



# HOKKAIDO UNIVERSITY

Title	STOICHIOMETRIC NUMBER AND MECHANISM OF THE HYDROGEN ELECTRODE REACTION ON RUTHENIUM AND RHENIUM AS STUDIED BY MEANS OF DEUTERIUM TRACER
Author(s)	SAITO, K. ; ENYO, M. ; MATSUSHIMA, T.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 23(1), 26-39
Issue Date	1976-01
Doc URL	<a href="https://hdl.handle.net/2115/24987">https://hdl.handle.net/2115/24987</a>
Type	departmental bulletin paper
File Information	23(1)_P26-39.pdf



# STOICHIOMETRIC NUMBER AND MECHANISM OF THE HYDROGEN ELECTRODE REACTION ON RUTHENIUM AND RHENIUM AS STUDIED BY MEANS OF DEUTERIUM TRACER

By

K. SAITO<sup>\*)</sup>, M. ENYO<sup>\*\*)</sup> and T. MATSUSHIMA<sup>\*\*)</sup>

(Received January 16, 1975)

## Abstract

A method was proposed for determining the reaction route of the hydrogen electrode reaction. It is based on congruence between the stoichiometric number determined from an isotope exchange rate and that from the isotopic composition of the hydrogen gas obtained by the exchange reaction. Deuterium exchange experiments were carried out on Ru and Re in 1 N H<sub>2</sub>SO<sub>4</sub>. On Ru, the discharge-combination route was concluded. The stoichiometric number was two. This indicates that the step between hydrogen adatom and proton in solution is rate-determining. The same route was concluded on Re with comparable magnitudes of the exchange rates of the two steps. Data obtained previously on other metals were reanalyzed by the present method. The analysis substantiated the reaction route concluded previously on Ni and Rh but was not conclusive on Pt, Ir, Ag, and Au.

## Introduction

Mechanistic studies of the hydrogen electrode reaction (*her*)



on Ru and Re are relatively scanty.<sup>1)</sup> Some reports available are mainly concerned with the polarization current (*I*) vs. overpotential ( $\eta$ ) relation of the *overall her*: Limited information only is obtained from such studies. JONCICH *et al.*<sup>2)</sup> measured the *I*– $\eta$  relation on Re in HCl solutions and reported the Tafel constant to be two. Combining this with the results that no pH dependence of the rate existed, they concluded the slow-combination (the catalytic) mechanism. GILES *et al.*<sup>3)</sup> used Ru electrodes elec-

<sup>\*)</sup> Present address: Denki Kagaku Kogyo, Ltd., Ōmi, Niigata, Japan.

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

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

trodeposited from  $\text{RuCl}_3$  solutions on C and Hg. The Tafel constant for the Ru/C electrode was 1.5. They thus concluded the ion+atom desorption mechanism. Similar data were also reported by SHMELEVA *et al.*<sup>4)</sup> on electrodeposited Ru in 2N  $\text{H}_2\text{SO}_4$ , or by KUHN and WRIGHT<sup>5)</sup> on Ru electrodes prepared by powder metallurgy.

Recently, MATSUSHIMA and ENYO<sup>6)</sup> employed a deuterium tracer technique in the mechanistic studies of the *her* on Ni, Rh, Pt, Ir, Ag, and Au. They could determine the reaction route and then rates of the constituent steps on Ni and Rh. The experiments indicated that the rate-determining step (*rds*) is often unclear, hence that the kinetics of the *overall her* does not represent that of any single step. This indicates, in order to establish the reaction mechanism, that we need to resolve the *her* into the constituent steps and investigate kinetics of the latter ones.

It is prerequisite to determine the reaction route in order to make such an analysis. This was made previously<sup>6)</sup> on the basis of constancy of a kinetic parameter throughout a range of the deuterium concentration in the *her* system. In the present work, another method based on the stoichiometric number concept is developed and applied to the *her* on Ru and Re. Previous data on various metals are also re-examined.

## Theoretical

### (A) Reaction Route

Four reaction routes will be considered below<sup>6)</sup> assuming hydrogen adatom,  $\text{H}(\text{a})$ , and hydrogen molecule-ion,  $\text{H}_2^+(\text{a})$ , as the possible reaction intermediates.

