A). Numbers on the Figure indicate the
sequence of the experiment.

with those obtained in the presence of 0.5 N K$_2$SO$_4$ (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 ν_{ex} and upon
isotopic composition of hydrogen gas were observed).[9]

Region B

Figure 6 shows results obtained in the solution of pH = 5.8 containing
0.5 N K$_2$SO$_4$; $i_{0(ex)}$ is dependent upon P_{H_2} and the value $\beta_{ex} \simeq 0.7$ is of similar
magnitude with both β_{ex} and β_{pol} observed in region A. In contrast with

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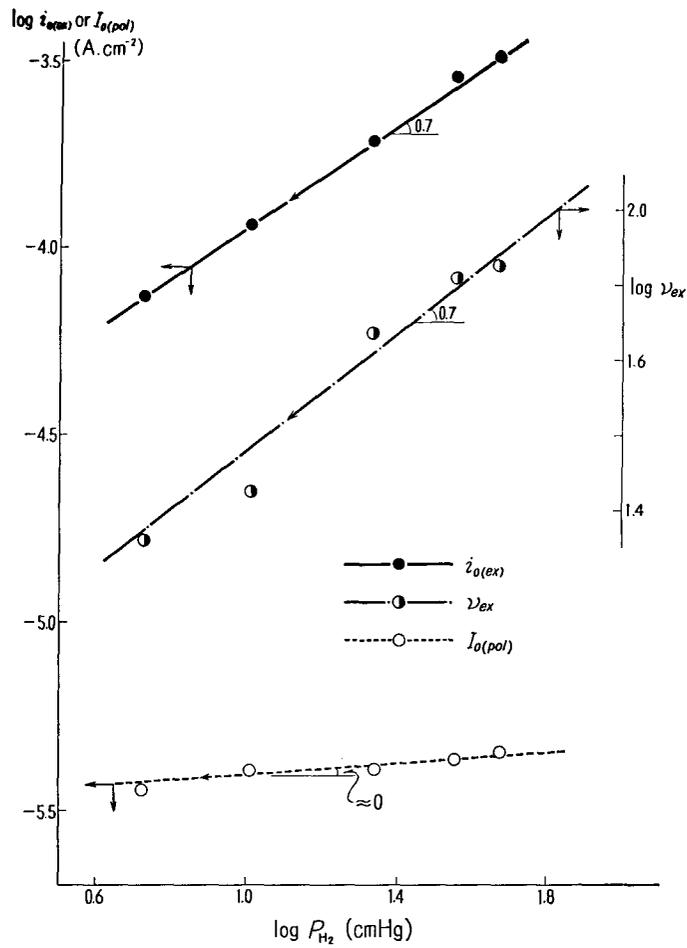
Fig. 6. Pressure dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in 0.5 N $K_2SO_4 + H_2SO_4$ (pH = 5.8); (region B, acidic side).

this, $I_{0(pol)}$ is independent of P_{H_2}, or $\beta_{pol} \simeq 0$. Consequently, ν_{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 ν_{ex} owing to poor conductance of the water.
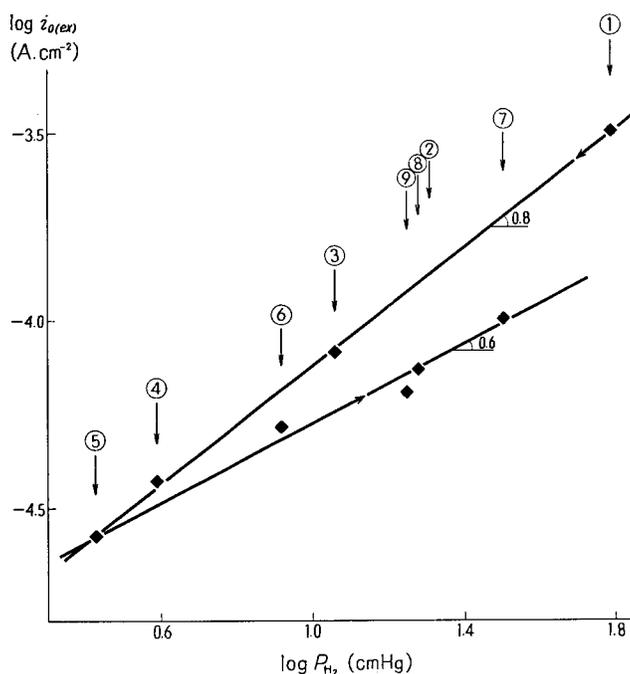

Fig. 7. Pressure dependence of $i_{0(ex)}$ in water containing no added electrolyte (pH = 5.4); (region B, acidic side).

