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

By

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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 H₂SO₄. 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)

\[ H_2 + 2B = 2H^+B + 2e \quad (B = H_2O \text{ or } OH^-) \]

on Ru and Re are relatively scanty. 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. 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. used Ru electrodes elec-

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trodeposited from RuCl₃ 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. on electrodeposited Ru in 2N H₂SO₄, or by Kuhn and Wright on Ru electrodes prepared by powder metallurgy.

Recently, Matsushima and Enyo 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 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 assuming hydrogen adatom, H(a), and hydrogen molecule-ion, H₄⁺(a), as the possible reaction intermediates.

I. \( H₂ \rightarrow 2H(a), H(a)+B \rightarrow H⁺B + e \)
II. \( H₂ + B \rightarrow H(a) + H⁺B + e, H(a) + B \rightarrow H⁺B + e \)
III. \( H₂ \rightarrow H₄⁺(a) + e, H₄⁺(a) + B \rightarrow H⁺B + H(a), H(a) + B \rightarrow H⁺B + e \)
IV. \( H₂ \rightarrow H₄⁺(a) + e, H₄⁺(a) + 2B \rightarrow 2H⁺B + e \)

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

(B) The Stoichiometric Number

The stoichiometric number of the rds, \( ν_r \), in a consecutive single-route reaction is given by,

\[
ν_r = -\frac{ΔG}{RT} \ln \left( \frac{V_+}{V_-} \right)
\]  

(1)

where \(-ΔG\) 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
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,

\[
\bar{\nu} = \sum_s \nu_s (-\Delta g_s) / \sum_s (-\Delta g_s)
\]  

(2)

where \(-\Delta g_s\) is the affinity for step \( s \).

The overall net rate \( V \) is

\[
V = V_+ - V_-
\]

(3)

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

\[
\bar{\nu} = V_o (1/RT) \left[ d(-\Delta G)/dV \right]_{\eta \to 0}
\]

(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, \( V_{o,\text{ex}} \), in the \( her \) system consisting of deuterium, electrolytic solution of light water, and the test electrode which catalyzes the exchange reaction, by

\[
V_{o,\text{ex}} = (N_o/\ell) \ln (X_o/X)
\]

(5)

where \( N_o \) 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,

\[
\bar{\nu}_{\text{ex}} = V_{o,\text{ex}} (1/RT) \left[ d(-\Delta G)/dV \right]_{\eta \to 0}
\]

(6)

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

\[
\left( \frac{d(-\Delta G)}{dV} \right)_{\eta \to 0} = (2F)^{\eta} \left( \frac{d\eta}{dI} \right)_{\eta \to 0}
\]

(7)

Note that \( \bar{\nu}_{\text{ex}} \) 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
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the step rates and the composition of the hydrogen isotopes to be obtained in the D_2/H_2O exchange reaction.

**Route I**

\[
\begin{align*}
\text{H}_3 & \underset{v_{+c}}{\overset{v_{-c}}{\longrightarrow}} \text{2H(a)}, & \quad \text{H(a)} + \text{B} & \underset{v_{+d}}{\overset{v_{-d}}{\longrightarrow}} \text{H}^+ \text{B} + \text{e}
\end{align*}
\]

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

\[
\frac{(v_{+c} - v_{-c})}{v_{+c}} = \frac{(v_{+d} - v_{-d})}{v_{+d}} = V
\]

(8)

where \(v_c\) and \(v_d\) are the stoichiometric number of step c and d, respectively (\(v_c = 1, v_d = 2\)). The affinities of the steps are related to the affinity of the overall reaction and to the step rates by

\[
-\Delta G = -v_c \Delta g_c - v_d \Delta g_d
\]

(9)

\[
-\Delta g_c = RT \ln\left(\frac{v_{+c}}{v_{-c}}\right)
\]

(10, c)

\[
-\Delta g_d = RT \ln\left(\frac{v_{+d}}{v_{-d}}\right)
\]

(10, d)