- I.  $\text{H}_2 \rightleftharpoons 2\text{H}(\text{a}), \text{H}(\text{a}) + \text{B} \rightleftharpoons \text{H}^+\text{B} + \text{e}$
- II.  $\text{H}_2 + \text{B} \rightleftharpoons \text{H}(\text{a}) + \text{H}^+\text{B} + \text{e}, \text{H}(\text{a}) + \text{B} \rightleftharpoons \text{H}^+\text{B} + \text{e}$
- III.  $\text{H}_2 \rightleftharpoons \text{H}_2^+(\text{a}) + \text{e}, \text{H}_2^+(\text{a}) + \text{B} \rightleftharpoons \text{H}^+\text{B} + \text{H}(\text{a}), \text{H}(\text{a}) + \text{B} \rightleftharpoons \text{H}^+\text{B} + \text{e}$
- IV.  $\text{H}_2 \rightleftharpoons \text{H}_2^+(\text{a}) + \text{e}, \text{H}_2^+(\text{a}) + 2\text{B} \rightleftharpoons 2\text{H}^+\text{B} + \text{e}$

It will be assumed that the *her* takes place through a single route.

### (B) The Stoichiometric Number

The stoichiometric number of the *rds*,  $\nu_r$ , in a consecutive single-route reaction is given by,<sup>7)</sup>

$$\nu_r = -\Delta G/RT \ln(V_+/V_-) \quad (1)$$

where  $-\Delta G$  is the affinity of the overall reaction and  $V_+$  and  $V_-$  are the uni-directional rates of the reaction in the forward and reverse directions, respectively. As all the quantities in the right-hand side of eq. (1) are

K. SAITO *et al.*

measurable, the stoichiometric number is calculable irrespective of whether or not there really exists a definite *rds*. In the case of no single *rds*, however, that formally obtained from eq. (1) is an average quantity. Thus,<sup>8)</sup>

$$\bar{\nu} = \sum_s \nu_s (-\Delta g_s) / \sum_s (-\Delta g_s) \quad (2)$$

where  $-\Delta g_s$  is the affinity for step *s*.

The overall net rate *V* is

$$V = V_+ - V_- \quad (3)$$

From eqs. (1) and (3), we have, near equilibrium,

$$\bar{\nu} = V_o(1/RT) \left[ d(-\Delta G)/dV \right]_{-\Delta G \rightarrow 0} \quad (4)$$

where  $V_o$  is the uni-directional rate at equilibrium, termed as the exchange rate, of the *her*.

We will deal with the  $V_o$  that is obtained by the isotope tracer method; this is only the method which directly detects the exchange rate. It is to be noted, however, that the isotope exchange does not necessarily employ *all* the steps involved in the reaction. We define the isotope exchange rate,  $V_{o,ex}$ , in the *her* system consisting of deuterium, electrolytic solution of light water, and the test electrode which catalyzes the exchange reaction, by

$$V_{o,ex} = (N_g/t) \ln(X_o/X) \quad (5)$$

where  $N_g$  is the total number of hydrogen molecules in the system, *X* the deuterium atomic fraction in gaseous hydrogen and subscript *o* signifies the initial value. Correspondingly, we denote the stoichiometric number determined from it in the form,

$$\bar{\nu}_{ex} = V_{o,ex}(1/RT) \left[ d(-\Delta G)/dV \right]_{-\Delta G \rightarrow 0} \quad (6)$$

The reaction resistance at the reversible potential,  $[d(-\Delta G)/dV]_{-\Delta G \rightarrow 0}$  is easily determined from the *I*- $\eta$  relation at  $\eta=0$ , *viz.*,

$$\left( \frac{d(-\Delta G)}{dV} \right)_{-\Delta G \rightarrow 0} = (2F)^2 \left( \frac{d\eta}{dI} \right)_{\eta \rightarrow 0} \quad (7)$$

Note that  $\bar{\nu}_{ex}$  is evaluated experimentally irrespective of our knowledge on the operative mechanism.

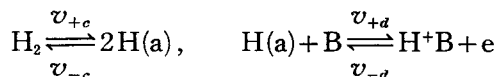
### (C) Step Rates and the Stoichiometric Number

We first examine the functional relationship between the stoichiometric number and the step rates for various reaction routes, and then between

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

the step rates and the composition of the hydrogen isotopes to be obtained in the  $D_2/H_2O$  exchange reaction.

*Route I*



$\nu_{+c}$  etc. denote the uni-directional rates of steps as specified. From the steady-state condition

$$(\nu_{+c} - \nu_{-c})/\nu_c = (\nu_{+d} - \nu_{-d})/\nu_d = V \quad (8)$$

where  $\nu_c$  and  $\nu_d$  are the stoichiometric number of step c and d, respectively ( $\nu_c=1, \nu_d=2$ ). The affinities of the steps are related to the affinity of the overall reaction and to the step rates by<sup>7,9)</sup>

$$-\Delta G = -\nu_c \Delta g_c - \nu_d \Delta g_d \quad (9)$$

$$-\Delta g_c = RT \ln(\nu_{+c}/\nu_{-c}) \quad (10, c)$$

$$-\Delta g_d = RT \ln(\nu_{+d}/\nu_{-d}) \quad (10, d)$$

From eqs. (8) and (10),

$$\frac{\nu_c}{v_c} = \frac{1}{RT} \left( \frac{d(-\Delta g_c)}{dV} \right)_{-\Delta g_c \rightarrow 0} \quad (11, c)$$

