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## STOICHIOMETRIC NUMBER AND THE MECHANISM OF THE HYDROGEN ELECTRODE REACTION ON NOBLE METALS IN ACIDIC SOLUTIONS

By

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### Abstract

The stoichiometric number,  $\nu_r$ , of the rate-determining step of the hydrogen electrode reaction on Rh, Ir, Au and Ag electrodes in aqueous sulfuric acid was determined by observing the exchange current density,  $i_0$ , from the rate of a deuterium exchange reaction and the reaction resistance at the isotopic mixed potential in the isotopically mixed system; the evaluation of  $i_0$  was performed without introducing any uncertainty due to the isotope effect.  $\nu_r$  was found unity for every electrode studied.

The pH-dependence of  $i_0$  was studied in terms of reaction resistance in solutions of various pH and constant ionic strength.  $i_0$  was found to be independent of pH within the range 0 to 3.5 for every electrode studied.

It was concluded from these results that recombination step of hydrogen adatoms is determining the overall rate of the hydrogen electrode reaction on these electrodes.

### Introduction

Mechanism of hydrogen electrode reaction (HER)



has been established as yet only for a few metal electrodes. The present work is concerned with elucidation of mechanism of HER on typical catalyst metals, Rh, Ir, Au and Ag, by determining two mechanistically important parameters, the stoichiometric number,  $\nu_r$ , of the rate-determining step,  $r$ , and the pH-dependence of the exchange current density,  $i_0$ .

Evaluation of  $i_0$  by extrapolating a linear portion of the Tafel line to zero value of overpotential, which was frequently used in the literature, is open to objections as pointed out previously<sup>1)</sup>; the Tafel line is often not sufficiently linear, even in the potential range sufficiently apart from the reversible potential, at which we may identify the observed current,  $i$ , with  $i_-$ , the unidirectional cathodic current. The evaluation is possible without un-

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certainty by utilizing a hydrogen isotope as a tracer, provided that due considerations are paid for the isotope effect which otherwise obscures the results.

Particular precautions have been paid in the present investigation to overcome the following two experimental difficulties; slow rate of diffusion of hydrogen molecule in the solution which may mask the rate of HER, and impurities in the solution, which disturb particularly the investigation on the pH-dependence of  $i_0$  of HER.

### Theoretical

#### (A) Mechanism and Mechanistic Parameters

Hydrogen adatom,  $H(a)$ , and adsorbed hydrogen-molecule ion,  $H_2^+(a)$ , are assumed to be possible intermediates of HER in acidic solution.\*) Hence,

TABLE 1. Possible reaction routes and appropriate mechanistic parameter values

| Reaction route | Steps and Mechanism   | $\nu_r$ | $\nu_{ex}$ | $\gamma$ |
|----------------|---|---------|------------|----------|
| I              | $H_2 \rightarrow 2H(a), H(a) \rightarrow H^+ + e^-$   |         |            |          |
|                | $\xrightarrow{\quad} \rightleftharpoons$  | 1       | 1          | 0        |
|                | $\rightleftharpoons \xrightarrow{\quad}$  | 2       | 2          | 0.5      |
| II             | $H_2 \rightarrow H(a) + H^+ + e^-, H(a) \rightarrow H^+ + e^-$                                |         |            |          |
|                | $\xrightarrow{\quad} \rightleftharpoons$  | 1       | 1          | 0.5      |
|                | $\rightleftharpoons \xrightarrow{\quad}$  | 1       | $\infty$   | 0.5      |
| III            | $H_2 \rightarrow H_2^+(a) + e^-, H_2^+(a) \rightarrow H(a) + H^+, H(a) \rightarrow H^+ + e^-$ |         |            |          |
|                | $\xrightarrow{\quad} \rightleftharpoons \rightleftharpoons$                                   | 1       | 1          | 0.5      |
|                | $\rightleftharpoons \xrightarrow{\quad} \rightleftharpoons$                                   | 1       | 1          | 1        |
|                | $\rightleftharpoons \rightleftharpoons \xrightarrow{\quad}$                                   | 1       | $\infty$   | 0.5      |
| IV             | $H_2 \rightarrow H_2^+(a) + e^-, H_2^+(a) \rightarrow 2H^+ + e^-$                             |         |            |          |
|                | $\xrightarrow{\quad} \rightleftharpoons$  | 1       | 1          | 0.5      |
|                | $\rightleftharpoons \xrightarrow{\quad}$  | 1       | 1          | 1.5      |

\*) According to HORIUTI,<sup>2)</sup> the energy of the state,  $H^-(a) + H^-(a)$ , is prohibitively high for being intermediate unless overpotential reaches below  $-1$  volt. Hence  $H^-(a)$  was excluded from the present discussion.

we have four possible reaction routes as listed in Table 1.

In Table 1,  $\nu_r$  is the stoichiometric number of the rate-determining step, denoted by  $\rightarrow$ , in the respective reaction route and  $\nu_{ex}$  is the value of  $\nu_r$  obtained by equating an isotopic exchange rate with the unidirectional rate of HER. If the isotopic tracer by-passes the rate-determining step of HER,  $\nu_{ex}$  should become far greater than  $\nu_r$ .<sup>3)</sup> This case is indicated by  $\infty$ .