From eqs. (8) and (10),

\[
\frac{v_c}{v_e} = \frac{1}{RT} \left(\frac{d(\Delta G)}{dV}\right)_{\Delta G=0}
\]

(11, c)

\[
\frac{v_d}{v_d} = \frac{1}{RT} \left(\frac{d(\Delta G)}{dV}\right)_{\Delta G=0}
\]

(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),

\[
\frac{1}{RT} \left(\frac{d(\Delta G)}{dV}\right)_{\Delta G=0} = \frac{v_c^2}{v_e} + \frac{v_d^2}{v_d}
\]

(12)

On the other hand, the isotope exchange rate, \(V_{v,c}\), for Route I is obtained as below. In the isotope exchange reaction, neglecting the isotope effect, we have

\[
2N_g \frac{dX}{dt} = -2v_c(X-Y)
\]

(13)

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

\[
2v_cX - (2v_c + v_d)Y = 0
\]

(14)

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

\[
v_c v_d/(2v_c + v_d) = (N_g/t) \ln(X_0/X)
\]

(15)
or, comparison with eq. (5) shows

\[ v_{o,ex} = v_o \frac{v_d}{2v_o + v_d} = v_d/2(m + 1) \]  

where

\[ m = \frac{v_d}{2v_o} \]  

As reported elsewhere, \( m \) is determined from the isotopic composition of the hydrogen gas obtained by the exchange reaction according to the relation

\[ \left[ \frac{X^{HD}}{X} - 2 + \frac{2X}{(m-1)^2} \right] X^{-\nu_m} = \left[ \frac{X^{HD}}{X_o} - 2 + \frac{2X_o}{(m-1)^2} \right] X_o^{-\nu_m} \]  

where \( X^{HD} \) 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

\[ \tilde{v}_{ex, I} = \frac{(m + 2)}{(m + 1)} \]  

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

**Route II**

\[ H_2 + B \xrightarrow{C} H(a) + H^*B + e, \quad H(a) + B \xrightarrow{f} H^*B + e \]

Analogously, we have

\[ \frac{1}{RT} \left( \frac{d(-AG)}{dV} \right)_{-\nu_o-0} = \frac{\nu_e}{v_e} + \frac{\nu_f}{v_f} \]  

where \( \nu_e = \nu_f = 1 \). The isotope exchange rate is given by

\[ V_{o,ex, II} = \frac{1}{2} \left[ \frac{v_e v_f}{v_e + v_f} + v_e \right] \]  

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). Substituting eqs. (20) and (21) into eq. (6), and defining \( l = v_f/v_e \) we find,

\[ \tilde{v}_{ex, II} = 1 + 1/2l \]  

If step e is the rds \( (l \rightarrow \infty) \), \( \tilde{v}_{ex, II} = 1 \), but if step f is \( (l \rightarrow 0) \), \( \tilde{v}_{ex, II} = \infty \). We can evaluate \( l \) from the composition data by the relation

\[ l = \frac{2 \ln(X_o/X) - \ln(X_o/X_o)}{2[\ln(X_o/X) - \ln(X_o/X)]]} \]
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Route III

\[ \text{H}_2 \xrightleftharpoons[i]{g} \text{H}_2^+(a) + e, \text{H}_2^+(a) + B \xrightleftharpoons[h]{1} \text{H}(a) + \text{H}^+ + B + e, \text{H}(a) + B \xrightleftharpoons[i]{i} \text{H}^+(B) + e \]

We obtain,

\[ \frac{1}{RT} \left( \frac{d(-\Delta G)}{dV} \right)_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_{_,2)}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}}
or, we find, irrespective of relative magnitudes of \( v_j \) and \( v_k \),

\[
\nu_{\text{ex,IV}} = 1
\]  

(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 \( \nu_{\text{ex}} \) on the one hand and \( \nu_{\text{ex,1}}, \nu_{\text{ex,II}}, \) and \( \nu_{\text{ex,III}} \) 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.**

