STOICHIOMETRIC NUMBER AND ELECTROLYTIC SEPARATION FACTOR OF DEUTERIUM ON NICKEL HYDROGEN ELECTRODE

By

Michio Enyo,*l Takamitsu Yokoyama*2
and Masamitsu Hoshi**

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Abstract

A detailed treatment of the method briefly reported previously is presented, which determines (without neglecting the isotope effect) the stoichiometric number \( \nu(r) \) of the rate-determining step \( r \) of the hydrogen electrode reaction from measurements of isotopic exchange reaction rate and reaction resistance. The method was applied to the nickel hydrogen electrode, and \( \nu(r) \) determined at unity from the two experimental parameters obtained in the system of light water (0.124 N NaOH) and pure deuterium at 25°C. Based on this value, the electrolytic separation factor of deuterium in the hydrogen ionization reaction, \( S_0 \), at the rest potential was determined at 1.5 from similar measurements of the two parameters at a deuterium content of 12.5% in the gaseous hydrogen. From this \( S_0 \), the electrolytic separation factor of deuterium in the hydrogen evolution reaction, \( S_1 \), was deduced to be approximately 6 using the relation \( S_1/S_0=S \) which holds at low deuterium content when the deuterium-containing hydrogen in contact with water is isotopically in equilibrium (\( S \) is the partition coefficient of deuterium between aqueous solution and gaseous hydrogen). This \( S \)-value compares well with data in the literature which were obtained at considerable cathodic polarizations. The results thus obtained support the theory that the hydrogen electrode reaction on nickel obeys the catalytic mechanism.

Introduction

Various efforts have been reported on determining the mechanism of the hydrogen electrode reaction,

\[ 2H^+ + 2e^- = H_2, \]  \hspace{1cm} (1)

where \( H^+ \) is a hydrogen ion associated with a Brønsted base \( H_2O \) or \( OH^- \) and \( e^- \) a metal electron. Among others, the stoichiometric number \( \nu(r) \) of the rate-determining step \( r \) of the reaction (1) and the electrolytic separation factor

**) M. H.: The Research Laboratory, TEIJIN Ltd., Tokyo, Japan.
of deuterium or tritium are powerful and frequently used means for the determination of the reaction mechanism\textsuperscript{13,14}.

The methods of determination of $\nu(r)$, as reported in the literature, are essentially based on the general equation\textsuperscript{13,14},

$$i_+ / i_- = \exp \left\{ -2F\eta / \nu(r)RT \right\},$$

where $i_+$ and $i_-$ are the forward and backward unidirectional rates of the reaction (1), respectively, $\eta$ is the overpotential\textsuperscript{*}, and the other notations have their usual meaning. At the reversible potential, Eq. (2) yields, as is well known,

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

where $i_0$ is the exchange current density or the particular value of $i_+$ or $i_-$ at the reversible potential and $i$ the net current density. Here, the measurement of the reaction resistance $(\partial \eta / \partial i)_{T=0}$ at the reversible potential can usually be made without difficulty, but the evaluation of $i_0$ requires a special technique. In several investigations reported\textsuperscript{2,13}, $i_0$ was evaluated by extrapolating the linear portion of the Tafel line to $\eta=0$. However, firstly, it is not quite safe to assume linearity over a wide range of $\eta$ especially before the establishment of the reaction mechanism, which is the very aim of the work, and secondly, this method appears not sufficiently accurate because the linearity observed experimentally was often not very reliable\textsuperscript{**}.

On the basis of the assumption that an isotopic exchange reaction between water and hydrogen in the presence of a metal electrode as catalyst is brought about only by the reaction (1) on the metal used, as is actually often found to be exactly the case\textsuperscript{1}, the value of $i_0$ can be determined from the transfer rate of a labelled isotope if one neglects the isotope effect, i.e., the difference in the specific rates between the isotopes. This method has the advantage over that described above that there is no basic ambiguity underlying it.

\textsuperscript{*} Potential of the test electrode referred to the reversible hydrogen electrode potential under the same conditions. In the following treatment where the isotope effect is taken into account, this is referred to the potential of the test electrode under the same conditions except that no current is flowing. This potential, at which the total forward and backward unidirectional rates of the hydrogen electrode reaction without isotopic discrimination exactly balance each other but the isotopically individual rates do not, will hereafter be called simply the rest potential of the electrode. In an isotopically pure system or one with no isotope effects, this becomes identical with the reversible potential.

\textsuperscript{**} The $i_0$ on, e.g., Ag or Cu as observed\textsuperscript{13} by an isotopic exchange reaction at the equilibrium potential was far smaller (e.g., by a factor of 10\textsuperscript{9}) than literature values obtained by the extrapolation method.
Neglect of the isotope effect, however, introduces indefinite errors into the results especially where hydrogen isotopes are concerned. Recently, a method has been proposed in which the isotope effect upon the determination of $\nu(r)$ of the hydrogen electrode reaction was avoided by taking the dependences of both the forward and the backward unidirectional transfer rates of a labelled isotope upon overpotential; the tacit assumption was made that the gaseous hydrogen taking part in an exchange reaction is isotopically in equilibrium. However, this method is restricted to a range of sufficiently low concentrations of the labelled isotope, and requires excellent constancy of the catalyst activity which, however, is one of the major experimental difficulties in the field.