The pH-dependence of  $i_0$ ,  $r$ , *i. e.*,

$$r \equiv -\partial \log i_0 / \partial \text{pH} \quad (2)$$

was calculated according to PARSONS<sup>4)</sup> with 0.5 transfer coefficient for the case of an excess amount of supporting electrolyte present in the solution.

#### (B) Method of the $\nu_{ex}$ -determination

We have in general<sup>5)</sup>

$$\frac{i_+}{i_-} = \exp\left(\frac{2F\eta}{\nu_r RT}\right) \quad (3)$$

for HER in system of any deuterium content, where  $i_+$  and  $i_-$  are, respectively, sum of the overall unidirectional rates (current density unit) of transfer of deuterium and light hydrogen from hydrogen gas to aqueous electrolyte and that of the reverse process,  $\eta$  is the potential of the test electrode as referred to the isotopic mixed potential of the same electrode in the same environment<sup>\*\*)</sup> and  $R$ ,  $T$  and  $F$  have their usual meaning.

Equation (3) gives the following equation at  $\eta=0$

$$\nu_r = i_0 \frac{2F}{RT} \left( \frac{\partial \eta}{\partial i} \right)_{\eta=0} \quad (4)$$

where  $i_0$ , the exchange current density, is the identical value of  $i_+$  and  $i_-$  at  $\eta=0$  and  $i$  is the net current density, *i. e.*,  $i = i_+ - i_-$ . The stoichiometric number  $\nu_r$  is thus derived from  $i_0$  and the reaction resistance,  $(\partial \eta / \partial i)_{\eta=0}$ .

The reaction resistance is readily determined by measuring  $\eta$  and  $i$  around the isotopic mixed potential. Evaluation of  $i_0$  at the isotopic mixed potential is possible by following an isotopic exchange between pure deuterium gas and aqueous electrolyte of light water. Thus, provided that atomic fraction  $X^a$

\*\* ) A steady potential of an electrode in a system composed of aqueous electrolyte and hydrogen gas of any deuterium contents at zero net current is here called the isotopic mixed potential of the electrode. This is not identical with the thermodynamic reversible potential of hydrogen electrode in a light hydrogen system of otherwise the same composition and the difference depends on magnitude of the isotope effect of HER, hence on the kind of electrode metal used, besides on the isotopic contents and other experimental conditions.<sup>6,7)</sup> The difference usually amounts 0~10 mV.<sup>6)</sup>

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of deuterium in hydrogen gas remains close to unity throughout the course of the exchange reaction and that the deuterium separation factor of HER in the forward (anodic) direction is of the order of magnitude of unity,<sup>\*\*\*)</sup> we have<sup>1)</sup>

$$A \int_0^t i_0 dt = 2nF(X_0^a - X^a) \quad (5)$$

where  $t$  is the reaction time,  $A$  is surface area of the test electrode,  $n$  is the number of moles of the total hydrogen gas and  $X_0^a$  is the value of  $X^a$  at  $t=0$ . Consequently, from Eqs. (4) and (5), we have the following expression for  $\nu_{ex}$ ,

$$\nu_{ex} = \frac{(2nF/At)(X_0^a - X^a)}{2F \left[ \left( \frac{\partial \eta}{\partial i} \right)_{\gamma=0}^{-1} \right]} \quad (6)$$

where the quantity

$$\left[ \left( \frac{\partial \eta}{\partial i} \right)_{\gamma=0}^{-1} \right] \equiv \frac{1}{t} \int_0^t \left( \frac{\partial \eta}{\partial i} \right)_{\gamma=0}^{-1} dt \quad (7)$$

can be evaluated graphically (see, Fig. 3).

## Experimental

### (A) Materials

**Hydrogen gas:** Light hydrogen gas was filtered through a Pd-Ag membrane (Japan Pure Hydrogen, Yokohama, Hydrogen Diffusion Purifier, Type LA 06S, capacity 60 l/hr) at 400°C. Deuterium gas was filtered through a Pd-thimble kept at 300°C. Both gases were passed through liquid nitrogen traps before use.

**Water:** Usual distilled water was further distilled five times (first two stages from potassium permanganate-sodium hydroxide solution) in an all glass apparatus under flow of nitrogen evaporated from liquid nitrogen. This water was used for washing and steaming of the cells, as well as preparation of aqueous electrolytes.

**Electrolytes:** Special grade  $H_2SO_4$  and  $K_2SO_4$  (Kanto Chemicals, Tokyo) were used.

**Metal catalyst:** Spirals of Rh and Ir (99.99%, Koch-Light Lab., England) and nets of Au and Ag (99.999%, Johnson-Matthey and Co., London) were used as catalysts for the exchange experiments. Wires of these metals were used for observations of  $\gamma$ .

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<sup>\*\*\*)</sup> This factor has been found to be  $1 \sim 2^{6,7)}$  and depends only slightly on  $X^a$ .