<table>
<thead>
<tr>
<th>Route</th>
<th>parameters</th>
<th>( \tilde{\nu} )</th>
<th>( \tilde{\nu}_{\text{ex,1 etc.}} )</th>
<th>production of HD</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. ( \text{H}_2 \longrightarrow 2\text{H} )</td>
<td>( m \equiv \nu_d/2\nu_c )</td>
<td>( m + 2 ) ( m+1 )</td>
<td>( m + 2 ) ( m+1 )</td>
<td>yes</td>
</tr>
<tr>
<td>( \text{H} \longrightarrow \text{H}^+ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II. ( \text{H}_2 \longrightarrow \text{H}^+ )</td>
<td>( l \equiv \nu_f/\nu_e )</td>
<td>1</td>
<td>( 1 + \frac{1}{2l} )</td>
<td>yes</td>
</tr>
<tr>
<td>( \text{H} \longrightarrow \text{H}^+ )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III. ( \text{H}_2 \longrightarrow \text{H}^+ )</td>
<td>( g_1 \equiv \nu_h/\nu_g )</td>
<td>1</td>
<td>( \frac{g}{g+1} \left( 1 + \frac{2}{g-(g_1+1)} \right) )</td>
<td>yes</td>
</tr>
<tr>
<td>( \text{H} \longrightarrow \text{H}^+ )</td>
<td>( g \equiv (g_1+1)(2g_2+1) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV. ( \text{H}_2 \longrightarrow 2\text{H}^+ )</td>
<td></td>
<td>1</td>
<td>1</td>
<td>no</td>
</tr>
</tbody>
</table>

**Experimental**

(A) Materials

Electrodeposition of Ru was performed from RuCl₃ solution of roughly \( 6 \times 10^{-4} \text{ mol/l} \) in 1 N H₂SO₄ with 3 mA for 120 hours onto Ag wire, 50 cm². Capacity measurements of the electrode thus prepared revealed the roughness factor of about 30. Rhenium electrode used was a ribbon \( 0.0254 \times \)
0.75 mm, H. Cross Co. U.S.A. purity 99.9% of 60 cm² apparent area. Hydrogen and deuterium were purified by filtering through Pd–Ag membranes.

(B) Cell

This was analogous to that reported elsewhere. The volume was ca. 400 ml. 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. The polarization measurements were made by a steady polarization method.

**Fig. 1.** Polarization resistance near equilibrium on Ru and Re in 1 N H₂SO₄, 21°C. Electrode Area; Ru = 50 cm², Re = 60 cm².

$I = 36.4$ cm Hg (Ru), 40.4 cm Hg (Re).
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 2A. The fact that significant amount of HD was produced excluded the possibility of Route IV. Comparison of various stoichiometric numbers is seen in Table 2A. Since \( m \) was ca. 10\(^{-2} \), \( \bar{\nu}_{\text{ex},1} \) was very close to two, in fair agreement with \( \bar{\nu}_{\text{ex}} \) of ca. 2.3. On the other hand, both \( \bar{\nu}_{\text{ex},II} \) and \( \bar{\nu}_{\text{ex},III} \) were 6 or possibly larger\(^*\). Based on the agreement between \( \bar{\nu}_{\text{ex}} \) and \( \bar{\nu}_{\text{ex},I} \), we conclude Route I to be

Table 2. Deuterium exchange reaction on Ru and Re  
1 N H\(_2\)SO\(_4\) ; 21°C ; \( X_{D}^{0} = 0.997 \), \( X_{D}^{\text{HD}} = 0.006 \).