$$\frac{\nu_d}{v_d} = \frac{1}{RT} \left( \frac{d(-\Delta g_d)}{dV} \right)_{-\Delta g_d \rightarrow 0} \quad (11, d)$$

where  $v_c$  and  $v_d$  are the exchange rate of step c and d, respectively. Differentiation of eq. (9) with  $V$  yields, by virtue of eqs. (11),

$$\frac{1}{RT} \left( \frac{d(-\Delta G)}{dV} \right)_{-\Delta G \rightarrow 0} = \frac{\nu_c^2}{v_c} + \frac{\nu_d^2}{v_d} \quad (12)$$

On the other hand, the isotope exchange rate,  $V_{o,ex}$ , for Route I is obtained as below. In the isotope exchange reaction, neglecting the isotope effect, we have

$$2N_o dX/dt = -2v_c(X - Y) \quad (13)$$

where  $Y$  is the deuterium atomic fraction in hydrogen adatoms. Also, the steady-state condition with respect to deuterium adatoms is expressed as,

$$2v_c X - (2v_c + v_d) Y = 0 \quad (14)$$

Integration of eq. (13), using (14), yields

$$v_c v_d / (2v_c + v_d) = (N_o/t) \ln(X_o/X) \quad (15)$$

or, comparison with eq. (5) shows

$$v_{o,ex} = v_e v_d / (2v_c + v_d) = v_d / 2(m+1) \quad (16)$$

where

$$m \equiv v_d / 2v_c \quad (17)$$

As reported elsewhere<sup>6)</sup>,  $m$  is determined from the isotopic composition of the hydrogen gas obtained by the exchange reaction according to the relation

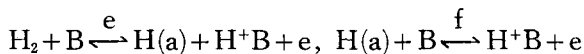
$$\left[ \frac{X^{\text{HD}}}{X} - 2 + \frac{2X}{(m-1)^2} \right] X^{-1/m} = \left[ \frac{X_o^{\text{HD}}}{X_o} - 2 + \frac{2X_o}{(m-1)^2} \right] X_o^{-1/m} \quad (18)$$

where  $X^{\text{HD}}$  is the mole fraction of HD. Thus,  $m$  is evaluated utilizing the isotopic composition data. Substitution of eqs. (12) and (16) into eq. (6) results in

$$\bar{v}_{ex,I} = (m+2)/(m+1) \quad (19)$$

If Route I is operative,  $\bar{v}_{ex,I}$  obtained from eq. (19) must agree with  $\bar{v}_{ex}$  obtained directly from the isotope exchange rate by eq. (6).

### Route II



Analogously, we have

$$\frac{1}{RT} \left( \frac{d(-\Delta G)}{dV} \right)_{-\Delta G \rightarrow 0} = \frac{v_e^2}{v_e} + \frac{v_f^2}{v_f} \quad (20)$$

where  $v_e = v_f = 1$ . The isotope exchange rate is given by<sup>10,11)</sup>

$$V_{o,ex,II} = \frac{1}{2} \left[ \frac{v_e v_f}{v_e + v_f} + v_e \right] \quad (21)$$

where the last term indicates that the exchange of isotope can take place through step e alone, as well as through the *overall her* (the multipath exchange<sup>9)</sup>). Substituting eqs. (20) and (21) into eq. (6), and defining  $l \equiv v_f/v_e$  we find,

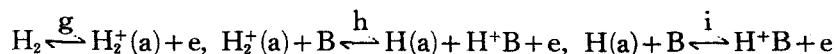
$$\bar{v}_{ex,II} = 1 + 1/2l \quad (22)$$

If step e is the *rds* ( $l \rightarrow \infty$ ),  $\bar{v}_{ex,II} = 1$ , but if step f is ( $l \rightarrow 0$ ),  $\bar{v}_{ex,II} = \infty$ . We can evaluate  $l$  from the composition data by the relation<sup>6)</sup>,

$$l = \frac{2 \ln(X_o/X) - \ln(X_o^{D_2}/X^{D_2})}{2 [\ln(X_o^{D_2}/X^{D_2}) - \ln(X_o/X)]} \quad (23)$$