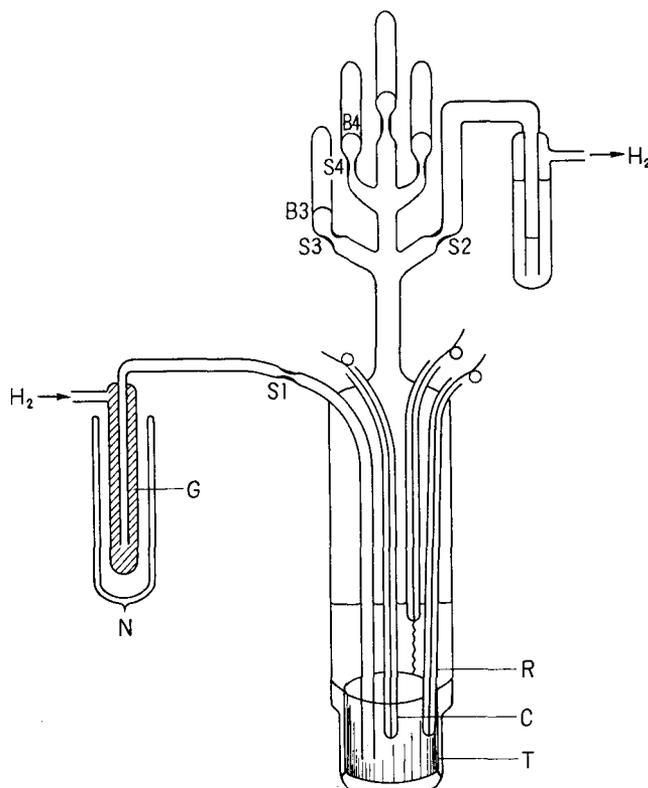
**(B) Potential measurements**

Steady state electrode potentials were measured by means of a vibrating-reed electrometer (Takeda Riken, Tokyo, TR-84B, input resistance  $>10^{15}$  ohm, sensitivity  $20 \mu\text{V}$ , accuracy  $\pm 1.3\%$ ).

Ohmic overpotentials, estimated by following galvanostatic transients with a c. r. oscilloscope, were eliminated from the total overpotential value observed. Corrections for concentration overpotentials, which were significant in the study of pH-dependence of  $i_0$ , were made as described later in detail.

**(C) Measurement of  $\nu_{ex}$** **Procedure**

Fig. 1 shows the exchange reaction vessel of about 400 ml volume. In



**Fig. 1.** Exchange reaction vessel (in the case of Ag)

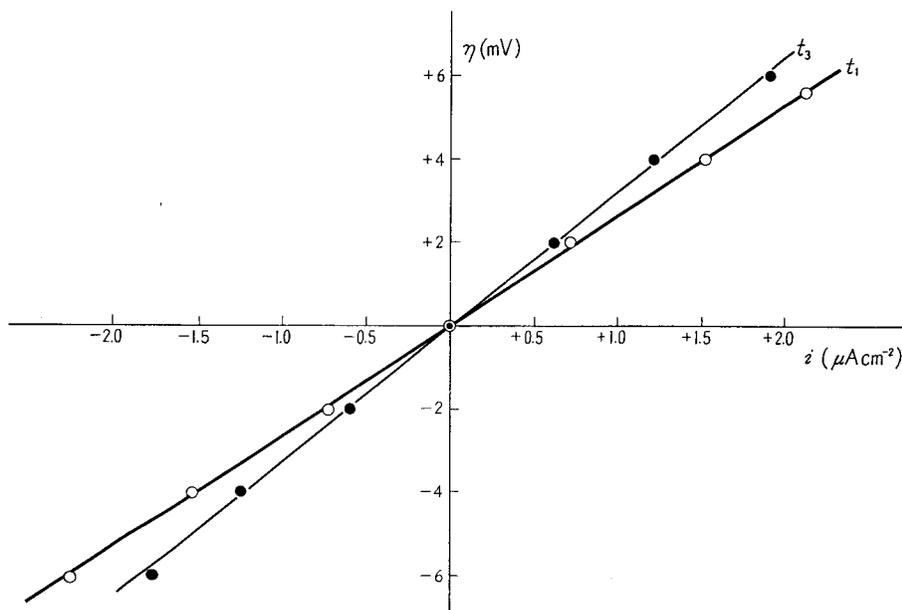
- |                        |                            |
|------------------------|----------------------------|
| B: Breakable joint     | T: Test electrode (Ag-net) |
| S: Constriction        | G: Glass wool              |
| R: Reference electrode | N: Liquid nitrogen trap    |
| C: Counter electrode   |                            |

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the vessel are the test electrode, T, of a net or a spiral of catalyst metal, the reference electrode, R, of Pt wire fused in glass with only its cross section of  $ca. 2 \times 10^{-3} \text{ cm}^2$  area exposed to the solution (to minimize its contribution to deuterium exchange) and the counter electrode, C, of similar construction.

The apparatus was filled with hot chromic acid mixture (or 2N NaOH aq. in the case of Ag test electrode) at least overnight, repeatedly rinsed with hot pure water prepared above and finally steamed for several hours under nitrogen gas flow. Thorough steaming of the cell was found indispensable in order to obtain stable and reproducible activity of catalyst.