Figure 8 shows data obtained at pH = 8.5; β_{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, ν_{ex} is close to unity and is independent of P_{H_2}.

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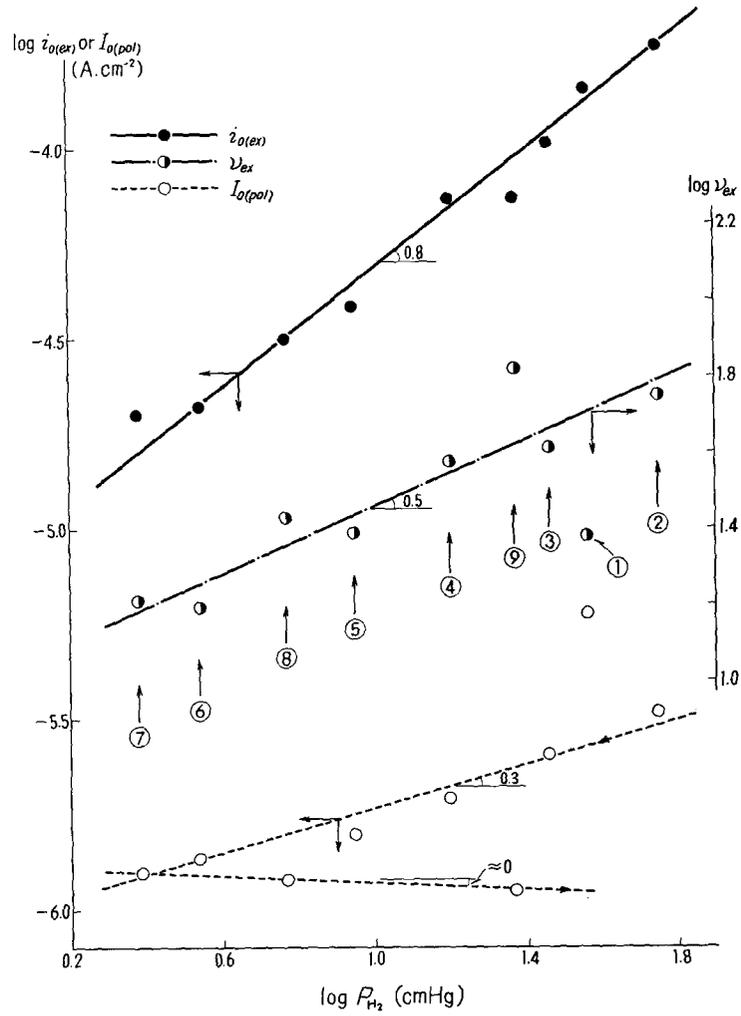
**Fig. 8.** Pressure dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in $0.5\,N$ $K_2SO_4 + KOH$ (pH = 8.4); (region B, alkaline side).
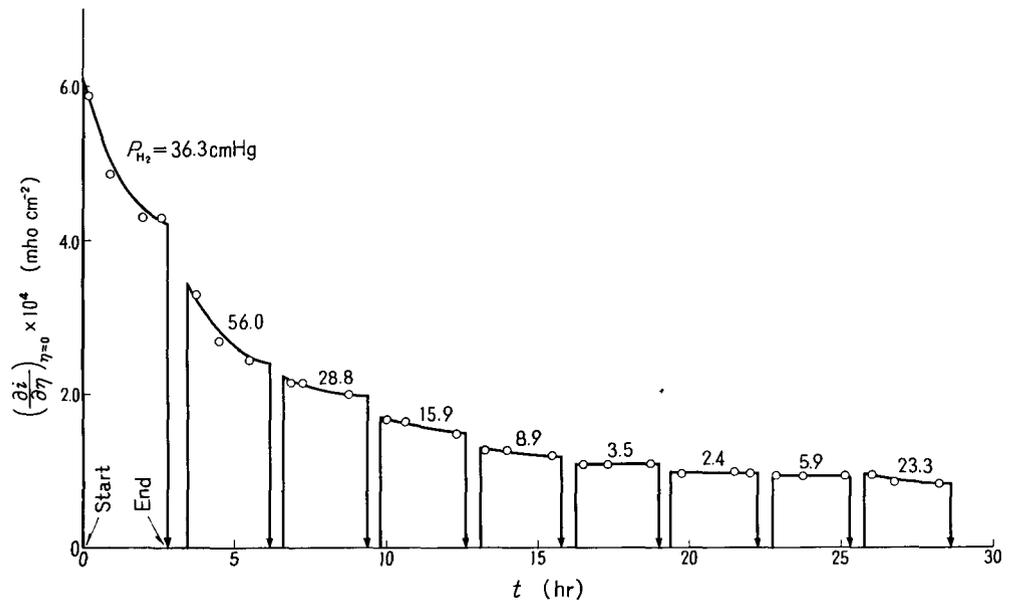
Fig. 9. Pressure and time dependences of reaction admittance in
0.5 N K_2SO_4+KOH (pH=9.4); (region B, alkaline side).