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

*Route III*



We obtain,

$$\frac{1}{RT} \left( \frac{d(-\Delta G)}{dV} \right)_{-d\theta \rightarrow 0} = \frac{\nu_g^2}{\nu_g} + \frac{\nu_h^2}{\nu_h} + \frac{\nu_i^2}{\nu_i} \quad (24)$$

where  $\nu_g = \nu_h = \nu_i = 1$ . The isotope exchange rate is obtained to be

$$V_{o,ex,III} = \frac{\nu_g g_1 (2g_2 + 1)}{2(g_1 + 1)(g_2 + 1) - g_1} \quad (25)$$

where  $g_1 \equiv \nu_h/\nu_g$  and  $g_2 \equiv \nu_i/\nu_h$ . Introducing eqs. (24) and (25) into eq. (6), and defining  $g \equiv (g_1 + 1)(2g_2 + 1)$ , we obtain

$$\bar{\nu}_{ex,III} = \frac{g}{g+1} \left\{ 1 + \frac{2}{g - (g_1 + 1)} \right\} \quad (26)$$

We can evaluate  $g$  from the isotopic composition data by<sup>6)</sup>

$$g = \frac{\ln(X_o/X)}{\ln(X_o^{D_2}/X^{D_2}) - \ln(X_o/X)} \quad (= 2l + 1) \quad (27)$$

In reality,  $g_1$  and  $g_2$  cannot be determined individually from the isotopic composition, or  $\bar{\nu}_{ex,III}$  is not determinable. Nevertheless, we may proceed by the criterion  $\bar{\nu}_{ex,III} > g/(g-1)$  or its minimum value at  $g_1 = 0$ ,

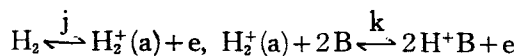
$$\bar{\nu}_{ex,III,min} = g/(g-1) \quad (28)$$

as obtained from eq. (26) with positive  $g_1$  and  $g_2$ . Comparing eq. (28) with (22), we find

$$\bar{\nu}_{ex,II} = \bar{\nu}_{ex,III,min} \quad (29)$$

It can easily be seen that Route III with  $\nu_g = \infty$  (hence  $g_1 = 0$ ) is practically the same as Route II.

*Route IV.*



In this case,

$$\frac{1}{RT} \left( \frac{d(-\Delta G)}{dV} \right)_{-d\theta \rightarrow 0} = \frac{\nu_j^2}{\nu_j} + \frac{\nu_k^2}{\nu_k} \quad (30)$$

where  $\nu_j = \nu_k = 1$ . The isotope exchange rate is given as

$$V_{o,ex,IV} = \nu_j \nu_k / (\nu_j + \nu_k) \quad (31)$$

or, we find, irrespective of relative magnitudes of  $v_j$  and  $v_k$ ,

$$\bar{v}_{ex,IV} = 1 \quad (32)$$

Various reaction routes and stoichiometric numbers are summarized in Table 1. It is important that we may distinguish the reaction route that is operative in a particular system by testing the harmony between  $\bar{v}_{ex}$  on the one hand and  $\bar{v}_{ex,I}$ ,  $\bar{v}_{ex,II}$ , and  $\bar{v}_{ex,III}$  on the other hand. It can be said that the test is based on the confirmation of a consistency between the deuterium exchange rate and isotopic composition of hydrogen gas obtained by the exchange reaction.

Route IV has particular characteristics that no HD can be formed in the exchange reaction between deuterium and light water (*cf.* Table 1). Thus, no information can be obtained of relative magnitudes of the exchange rates of the constituent steps from the isotopic composition data.

TABLE 1. Various reaction routes and stoichiometric numbers.

Route	parameters	$\bar{v}$	$\bar{v}_{ex,I}$ etc.	production of HD
I. $\begin{array}{l} \text{H}_2 \xrightleftharpoons{c} 2\text{H} \\ \text{H} \xrightleftharpoons{d} \text{H}^+ \end{array}$	$m \equiv v_d/2v_c$	$\frac{m+2}{m+1}$	$\frac{m+2}{m+1}$	yes
II. $\begin{array}{l} \text{H}_2 \xrightleftharpoons{e} \text{H} + \text{H}^+ \\ \text{H} \xrightleftharpoons{f} \text{H}^+ \end{array}$	$l \equiv v_f/v_e$	1	$1 + \frac{1}{2l}$	yes
III. $\begin{array}{l} \text{H}_2 \xrightleftharpoons{g} \text{H}_2^+ \\ \text{H}_2^+ \xrightleftharpoons{h} \text{H} + \text{H}^+ \\ \text{H} \xrightleftharpoons{i} \text{H}^+ \end{array}$	$g_1 \equiv v_h/v_g$ $g_2 \equiv v_i/v_h$ $g \equiv (g_1+1)(2g_2+1)$	1	$\frac{g}{g+1} \left\{ 1 + \frac{2}{g-(g_1+1)} \right\}$	yes
IV. $\begin{array}{l} \text{H}_2 \xrightleftharpoons{} \text{H}_2^+ \\ \text{H}_2^+ \xrightleftharpoons{} 2\text{H}^+ \end{array}$		1	1	no