About 100 ml of aqueous electrolyte was admitted into the reaction vessel thus cleaned and light hydrogen gas was passed through the solution for two days or more until the electrode potentials of T and R agreed within  $20 \mu\text{V}$ . The vessel was then sealed off at constriction S1 and S2, connected to a vacuum line at breakable joint B3 via a liquid nitrogen trap, light hydrogen inside was replaced with  $ca. 20 \text{ cmHg}$  deuterium gas at room temperature and sealed off at constriction S3. The vessel was shaken for about one hour to purge light hydrogen dissolved in the solution, connected again to the vacuum line at breakable joint B4, the hydrogen was replaced with fresh deuterium gas ( $ca. 20 \text{ cmHg}$ ) and then finally sealed off. The vessel was shaken 400 times per



**Fig. 2.** A typical  $\eta$ - $i$  relation near the isotopic mixed potential (Au, Run 2, No. 3)  $t_1$ , 7 min, and  $t_3$ , 4 hr, after initiation of the exchange reaction

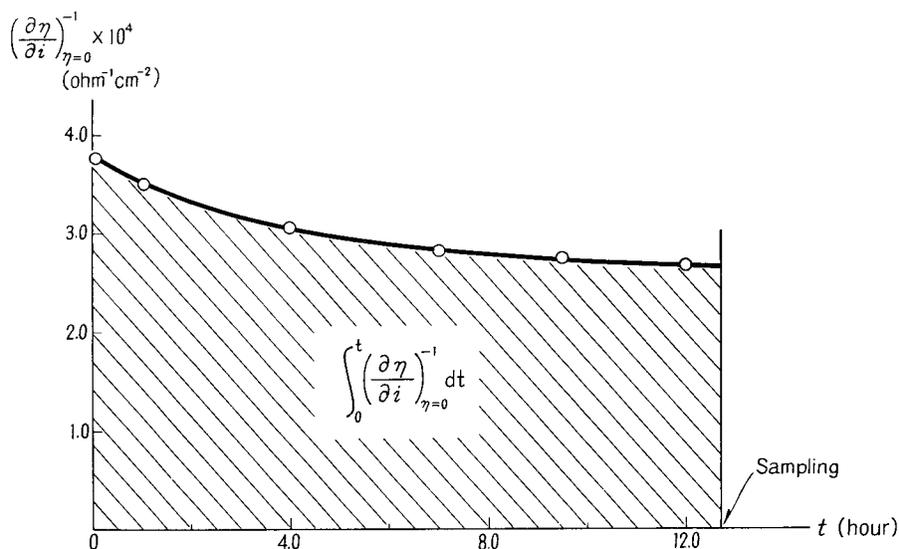


Fig. 3. A typical relation between  $(\partial\eta/\partial i)_{\eta=0}^{-1}$  and reaction time (Au, Run 2. No. 3)

minute with 2 cm amplitude while keeping at a fixed temperature by means of a super-thermostat. The reaction resistance was measured frequently during the shaking. Typical results of measurement of the reaction resistance and its change with time are respectively shown in Fig. 2 and 3. After a recorded time, the reacted gas was sampled through a breakable joint. The reaction was repeated similarly after replacing the remnant gas with fresh deuterium gas.

The sampled gases were analyzed by means of a gas-chromatograph with ferric oxide-coated alumina column at liquid nitrogen temperature.<sup>8)</sup> Relative error in the  $X^a$ -determination was within 0.2%.

#### Isotopic mixed potential during exchange reaction

Potential,  $E_{\text{obs}}$ , of the test electrode under the shaking without net current flow was measured against R in the course of the exchange reaction. The data are listed on the first row of Table 2. This  $E_{\text{obs}}$  gives the excess of the isotopic mixed potential,  $E_m$ , of the test electrode over that of Pt reference electrode, but not over the reversible hydrogen electrode potential in light hydrogen system. In order to evaluate  $E_m$ -value of the test electrode from  $E_{\text{obs}}$ , therefore, we need to add to the latter the  $E_m$ -value of the Pt reference electrode which is known to amount 1.5 mV.<sup>6)</sup> The value thus corrected are given by  $E_m(\text{calc.})$  on the second row of Table 2. It is seen, however, that  $E_{\text{obs}}$ , rather than  $E_m(\text{calc.})$ , closely agrees with the  $E_m$ -value determined previ-

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TABLE 2. Potential of the test electrode,  $E_{\text{obs}}$ , during the exchange reaction ( $X^{\text{e}} \simeq 1$ , 1.0N  $\text{H}_2\text{SO}_4$ , 12°C, potentials in mV)  
 $E_m(\text{calc.}) = E_{\text{obs}} + 1.5$  mV, see text, and  $E_m(\text{lit.})$ , literature value of the isotopically mixed potential in deuterium-light water system.<sup>6,9)</sup>

| Electrode metal           | Rh      | Ir      | Au      | Ag      |
|---------------------------|---------|---------|---------|---------|
| $E_{\text{obs}}$          | 6.0~4.0 | 3.0~1.6 | 6.2~5.8 | 7.0~4.6 |
| $E_m(\text{calc.})$       | 7.5~5.9 | 4.5~3.1 | 7.7~7.3 | 8.5~6.1 |
| $E_m(\text{lit.})$ (25°C) | 4.6     | 1.5~2.1 | 5.3     | 8.2     |

ously<sup>6,9)</sup> (last row of Table 2). This fact is well attributed to the fall of potential of R below its  $E_m$ -value on account of its high activity for deuterium exchange, caused by a preliminary activation with anodic treatment, which reduces locally the concentration of deuterium near its surface by rapid exchange.\*)

The agreement of  $E_{\text{obs}}$  with  $E_m(\text{lit.})$  indicates that diffusion of deuterium in solution towards the test electrode is sufficiently rapid as compared with that of the exchange reaction.