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

Figure 11 summarizes the temperature dependences observed at pH=5.7 (region B); ν_{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^{-1}, respectively.
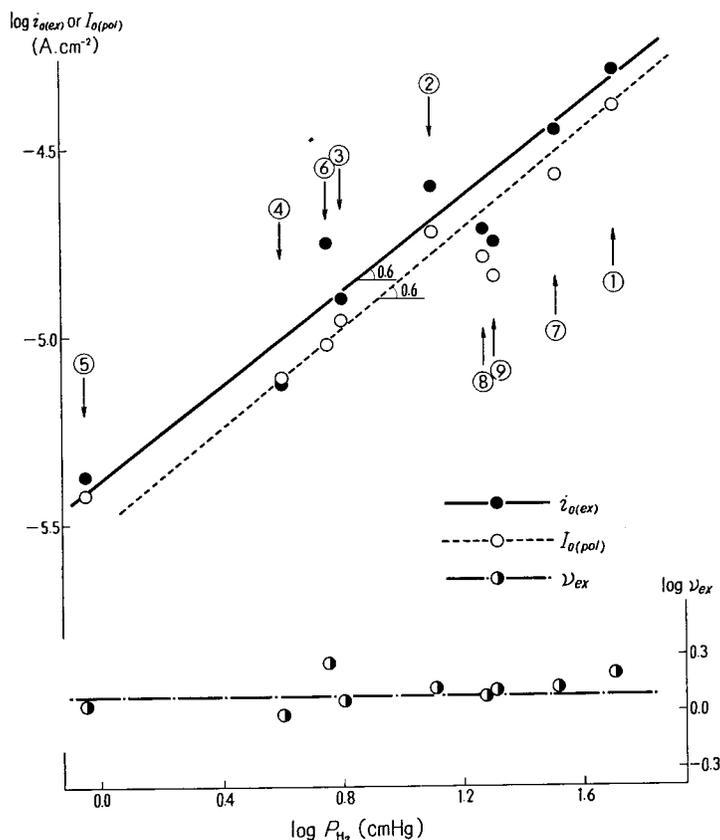
Fig. 10. Pressure dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in 0.5 N K$_2$SO$_4$+KOH (pH=13.5); (region C). Numbers on the Figure indicate the sequence of the experiment.
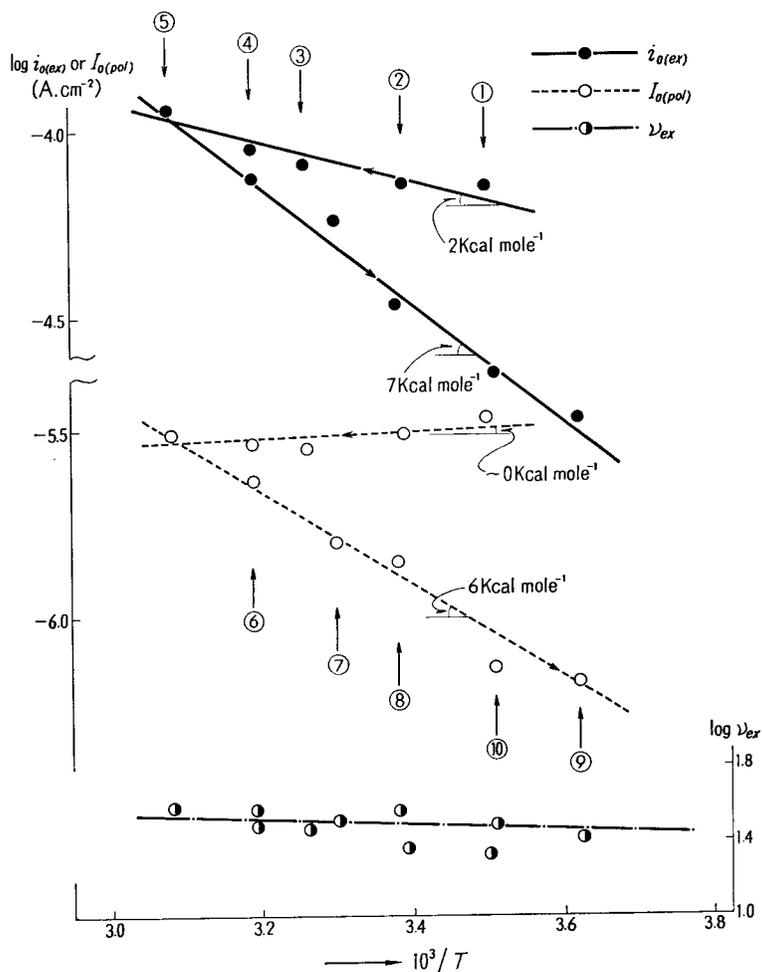
Fig. 11. Temperature dependences of $i_{0(ex)}$, $I_{0(pol)}$ and ν_{ex} in 0.5 N $K_2SO_4 + H_2SO_4$ (pH = 4.7), $P_{H_2} = 20 \pm 2$ cmHg; (region B). Numbers on the Figure indicate the sequence of the experiment.