## Experimental

### (A) Materials

Electrodeposition of Ru was performed from  $\text{RuCl}_3$  solution of roughly  $6 \times 10^{-4}$  mol/l in 1 N  $\text{H}_2\text{SO}_4$  with 3 mA for 120 hours onto Ag wire, 50 cm<sup>2</sup>. Capacity measurements of the electrode thus prepared revealed the roughness factor of about 30. Rhenium electrode used was a ribbon ( $0.0254 \times$

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

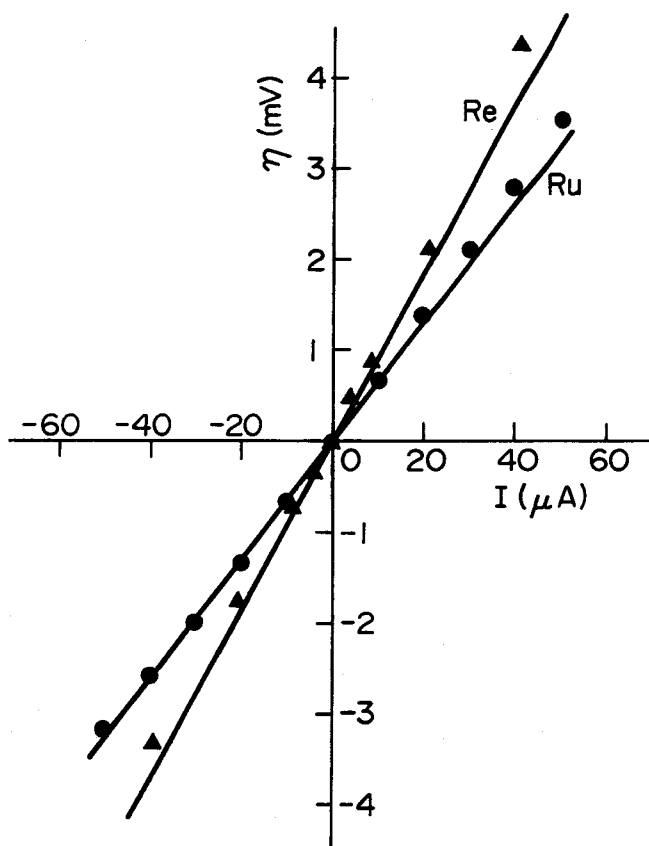
0.75 mm, H. Cross Co. U.S.A. purity 99.9%) of 60 cm<sup>2</sup> apparent area. Hydrogen and deuterium were purified by filtering through Pd-Ag membranes.

(B) Cell

This was analogous to that reported elsewhere.<sup>6)</sup> The volume was *ca.* 400m ℓ. The reference and counter electrodes were 0.3 mm Pt wires exposing only the cross sections to the solution.

(C) Procedure

Procedure employed was essentially the same as reported elsewhere.<sup>6)</sup> The polarization measurements were made by a steady polarization method.



**Fig. 1.** Polarization resistance near equilibrium on Ru and Re in 1 N H<sub>2</sub>S<sub>4</sub>O, 21°C. Electrode Area; Ru=50 cm<sup>2</sup>, Re=60 cm<sup>2</sup>.  $P=36.4$  cm Hg (Ru), 40.4 cm Hg (Re).

K. SAITO *et al.*

Typical results are given in Fig. 1. Corrections for the ohmic pseudo-overpotential was made after evaluating by a transient technique. The cell was shaken 120 times per min. with 2 cm amplitude. Temperature was kept at 21°C. Hydrogen isotopes were analyzed by a gas-chromatograph.

### Results and Discussion

#### (A) Ru

Typical results are listed in Table 2 A. The fact that significant amount of HD was produced excluded the possibility of Route IV. Comparison of various stoichiometric numbers is seen in Table 2 A. Since  $m$  was *ca.*  $10^{-2}$ ,  $\bar{v}_{ex,I}$  was very close to two, in fair agreement with  $\bar{v}_{ex}$  of *ca.* 2.3. On the other hand, both  $\bar{v}_{ex,II}$  and  $\bar{v}_{ex,III}$  were 6 or possibly larger\*). Based on the agreement between  $\bar{v}_{ex}$  and  $\bar{v}_{ex,I}$ , we conclude Route I to be

TABLE 2. Deuterium exchange reaction on Ru and Re  
1 N H<sub>2</sub>SO<sub>4</sub>; 21°C; X<sub>0</sub><sup>D<sub>2</sub></sup>=0.997, X<sub>0</sub><sup>HD</sup>=0.006.