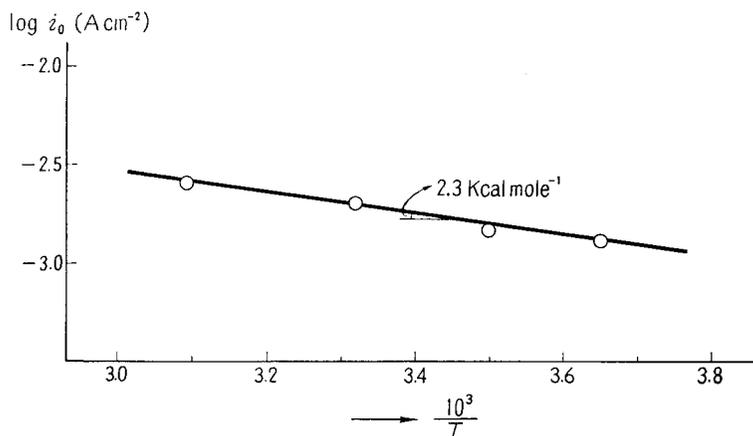


Fig. 4. The exchange rate on an activated Pt electrode.  
 (20 cmHg  $\text{D}_2$  at the working temperature,  
 Shaking condition; 400  $\text{min}^{-1}$ ).

\*) The fall of  $E_m$  of this sort should occur to the test electrode as well if we stop the shaking; deuterium concentration near the test electrode as well as the reference electrode should be locally diminished by the exchange and hence  $E_{\text{obs}}$  should vanish. This was actually observed.

### Diffusion of hydrogen molecule

Further investigation on whether the diffusion of hydrogen molecule in solution is sufficiently rapid as compared with the overall rate of HER under the present shaking condition was carried out using a reaction vessel provided with a Pt-net test electrode of 20 cm<sup>2</sup> surface area. The electrode was preliminarily activated by applying anodic and cathodic polarizations in 1 N H<sub>2</sub>SO<sub>4</sub> and then deuterium exchange rate was measured at various temperatures. The results are shown in Fig. 4. The value of the exchange rate, which is the lower limit of the diffusion rate, was found ten times as large as that on Rh which showed the highest value of  $i_0$  among four electrode metals on which  $\nu_{ex}$ 's were determined. It follows that the diffusion cannot be rate-determining on all the electrodes used in the latter experiment.

### Blank tests

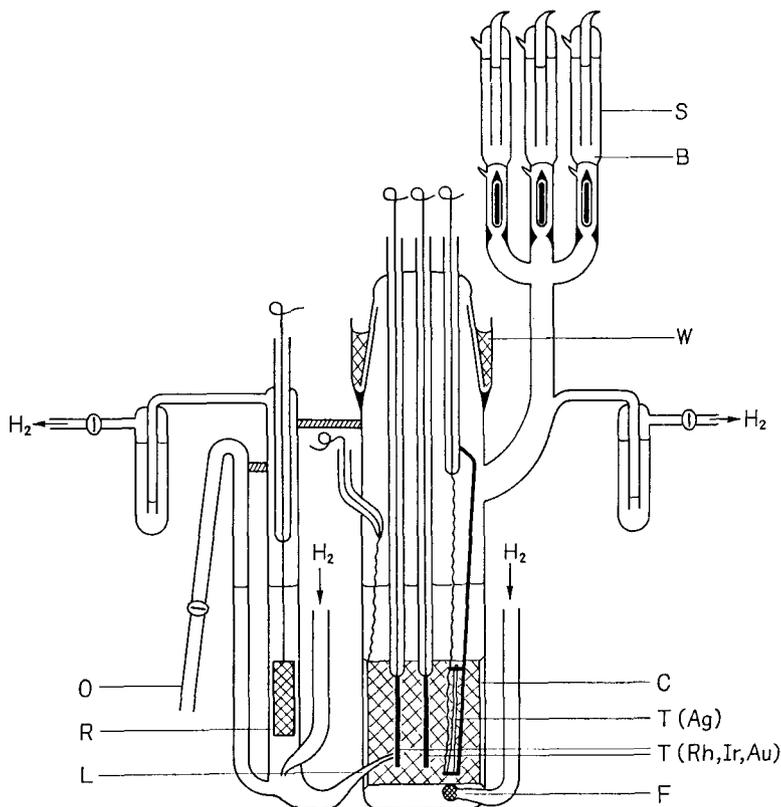
Blank tests were conducted with regard to the exchange between deuterium and water and the isotopic equilibration,  $P_2 + D_2 = 2PD$ , in 1 N H<sub>2</sub>SO<sub>4</sub> at various temperatures (11, 30 and 50°C) using a similar reaction vessel but with no catalyst. Starting with either pure deuterium ( $X^D=0.997$ ) or with a mixture gas of P<sub>2</sub>+D<sub>2</sub> ( $X^D=0.502$ , free from PD), no change was observed in the  $X^D$ -value nor in the isotopic composition in the respective case after 50 hours of shaking. The facts verify that both the exchange and equilibration reactions are effected solely by catalyst metals.