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>( P(21^\circ C) ) (cm Hg)</th>
<th>( t ) (hr : min)</th>
<th>( X_{D}^{0} )</th>
<th>( X_{D}^{\text{HD}} )</th>
<th>( \bar{\nu}_{\text{ex}} )</th>
<th>( \bar{\nu}_{\text{ex},I} )</th>
<th>( \bar{\nu}_{\text{ex},II} )</th>
<th>( \bar{\nu}_{\text{ex},III} )</th>
<th>( \bar{\nu}_{\text{ex}^{-}} ) (ohm)</th>
<th>( (d\bar{\nu}/dI)_{\nu=0} )</th>
<th>Route I</th>
<th>Route II, III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 36.4</td>
<td>48:00</td>
<td>0.197</td>
<td>0.790</td>
<td>65.2</td>
<td>2.36</td>
<td>~0.03</td>
<td>0.0725</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 18.6</td>
<td>46:00</td>
<td>0.214</td>
<td>0.771</td>
<td>111</td>
<td>2.31</td>
<td>~0.02</td>
<td>0.0206</td>
<td>18.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 56.9</td>
<td>47:00</td>
<td>0.130</td>
<td>0.865</td>
<td>75.0</td>
<td>2.54</td>
<td>&lt;0.01</td>
<td>0.0354</td>
<td>15.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 12.4</td>
<td>40:00</td>
<td>0.189</td>
<td>0.800</td>
<td>183</td>
<td>2.34</td>
<td>&lt;0.01</td>
<td>0.0258</td>
<td>20.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 27.2</td>
<td>44:00</td>
<td>0.108</td>
<td>0.899</td>
<td>164</td>
<td>2.25</td>
<td>&lt;0.01</td>
<td>0.115</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 7.2</td>
<td>44:00</td>
<td>0.191</td>
<td>0.801</td>
<td>324</td>
<td>2.18</td>
<td>&lt;0.01</td>
<td>0.0237</td>
<td>12.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 32.9</td>
<td>47:00</td>
<td>0.100</td>
<td>0.898</td>
<td>183</td>
<td>2.39</td>
<td>&lt;0.01</td>
<td>0.256</td>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(B) Re, apparent surface area 60 cm\(^2\)

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>( P(21^\circ C) ) (cm Hg)</th>
<th>( t ) (hr : min)</th>
<th>( X_{D}^{0} )</th>
<th>( X_{D}^{\text{HD}} )</th>
<th>( \bar{\nu}_{\text{ex}} )</th>
<th>( \bar{\nu}_{\text{ex},I} )</th>
<th>( \bar{\nu}_{\text{ex},II} )</th>
<th>( \bar{\nu}_{\text{ex},III} )</th>
<th>( \bar{\nu}_{\text{ex}^{-}} ) (ohm)</th>
<th>( (d\bar{\nu}/dI)_{\nu=0} )</th>
<th>Route I</th>
<th>Route II, III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 43.2</td>
<td>39:00</td>
<td>0.066</td>
<td>0.915</td>
<td>79.0</td>
<td>2.07</td>
<td>0.57</td>
<td>1.64</td>
<td>3.64</td>
<td>2.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 40.4</td>
<td>43:00</td>
<td>0.067</td>
<td>0.915</td>
<td>91.5</td>
<td>1.99</td>
<td>0.53</td>
<td>1.65</td>
<td>3.97</td>
<td>3.28</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 54.1</td>
<td>46:00</td>
<td>0.066</td>
<td>0.919</td>
<td>76.5</td>
<td>1.94</td>
<td>0.47</td>
<td>1.68</td>
<td>4.40</td>
<td>3.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 29.1</td>
<td>68:07</td>
<td>0.104</td>
<td>0.870</td>
<td>129</td>
<td>1.98</td>
<td>0.46</td>
<td>1.68</td>
<td>4.71</td>
<td>3.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 21.5</td>
<td>40:00</td>
<td>0.068</td>
<td>0.910</td>
<td>183</td>
<td>2.19</td>
<td>0.49</td>
<td>1.67</td>
<td>4.26</td>
<td>3.13</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^*\) Evaluation of \( l \) and \( g \) from the data in Table 2A 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 2A were obtained from such GC data among repeated GC analyses that would result in smallest possible values of \( \bar{\nu}_{\text{ex},II} \) and \( \bar{\nu}_{\text{ex},III} \).
operative on Ru**. Thus, the present results did not support the conclusions proposed in the literature

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 Ni6,11.