(A) Electrodeposited Ru, apparent surface area 50 cm<sup>2</sup>

Exp. no.	P(21°C) (cm Hg)	t (hr : min)	X <sup>HD</sup>	X <sup>D<sub>2</sub></sup>	(dη/dl) <sub>τ→0</sub> (ohm)	$\bar{v}_{ex}$	Route I		Route II, III	
							m	$\bar{v}_{ex,I}$	l	$\frac{\bar{v}_{ex,II}}{\bar{v}_{ex,III, min.}}$
1	36.4	48:00	0.197	0.790	65.2	2.36	~0.03	} 2.0	0.0725	7.9
2	18.6	46:00	0.214	0.771	111	2.31	~0.02		0.0206	18.4
2	56.9	47:00	0.130	0.865	75.0	2.54	<0.01		0.0354	15.2
4	12.4	40:00	0.189	0.800	183	2.34	<0.01		0.0258	20.4
5	27.2	44:00	0.108	0.899	164	2.25	<0.01		0.115	6.8
6	7.2	44:00	0.191	0.801	324	2.18	<0.01		0.0237	12.8
7	32.9	47:00	0.100	0.898	183	2.39	<0.01		0.256	3

(B) Re, apparent surface area 60 cm<sup>2</sup>

1	43.2	39:00	0.066	0.915	79.0	2.07	0.57	1.64	3.64	2.82
2	40.4	43:00	0.067	0.915	91.5	1.99	0.53	1.65	3.97	3.28
2	54.1	46:00	0.066	0.919	76.5	1.94	0.47	1.68	4.40	3.22
4	29.1	68:07	0.104	0.870	129	1.98	0.46	1.68	4.71	3.36
5	21.5	40:00	0.068	0.910	183	2.19	0.49	1.67	4.26	3.13

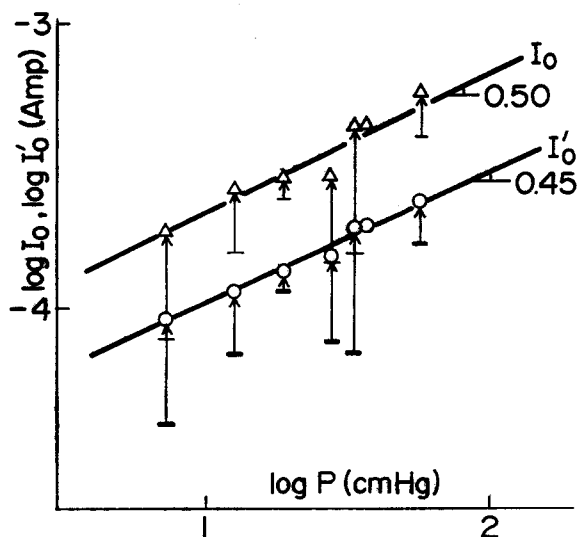
\*) Evaluation of  $l$  and  $g$  from the data in Table 2 A often resulted in negative, thus meaningless, values. These directly exclude Route II or III. In order to see the data under most severe conditions, values in Table 2 A were obtained from such GC data among repeated GC analyses that would result in smallest possible values of  $\bar{v}_{ex,II}$  and  $\bar{v}_{ex,III}$ .

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

operative on Ru\*\*). Thus, the present results did not support the conclusions proposed in the literature<sup>3-5</sup>.

In Table 2 A,  $m$  is much smaller than unity or, in other words, step d in Route I is practically rate-determining. As seen from comparison of nos. 1 and 7, the catalytic activity of Ru decreased by a factor of three (during the period of two weeks). Along with this activity decrease, a decrease of  $m$  is noted. Thus, a decrease of the catalytic activity is associated with decrease of the exchange rate of step d, as was also observed on Ni<sup>6,11</sup>.

Due to the activity decrease, no direct data was obtained of the dependence of the rates of the overall exchange rate or that of step d upon total hydrogen pressure,  $P$ . Nevertheless, after a correction for the activity decrease assuming an exponential decay<sup>12</sup>, an acceptable behaviour was seen (Fig. 2). The slope,  $d \ln I_0/d \ln P$  (and  $d \ln I'_0/d \ln P$ ) which now represents  $d \ln v_d/d \ln P$  because of step d being practically rate-determining



**Fig. 2.** Pressure dependences of  $I_0$  and  $I'_0$  on Ru, 1 N  $H_2SO_4$ , 21°C  
(After correction for decrease of the catalytic activity, see text).  
 $I_0$ ; from isotope exchange rate.  
 $I'_0$ ; from polarization data, viz.,  $I'_0 \equiv (RT/2F)(dI/d\eta)_{\eta \rightarrow 0}$ .