### (D) pH-dependence of $i_0$

The pH-dependence was observed using an all-glass cell (shown in Fig. 5) provided with test electrodes of wire of 0.2~1 cm<sup>2</sup> surface area and a counter electrode of Pt-net of *ca.* 200 cm<sup>2</sup> surface area in the main compartment and a reference electrode of another Pt-net in the side compartment. The cell was thoroughly cleaned similarly to the case of the exchange reaction vessel. The reaction resistance measurements were made after passing light hydrogen through the solution for two days. The solution was sulfuric acid of various concentrations and contained 1 N K<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte. Potential of the test electrode under constant current condition was followed by means of a c.r. oscilloscope except in the case of Ag where the electrometer was used.

The solution pH was shifted, without opening the cell, by adding to the solution an amount of aqueous electrolyte of proper concentration separately prepared and saturated with hydrogen (in containers S in Fig. 5) through a breakable joint. The solution pH in the cell was measured by means of a glass electrode pH-meter, after sampling a portion of the solution from outlet

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**Fig. 5.** The cell for measurements of pH-dependence of  $i_0$

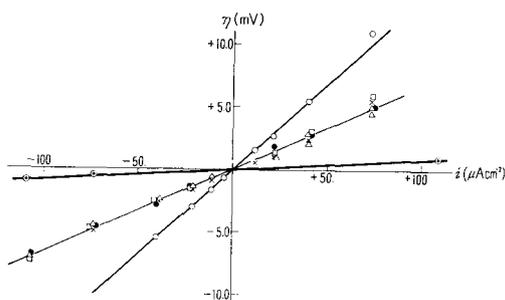
- |   |                        |
|---|------------------------|
| S: Solution container                         | F: Sintered frit       |
| B: Breakable joint                            | L: Luggin capillary    |
| W: Water seal                                 | R: Reference electrode |
| C: Counter electrode                          | O: Solution outlet     |
| T(Ag): Test electrode of Ag                   |                        |
| T(Rh, Ir, Au): Test electrode of Rh, Ir or Au |                        |

O by applying a hydrogen pressure. The value of  $i_0$  was calculated by Eq. (4) from the observed reaction resistance and of  $\nu_r$  already determined.

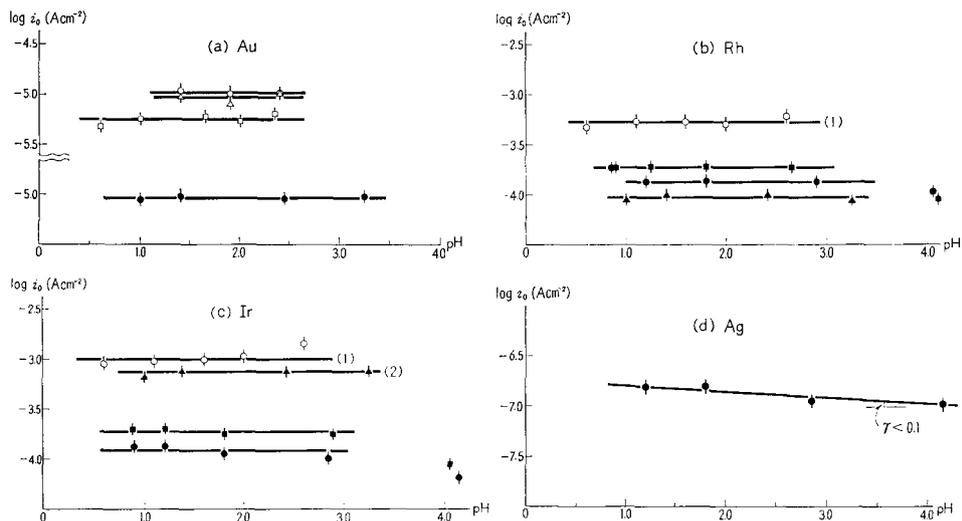
Correction for the concentration overpotential in the overpotential measurements was made in the following way. After completion of the galvanostatic observation of the  $\eta-t$  relations in solutions of various concentrations of sulfuric acid, the test electrode was strongly activated in the solution used in the last run by repeated anodic and cathodic polarizations. Galvanostatic transient curves were then taken on the activated electrode. A linear relation to  $t^{1/2}$  of the potential increment of the galvanostatic transient curve on the

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activated electrode was observed, which verifies<sup>10)</sup> that the potential is practically composed of the concentration overpotential. Now, the curve was found to run parallel with the corresponding one obtained with the non-activated electrode in any solution of different pH at the same value of the current density, except for the initial rapidly rising portion of the latter curve. The parallel shift was hence taken as the activation overpotential of the non-activated electrode. No appreciable correction was needed in the case of Ag-electrode because of extremely small value of  $i$  applied.