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 decay12, an acceptable behaviour was seen (Fig. 2). The slope, \( d \ln I_d/d \ln P \) (and \( d \ln I'_d/d \ln P \)) which now represents \( d \ln v_d/d \ln P \) because of step d being practically rate-determining

\[
\text{Fig. 2. Pressure dependences of } I_0 \text{ and } I'_0 \text{ on Ru, } 1 \text{ N } H_2SO_4, 21^\circ C \text{ (After correction for decrease of the catalytic activity, see text).}
\]

\( I_0 \); from isotope exchange rate.

\( I'_0 \); from polarization data, viz., \( I'_0 = (RT/2F)(dl/d\bar{v})_{\infty} \).

***) 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 \( \bar{v}_\text{ex} \). Hence, \( \bar{v}_\text{ex} \) should in reality be somewhat smaller than the figures here obtained, or in better agreement with \( \bar{v}_\text{ex, L} \).
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was ca. 0.5: This is somewhat larger than the value expected for a charge-transfer control of the her\(^{13}\), 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, \(E_r=19.0\sim24.6\ \text{mV}\), can be analyzed according to the relation derived by Enyo and Yokoyama\(^{14}\). At \(X_o\approx X\approx1, S_+\approx\exp\left(\frac{F E_r}{R T}\right)\) where \(S_+\) is the deuterium separation factor in the direction of hydrogen ionization. Hence, we obtain \(S_+ = 2.1\sim2.7\) which is far greater than the data obtained on Pt, Au, Ag, or Ni, 1.1\sim1.6\(^{14}\). The separation factor \(S_-\) in the hydrogen evolution reaction reaction is then obtained according to the relation derived for the slow-discharge mechanism\(^{16}\), \(S_- = Q S_+ K/4\) where \(Q\) is the partition coefficient of deuterium between hydrogen gas and water at \(X=0, i.e., ca. 3.9^{16-18}\) and \(K\) is the equilibrium constant of the reaction \(H_2 + D_2 = 2HD, i.e., ca. 3.26\) at 25\(^\circ\)C. It is interesting that \(S_-\) on Ru is deduced to be rather high, 6.6\sim8.5. 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, \(\bar{v}_{ex,1}\) obtained to be 1.7 was in fair agreement with \(\bar{v}_{ex}\approx2.0\). On the other hand, \(\bar{v}_{ex,11} = \bar{v}_{ex,11,\text{min}} = 3.1\) is much larger than \(\bar{v}_{ex}\). Accordingly, Route I is again concluded to be acceptable. The result \(m=0.5\) 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 unsuccesful 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 \(\bar{v}_{ex}\) values obtained from the data reported\(^{9}\) on Ni and Rh are listed in Table 3. It is seen that \(\bar{v}_{ex,11} = \bar{v}_{ex,11,\text{min}}\) is much larger than \(\bar{v}_{ex}\) whereas \(\bar{v}_{ex,1}\) 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 MATSUSIMA and ENY06)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{v}_{ex}$</th>
<th>$m$</th>
<th>$\bar{v}_{ex,1}$</th>
<th>$l$</th>
<th>$\bar{v}<em>{ex,II}$, $\bar{v}</em>{ex,III}$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.38</td>
<td>0.40</td>
<td>1.71</td>
<td>0.170</td>
<td>3.94</td>
</tr>
<tr>
<td>2</td>
<td>1.46</td>
<td>0.46</td>
<td>1.69</td>
<td>0.191</td>
<td>3.63</td>
</tr>
<tr>
<td>3</td>
<td>1.33</td>
<td>0.72</td>
<td>1.58</td>
<td>0.306</td>
<td>2.63</td>
</tr>
<tr>
<td>4</td>
<td>1.13</td>
<td>1.3</td>
<td>1.44</td>
<td>0.536</td>
<td>1.93</td>
</tr>
<tr>
<td>5</td>
<td>1.28</td>
<td>0.39</td>
<td>1.72</td>
<td>0.168</td>
<td>3.98</td>
</tr>
</tbody>
</table>