Discussion

Results are summarized in Table 2; the value ∞ of ν_{ex} represents that ν_{ex} is much larger than the theoretically expected value[4] of $\nu(r)$, 1 or 2, and γ_{ex} and γ_{pol} represent the pH-dependences of $i_{0(ex)}$ and $I_{0(pol)}$, defined respectively as

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

(β and γ 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)
ν_{ex}	1	∞	1
β_{ex}	0.9~0.6	0.8~0.6	0.6
β_{pol}	0.9~0.6	0	0.6
γ_{ex}	0	0	0
γ_{pol}	0	~ 1 (acidic side) ~ −1 (alkaline side)	0

$$\gamma_{ex} \equiv - d \log i_{0(ex)} / d \, \mathrm{pH} \qquad (9)$$

and

$$\gamma_{pol} \equiv - d \log I_{0(pol)} / d \, \mathrm{pH} . \qquad (10)$$

In region A, the HER on Rh was previously reported[4] to obey the catalytic mechanism,

$$\begin{cases} H_2 \leftrightarrow 2\,H(a) & \text{(rate-determining)} \\ H(a) \rightleftharpoons H^+ + e & \text{(rapid)} , \end{cases}$$
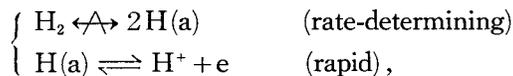
where $H(a)$ is a hydrogen adatom on the electrode surface. The results in region A (Table 2), $\nu_{ex}=1$, $\gamma_{ex} \simeq \gamma_{pol} \simeq 0$, are in agreement with previous data and are consistent with the catalytic mechanism but not with other mechanisms such as the slow-discharge and the electrochemical.[4] 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: β is expressed as[10,11],

$$\beta \equiv \frac{d \ln i_0}{d \ln P_{H_2}} = \left(\frac{\partial \ln i_+}{\partial \ln P_{H_2}} \right)_\varphi - \frac{RT}{2F} \left(\frac{\partial \ln i_+}{\partial \varphi} \right)_{P_{H_2}} \qquad (11)$$

where φ 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~ 0.4 at $\eta = 0$.[9] Hence, from the above value of β, 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 1.2~0.8, 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

A and accordingly the HER on Rh in this region is also concluded to obey the catalytic mechanism.