**Fig. 6.**  $\eta$ - $i$  relation near the reversible potential on Rh in solutions  $x$  N  $\text{H}_2\text{SO}_4$ +1 N  $\text{K}_2\text{SO}_4$  (temp.  $12^\circ\text{C}$ )  
pH;  $\circ$ : 4.10  $\times$ : 2.65  $\triangle$ : 1.80  $\bullet$ : 1.25  
 $\square$ : 0.9  $\odot$ : 0.9 after activation



**Fig. 7.** pH dependence of exchange current density  $i_0$  (temp.  $12^\circ\text{C}$ )

$\circ$   $\square$   $\triangle$ :  $x$  N  $\text{H}_2\text{SO}_4$   
 $\bullet$   $\blacksquare$   $\blacktriangle$ :  $x$  N  $\text{H}_2\text{SO}_4$ +1 N  $\text{K}_2\text{SO}_4$

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Fig. 6 shows a typical  $\eta$  vs.  $i$  relation as observed on Rh test electrode together with that on the activated Rh electrode. The correction for the concentration overpotential was usually within ten per cent of the total one except for curve 1 of Rh in Fig. 7(b), and curves 1 and 2 of Ir in Fig. 7(c), where it was a few tens per cent.

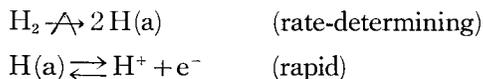
### Results and Discussion

The results obtained are summarized in Table 3 and Fig. 7. The observed value of  $\nu_r$  was unity on every electrode studied within the experimental error of  $\pm 0.2$  (or  $\pm 0.4$  for Ir). The observed value of  $\nu_r$  on Ir was associated with a considerable fluctuation, which was due partly to instability of activity of Ir electrode and partly to small values of  $X_0^a - X^a$  which introduced relatively a large error in its determination.

SCHULDINER<sup>11)</sup> obtained  $\nu_r$  of HER on Rh and Pt to be unity by comparing the slope of the  $i$  vs.  $(1 - e^{2nE/RT})$  curve with the reaction resistance. However, his method does not appear to be justifiable since the mechanism and in consequence the  $\nu_r$ -value was *a priori* premised in his analysis. Bockris and others reported  $\nu_r$  of HER on Rh, Au and Ag electrodes to be unity<sup>12,13)</sup>, or two<sup>14)</sup>. In these reports, however, the  $i_0$ -value was determined by the extrapolation method which is not reliable as mentioned in the Introduction. The present investigation first confirmed the value to be unity for these electrodes.

The  $\gamma$  was found to be zero in the pH-range from 0 to 3.5 in every case of electrode studied. Many investigators concluded a rate-determining discharge step on these metals; the absence of pH-effect on  $i_0$  has been there interpreted in terms of change of the so-called  $\phi_1$ -potential with pH, which would cancel the pH-effect according to a double-layer theory.<sup>15-17)</sup> This interpretation, however, does not apply to the present case where  $\phi_1$ -potential is practically kept constant along with the ionic strength of the solution. The present result denies the possibility of the rate-determining discharge step.

We conclude from the present results of  $\nu_r=1$  and  $\gamma=0$ , with reference to possible reaction mechanisms in Table 1, that HER on these electrodes in acidic solution obeys the catalytic mechanism, *i. e.*,



We define the degree of equilibration,  $\rho$ , of the gaseous hydrogen isotopes as,