\*\*\*) There may exist various factors, e.g., contribution of the reference and the counter electrodes to the isotope exchange (possibly up to 3%), or inaccuracies associated with the polarization resistance measurements, which would give rise to a systematic positive shift of  $\bar{v}_{ex}$ . Hence,  $\bar{v}_{ex}$  should in reality be somewhat smaller than the figures here obtained, or in better agreement with  $\bar{v}_{ex,I}$ .

K. SAITO *et al.*

was *ca.* 0.5: This is somewhat larger than the value expected for a charge-transfer control of the *her*<sup>13)</sup>, 0.25, but it appears difficult to judge the significance of the discrepancy seeing from the extent of the corrections (vertical lines in Fig. 2) made for the activity decrease.

Since step d is practically rate-determining on Ru, the isotopic mixed potential observed,  $E_r=19.0\sim 24.6$  mV, can be analyzed according to the relation derived by ENYO and YOKOYAMA<sup>14)</sup>. At  $X_o \simeq X \simeq 1$ ,  $S_+ \simeq \exp \{FE_r/RT\}$  where  $S_+$  is the deuterium separation factor in the direction of hydrogen ionization. Hence, we obtain  $S_+=2.1\sim 2.7$  which is far greater than the data obtained on Pt, Au, Ag, or Ni, 1.1~1.6<sup>14)</sup>. The separation factor  $S_-$  in the hydrogen evolution reaction reaction is then obtained according to the relation derived for the slow-discharge mechanism<sup>15)</sup>,  $S_- = QS_+K/4$  where  $Q$  is the partition coefficient of deuterium between hydrogen gas and water at  $X=0$ , *i.e.*, *ca.* 3.9<sup>16~18)</sup> and  $K$  is the equilibrium constant of the reaction  $H_2 + D_2 = 2HD$ , *i.e.*, *ca.* 3.26 at 25°C. It is interesting that  $S_-$  on Ru is deduced to be rather high, 6.6~8.5. No data appeared to be available of  $S_-$  on Ru by direct electrolysis.

## (B) Re

This was found to be a very difficult system to realize high and reproducible catalytic activity. Fragmentary information only was thus obtained (Table 2 B). Nevertheless,  $\bar{\nu}_{ex,I}$  obtained to be 1.7 was in fair agreement with  $\bar{\nu}_{ex} \simeq 2.0$ . On the other hand,  $\bar{\nu}_{ex,II} = \bar{\nu}_{ex,III,min} \simeq 3.1$  is much larger than  $\bar{\nu}_{ex}$ . Accordingly, Route I is again concluded to be acceptable. The result  $m \simeq 0.5$  indicates that no single rds exists in the *her* on Re under ordinary conditions. Thus, Re is found rather similar to Ni and Rh with regard to the *her* mechanism. Experiments were unsuccessful in obtaining reliable results on the pressure dependence of the exchange rate.

## Analysis of Previous Results

The data of the deuterium exchange experiments on some other metals reported previously were analyzed by the present method.

## (A) Ni and Rh

Various  $\bar{\nu}_{ex}$  values obtained from the data reported<sup>6)</sup> on Ni and Rh are listed in Table 3. It is seen that  $\bar{\nu}_{ex,II} = \bar{\nu}_{ex,III,min}$  is much larger than  $\bar{\nu}_{ex}$  whereas  $\bar{\nu}_{ex,I}$  is in fair agreement with the latter. Thus, the present analysis substantiates the previous conclusion that the discharge-combination route is applicable to the *her* on Ni and Rh.

## Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction

TABLE 3. Analysis of previous data on Ni and Rh

(A) Ni (data from MATSUSMIMA and ENYO<sup>6)</sup>)

Run	$\bar{\nu}_{\text{ex}}$	$m$	$\bar{\nu}_{\text{ex,I}}$	$l$	$\bar{\nu}_{\text{ex,II}}, \bar{\nu}_{\text{ex,III, min.}}$
1	1.38	0.40	1.71	0.170	3.94
2	1.46	0.46	1.69	0.191	3.63
3	1.33	0.72	1.58	0.306	2.63
4	1.13	1.3	1.44	0.536	1.93
5	1.28	0.39	1.72	0.168	3.98

(B) Rh (data from MATSUSHIMA and ENYO<sup>12)</sup>)

1	1.03	0.53	1.65	0.221	3.26
2	1.11	0.52	1.66	0.206	3.43
3	1.17	0.47	1.68	0.176	3.84
4	0.99	0.46	1.69	0.212	3.35
5	1.21	0.51	1.66	0.230	3.17

(B) Pt, Ir, Ag and Au

Typical results of the analysis are given in Table 4. No clear distinction could be made among various  $\bar{\nu}$ 's. It is considered that the previous technique of determination of the reaction route based on a constancy of