In region B, the results of γ_{ex} and β_{ex} are the same with those obtained in regions A and C. The facts indicate that the mechanism of the exchange reaction is unaltered throughout the whole pH range. Now, the value $\nu_{ex} = \infty$ indicates[6] that, in this region, the exchange reaction takes place without passing through the rate-determining step of the HER. Also, it is clear from $\beta_{pol} \simeq 0$ that the rate-determining step of the HER in this region does not involve hydrogen molecule or hydrogen adatom*[*]. It is hence very likely that here the diffusion of H^+ or OH^- is controlling the overall rate. This view is supported by the fair agreement of the value of the activation energy obtained from $I_{0(pol)}$ in this region with that reported[12] for diffusion of H^+ in aqueous solution. Further, it is well substantiated by the fact that, in both acidic and alkaline side, $I_{0(pol)}$ showed general tendency with decreasing acidity or alkalinity of the solution to approach asymptotically the lines with $|\text{slope}| = 1$ in log $I_{0(pol)}$ vs. pH diagram (*cf.* line 1 in Fig. 1 and line 3 in Fig. 2). We may therefore conclude that the rate-determining step of the HER in this region is the diffusion of H^+ or OH^- and that the deuterium exchange reaction takes place without passing through this step.

The dotted straight lines (1) in Fig. 1 and (3) in Fig. 2 give the limiting rates of diffusion of H^+ and OH^-, respectively, as calculated from the known values of diffusion coefficient[12,13] of H^+ and OH^- and the thickness of the diffusion layer (*ca.* 1×10^{-3} cm under the present shaking condition as estimated from the previous data[3] on the limiting rate of diffusion of H_2). Values of the stoichiometric number calculated from the dotted lines and $i_{0(ex)}$ (which is pH-independent) are shown by the dotted curved lines (2) in Fig. 1 and (4) in Fig. 2; these are in good agreement with the observed values of ν_{ex}.

Summarizing the above, the operative mechanism may be presented as follows. The entire reaction is expressed by the scheme,

$$
\begin{array}{ccc}
\text{(I)} & \text{(II)} & \text{(III)} \\
H_2 \longleftrightarrow \{H(a) \rightleftharpoons H^+(S) \longleftrightarrow H^+(B) \\
\quad\quad \{H(a) \quad (D^+) \\
\quad\quad\quad \text{(IV)} \updownarrow + OH^- \text{ or } H_2O \\
\quad\quad\quad\quad \text{(V)} \\
\quad\quad H_2O(S) \rightleftharpoons H_2O(B) \\
\quad\quad (PDO) \quad\quad (PDO)
\end{array}
$$

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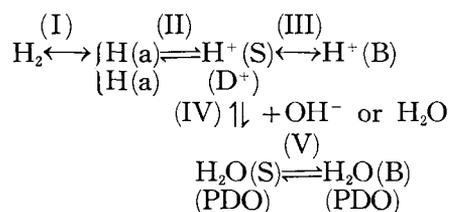
*) It is not *a priori* impossible to interprete $\beta_{pol} = 0$ on the basis of the catalytic mechanism, if one assumes the surface coverage of H(a) to be nearly complete. However, there is no possibility along this line of interpreting the other experimental data, $\nu_{ex} = \infty$ and $|d \log I_{0(pol)} / d \text{pH}| = 1$.

Step (I) is the dissociation of hydrogen molecule to hydrogen adatoms and this plays the role of the common rate-detrmining 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[14]; 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 1^{-1}. Thus, the route of the deuterium exchange reaction is constructed of steps (I)↔(II)↔(IV)↔(V), in which step (I) is rate-determining in the whole pH-range. The route of the HER is constructed of steps (I)↔(II)↔(III), in which step (I) is rate-determining in regions A and C and step (III) in region B. As a result, ν_{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 meaurements is not secured in the netural 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[6] 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[15], 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, $P_2 + D_2 = 2PD$, 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[15] to be due to concurrent occurrence of a side reaction which independently equilibrates hydrogen isotopes. Further works are, however, required to assertain this assumption and to clarify its mechanism.

Stoichiometric number of hydrogen electrode reaction

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