(B) Rh (data from MATSUSIMA and ENYO12)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{v}_{ex}$</th>
<th>$m$</th>
<th>$\bar{v}_{ex,1}$</th>
<th>$l$</th>
<th>$\bar{v}<em>{ex,II}$, $\bar{v}</em>{ex,III}$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.03</td>
<td>0.53</td>
<td>1.65</td>
<td>0.221</td>
<td>3.26</td>
</tr>
<tr>
<td>2</td>
<td>1.11</td>
<td>0.52</td>
<td>1.66</td>
<td>0.206</td>
<td>3.43</td>
</tr>
<tr>
<td>3</td>
<td>1.17</td>
<td>0.47</td>
<td>1.68</td>
<td>0.176</td>
<td>3.84</td>
</tr>
<tr>
<td>4</td>
<td>0.99</td>
<td>0.46</td>
<td>1.69</td>
<td>0.212</td>
<td>3.35</td>
</tr>
<tr>
<td>5</td>
<td>1.21</td>
<td>0.51</td>
<td>1.66</td>
<td>0.230</td>
<td>3.17</td>
</tr>
</tbody>
</table>

(B) Pt, Ir, Ag and Au

Typical results of the analysis are given in Table 4. No clear distinction could be made among various $\bar{v}$'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 MATSUSIMA and ENYO10)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{v}_{ex}$</th>
<th>$m$</th>
<th>$\bar{v}_{ex,1}$</th>
<th>$l$</th>
<th>$\bar{v}<em>{ex,II}$, $\bar{v}</em>{ex,III}$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.06</td>
<td>4.29</td>
<td>1.19</td>
<td>2.35</td>
<td>1.21</td>
</tr>
<tr>
<td>2</td>
<td>1.90</td>
<td>4.51</td>
<td>1.18</td>
<td>2.78</td>
<td>1.18</td>
</tr>
<tr>
<td>3</td>
<td>1.04</td>
<td>2.21</td>
<td>1.31</td>
<td>3.27</td>
<td>1.15</td>
</tr>
<tr>
<td>4</td>
<td>1.09</td>
<td>3.51</td>
<td>1.22</td>
<td>2.30</td>
<td>1.22</td>
</tr>
</tbody>
</table>

(B) Ir (data from MATSUSIMA and ENYO12; Run 7)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{v}_{ex}$</th>
<th>$m$</th>
<th>$\bar{v}_{ex,1}$</th>
<th>$l$</th>
<th>$\bar{v}<em>{ex,II}$, $\bar{v}</em>{ex,III}$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.37</td>
<td>—</td>
<td>—</td>
<td>1.20</td>
<td>1.42</td>
</tr>
<tr>
<td>3</td>
<td>1.48</td>
<td>11.5</td>
<td>1.08</td>
<td>1.08</td>
<td>1.46</td>
</tr>
</tbody>
</table>

(C) Ag (data from MATSUSIMA and ENYO12; Run 9)

<table>
<thead>
<tr>
<th>Run</th>
<th>$\bar{v}_{ex}$</th>
<th>$m$</th>
<th>$\bar{v}_{ex,1}$</th>
<th>$l$</th>
<th>$\bar{v}<em>{ex,II}$, $\bar{v}</em>{ex,III}$, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.96</td>
<td>5.89</td>
<td>1.15</td>
<td>1.94</td>
<td>1.26</td>
</tr>
<tr>
<td>2</td>
<td>1.08</td>
<td>3.57</td>
<td>1.22</td>
<td>1.74</td>
<td>1.29</td>
</tr>
<tr>
<td>3</td>
<td>1.01</td>
<td>3.14</td>
<td>1.24</td>
<td>1.39</td>
<td>1.36</td>
</tr>
</tbody>
</table>
reaction parameters with $X$ meets a difficulty when $X^{HD}$ 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 $i$'s meets a difficulty when again $X^{HD}$ is so small that those $v$'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

Stoichiometric Number and Mechanism of the Hydrogen Electrode Reaction