$$\rho \equiv X_{\text{PD}} / X_{\text{PD,eq}}$$

TABLE 3. Results of exchange reaction between light water and deuterium

| Run 1. Au 0.2 N H <sub>2</sub> SO <sub>4</sub> , surface area 172 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.994  |               |                                      |               |            |                |  |  |                 |      |
|---|---------------|--------------------------------------|---------------|------------|----------------|--|--|-----------------|------|
| No.   | Temp.<br>(°C) | P <sub>H<sub>2</sub></sub><br>(cmHg) | n<br>(m mole) | t<br>(h:m) | X <sup>g</sup> | i <sub>0</sub> <sup>(*)</sup><br>(A cm <sup>-2</sup> ) | (∂η/∂i) <sub>i=0</sub><br>(ohm cm <sup>2</sup> ) | ν <sub>ex</sub> | ρ    |
| 1   | 11.0          | 20.6                                 | 4.36          | 20:15      | 0.977          | 0.114×10 <sup>-5</sup>                                 | 7.46×10 <sup>3</sup>                             | 0.69            | —    |
| 3   | 11.0          | 18.5                                 | 3.90          | 8:00       | 0.908          | 1.31   | 1.09   | 1.16            | 0.32 |
| 4   | 11.0          | 19.1                                 | 4.01          | 10:05      | 0.935          | 0.731  | 1.81   | 1.07            | 0.23 |
| Run 2. Au 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 172 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.994  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 10.6          | 20.7                                 | 3.74          | 11:00      | 0.970          | 2.54×10 <sup>-6</sup>                                  | 3.69×10 <sup>3</sup>                             | 0.76            | 0.40 |
| 2   | 10.2          | 20.7                                 | 3.72          | 9:40       | 0.956          | 4.56   | 2.88   | 1.07            | 0.30 |
| 3   | 10.2          | 19.5                                 | 3.49          | 12:37      | 0.956          | 3.29   | 3.41   | 0.91            | 0.25 |
| 4   | 10.3          | 20.7                                 | 3.69          | 10:01      | 0.955          | 4.49   | 2.74   | 1.00            | 0.23 |
| 5   | 10.0          | 19.0                                 | 3.40          | 8:02       | 0.945          | 6.49   | 2.13   | 1.12            | 0.24 |
| Run 3. Au 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 172 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.998  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 11.5          | 16.5                                 | 2.98          | 87:00      | 0.920          | 8.33×10 <sup>-6</sup>                                  | 15.7 ×10 <sup>3</sup>                            | 1.07            | 0.16 |
| 4   | 51.5          | 22.0                                 | 3.34          | 47:00      | 0.922          | 1.69   | 7.80   | 0.94            | 0.12 |
| Run 4. Rh 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 4.4 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.998  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 11.5          | 18.1                                 | 3.22          | 9:20       | 0.959          | 1.64×10 <sup>-4</sup>                                  | 7.75×10  | 1.03            | 0.70 |
| 2   | 11.5          | 15.7                                 | 2.78          | 15:20      | 0.927          | 1.57   | 8.72   | 1.11            | 0.72 |
| 3   | 11.5          | 18.4                                 | 3.22          | 18:00      | 0.916          | 1.79   | 8.02   | 1.17            | 0.75 |
| 4   | 11.5          | 21.3                                 | 3.27          | 11:30      | 0.961          | 1.28   | 9.55   | 0.99            | 0.73 |
| 5   | 11.5          | 17.8                                 | 3.23          | 15:45      | 0.949          | 1.22   | 12.2   | 1.21            | 0.71 |
| Run 5. Ir 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 2.1 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.992  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 12.0          | 21.5                                 | 3.63          | 27:05      | 0.986          | 2.04×10 <sup>-5</sup>                                  | 8.40×10 <sup>2</sup>                             | 1.39            | —    |
| 2   | 12.0          | 21.8                                 | 3.57          | 25:20      | 0.986          | 2.16   | 6.76   | 1.19            | 0.74 |
| Run 6. Ir 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 2.1 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.994  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 12.0          | 24.4                                 | 3.70          | 32:20      | 0.983          | 3.22×10 <sup>-5</sup>                                  | 3.17×10 <sup>2</sup>                             | 0.83            | —    |
| Run 7. Ir 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 11.1 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.995 |               |                                      |               |            |                |  |  |                 |      |
| 2   | 2.5           | 20.8                                 | 3.09          | 1:00       | 0.988          | 1.04×10 <sup>-4</sup>                                  | 1.56×10 <sup>2</sup>                             | 1.37            | 0.58 |
| 3   | 13.2          | 20.3                                 | 2.90          | 24:00      | 0.982          | 0.0759   | 24.0   | 1.48            | 0.50 |
| Run 8. Ag 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 505 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.998  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 12.0          | 20.5                                 | 3.90          | 24:00      | 0.990          | 1.38×10 <sup>-7</sup>                                  | 8.48×10 <sup>4</sup>                             | 0.95            | 0.45 |
| Run 9. Ag 1.0 N H <sub>2</sub> SO <sub>4</sub> , surface area 505 cm <sup>2</sup> , X <sub>0</sub> <sup>g</sup> =0.994  |               |                                      |               |            |                |  |  |                 |      |
| 1   | 12.0          | 20.6                                 | 3.48          | 6:30       | 0.947          | 2.67×10 <sup>-6</sup>                                  | 4.41×10 <sup>3</sup>                             | 0.96            | 0.29 |
| 2   | 12.0          | 17.6                                 | 2.98          | 13:50      | 0.951          | 1.01   | 13.2   | 1.08            | 0.33 |
| 3   | 12.0          | 21.9                                 | 3.69          | 48:50      | 0.950          | 0.355  | 35.1   | 1.01            | 0.35 |

$$*) i_0 \equiv \frac{2nF}{At}(X_0^g - X^g)$$

*Mechanism of Hydrogen Electrode Reaction*

where  $X_{PD}$  is the mole fraction of PD in hydrogen gas and  $X_{PD,eq}$  is that of the same gas in equilibrium of the reaction,  $P_2 + D_2 = 2 PD$ . It is readily demonstrated<sup>18)</sup> that no equilibration reaction should be effected by the catalytic mechanism, since no PD would be created under the present condition where  $P_2 + D_2$  coexists with electrolyte solution in light water. As seen in the last column of Table 3, however, amount of PD observed corresponded to 10~70% of the value in the equilibrium. It is considered that such a PD formation was effected by a side reaction,<sup>18)</sup> but further investigations are required to clarify the reaction in detail.

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