TABLE 4. Analysis of previous data on Pt, Ir, Ag and Au

(A) Pt (data from MATSUSHIMA and ENYO<sup>19)</sup>)

	$\bar{\nu}_{\text{ex}}$	$m$	$\bar{\nu}_{\text{ex,I}}$	$l$	$\bar{\nu}_{\text{ex,II}}, \bar{\nu}_{\text{ex,III, min.}}$
1	1.06	4.29	1.19	2.35	1.21
2	1.90	4.51	1.18	2.78	1.18
3	1.04	2.21	1.31	3.27	1.15
4	1.09	3.51	1.22	2.30	1.22

(B) Ir (data from MATSUSHIMA and ENYO<sup>12)</sup>: Run 7)

2	1.37	—	—	1.20	1.42
3	1.48	11.5	1.08	1.08	1.46

(C) Ag (data from MATSUSHIMA and ENYO<sup>12)</sup>: Run 9)

1	0.96	5.89	1.15	1.94	1.26
2	1.08	3.57	1.22	1.74	1.29
3	1.01	3.14	1.24	1.39	1.36

K. SAITO *et al.*(D) Au (data from MATUSHIMA and ENYO<sup>12</sup>): Run 2)

	$\bar{\nu}_{\text{ex}}$	$m$	$\bar{\nu}_{\text{ex},\text{I}}$	$l$	$\bar{\nu}_{\text{ex},\text{II}}, \bar{\nu}_{\text{ex},\text{III}}, \text{min.}$
1	0.76	3.27	1.23	1.41	1.36
2	1.07	4.77	1.17	2.06	1.24
3	0.91	7.33	1.12	3.04	1.16
4	1.00	8.75	1.10	3.98	1.13
5	1.12	6.62	1.13	3.26	1.15

reaction parameters with  $X$  meets a difficulty when  $X^{\text{HD}}$  is too small to be analyzed reliably or the catalytic activity is too low to allow detailed investigations, whereas the present technique based on comparison of various  $\bar{\nu}$ 's meets a difficulty when again  $X^{\text{HD}}$  is so small that those  $\bar{\nu}$ 's are numerically close with each other. The present method is found useful in cases such as on Re where the catalytic activity is rather low but production of HD is not extremely little.

### References

- 1) K. J. VETTER, *Electrochemical Kinetics*, Academic Press, New York (1967), p. 516.
- 2) M. J. JONCICH, L. S. STEWART, and F. A. POSEY, *J. Electrochem. Soc.*, **112**, 717 (1965).
- 3) R. D. GILES, J. A. HARRISON, and H. R. THIRSK, *J. Electroanal. Chem.*, **20**, 47 (1969).
- 4) N. M. SHMELEVA, E. D. LEVIN, and A. L. ROTINIAN, *Elektrokhim.*, **7**, 1539 (1971).
- 5) A. T. KHUN and P. M. WRIGHT, *J. Electroanal. Chem.*, **27**, 319 (1970).
- 6) T. MATSUSHIMA and M. ENYO, *Electrochim. Acta*, **19**, 117, 125, 131 (1974).
- 7) J. HORIUTI and T. NAKAMURA, *Adv. in Catalysis*, Vol. 17, p.1, Academic Press, New York (1967).
- 8) M. I. TEMKIN, *Doklady Akad. Nauk, SSSR*, **152**, 156 (1963).
- 9) A. MATSUDA and J. HORIUTI, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **10**, 14 (1962).
- 10) J. A. CHRISTIANSEN, *Adv. in Catalysis*, Vol. 5, p. 311, Academic Press, New York (1953).
- 11) T. MATSUSHIMA and M. ENYO, *Electrochim. Acta*, in press.
- 12) T. MATSUSHIMA and M. ENYO, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **17**, 14 (1969).
- 13) A. N. FRUMKIN, *Adv. in Electrochem. and Electrochem. Engineering*, P. DELAHAY and C. W. TOBIAS ed., Intersci., New York (1961), Vol. 1, p. 65.
- 14) M. ENYO and T. YOKOYAMA, *Electrochim. Acta*, **12**, 1641 (1967).
- 15) T. YOKOYAMA and M. ENYO, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **15**, 207 (1967); M. ENYO, *ibid.*, **22**, 195 (1974).

*Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction*

- 16) G. OKAMOTO, *Sci. Papers, Inst. Phys. Chem. Res. Tokyo*, **31**, 211 (1937).
- 17) W. M. LATIMER, *Oxidation Potentials*, 2nd ed., p. 37, Prentice-Hall, New York (1952).
- 18) M. v. STACKELBERG and W. JAHNS, *Z. Elektrochem.*, **62**, 349 (1958).
- 19) T. MATSUSHIMA and M. ENYO, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **17**, 165 (1969).