Besides those works on $\nu(r)$, Horiuti and Okamoto have examined the electrolytic separation factor of deuterium in the hydrogen evolution reaction, $S$, on various metals and found that the values fall into two distinct groups depending on the electrode metal and the experimental conditions. Later, this finding was confirmed by Walton and Wolfenden. After those pioneer works, the separation factor was widely accepted as characteristic of the reaction mechanism, and hence many efforts have been devoted to both the experimental determination and the theoretical interpretation of its value.

A method has been reported in a previous paper by which $\nu(r)$ of the reaction (1) could be determined more conveniently and dependably without neglecting the isotope effect, and where the isotope effect was evaluated simultaneously in terms of the electrolytic separation factor. This method, which thus determines the two diagnostically important parameters at the same time, was treated in detail and successfully applied to the hydrogen electrode reaction on nickel in alkaline solution as reported below.

**Theoretical**

The relation between the reaction resistance of reaction (1) and the rate of isotopic transfer between light water and deuterium-containing hydrogen in the presence of a metal catalyst is derived as follows without neglecting the isotope effect. The rate of isotopic transfer at the rest potential (see footnote, p. 223), $V_o$ (atom/sec), which is a function of the deuterium contents in the two phases and hence of time in an exchange reaction, is given as,

$$V_o = V_{-}(P) + V_{-}(D), \quad (2. a)$$

or,

$$V_o = V_{+}(P) + V_{+}(D), \quad (2. b)$$

where $V_{-}(P)$ and $V_{-}(D)$ are, respectively, the unidirectional rates of protium and deuterium transfer from hydrogen to water at the rest potential, and $V_{+}(P)$ and $V_{+}(D)$ are those of the reverse process. The net rate of decrease of deu-
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terium in hydrogen is given by \( V_-(D) - V_+(D) \). However, \( V_+(D) \) can be taken here as practically constant, as water is so abundant in comparison with gaseous hydrogen in usual experimental designs that the variation of its deuterium content during the exchange reaction can be completely ignored. Further, the experimental conditions were chosen, for the sake of simplicity, so that the deuterium content in the solution is always practically zero, hence \( V_-(D) - V_+(D) \) is equal to \( V_-(D) \). We have thus,

\[-d(NX_g)/dt = V_-(D), \quad (3)\]

where \( N \) is the total number of hydrogen atoms without isotopic discrimination in the gaseous hydrogen, which is kept constant throughout the exchange reaction because of absence of net current*, and \( X_g \) is the atomic fraction of deuterium in it at time \( t \). The deuterium separation factor in the hydrogen ionization reaction, \( S_g \), is defined as,

\[ S_g = f \frac{V_-(P)}{1-X_g} \left/ f \frac{V_-(D)}{X_g} \right., \quad (4)\]

which represents the isotope effect in the hydrogen electrode reaction. Eliminating \( V_-(P) \) and \( V_-(D) \) from Eqs. (2.a), (3) and (4), we have,

\[ S_g (1-X_g)+X_g \frac{dX_g}{X_g} = - \frac{V_o}{N} dt, \]

which is immediately integrated with the boundary condition that \( X_g = X_{g0} \) at \( t=0 \). Thus we have, finally,

\[ S_g = \frac{(\bar{V}_o/N)t - (X_{g0}-X_g)}{\ln (X_{g0}/X_g) - (X_{g0}-X_g)} \quad (5)\]

Here, \( \bar{V}_o \) is the average value of \( V_o \) during the course of the exchange reaction started with \( X_{g0} \) and terminated at \( X_g \) at time \( t \), and is given in terms of the corresponding average exchange current density, \( \bar{i}_e \), on the basis of the assumption mentioned in the Introduction that the exchange reaction is brought about only by the hydrogen electrode reaction, as,

\[ \bar{V}_o = AN_A \bar{i}_e/F, \quad (6)\]

where \( A \) is the apparent surface area of the electrode, \( N_A \) the Avogadro number and \( F \) the Faraday. Further, \( \bar{i}_e \) is given by the average of reciprocal of the reaction resistance at the rest potential of the reaction (1) on the electrode as,

*) The amounts of hydrogen evolved or ionized during the measurements of the reaction resistance conducted as described below were entirely negligible.
The relation (7) holds, as verified in a previous paper\textsuperscript{16}, irrespective of the deuterium content in the system and of the extent of the isotope effect by defining $\eta$ as the potential of the test electrode referred to its rest potential, provided that neither $S_t$ nor $S_q$ vary with the electrode potential. This requirement must be fulfilled in the present case since the value of $S_t$ obtained below at the rest potential on the nickel hydrogen electrode is close to literature values obtained under high cathodic polarizations; here, the electrode was polarized only within the range where $|\eta| < 5 \text{ mV}$. The last factor in Eq. (7) was evaluated from the experimentally observed reaction resistances at the beginning and at the end of the exchange reaction as\textsuperscript{11},

\begin{equation}
\frac{1}{i_0} = -\nu(r)\frac{RT}{2F} \left( \frac{\partial \eta}{\partial i} \right)_{\gamma=0}^{-1}.
\end{equation}

Eq. (5) thus contains $S_q$ and $\nu(r)$ as two unknowns. The $\nu(r)$ alone is determined from a special case of Eq. (5) as follows. Consider an exchange reaction between pure (~100\%) deuterium and light water which reduces $X_q$ only slightly so that $X_q \approx X_{q,0} \approx 1$. Expanding $\ln \left( X_{q,0} - X_q \right)$ in Eq. (5) under this condition as $(X_{q,0}/X_q) - 1$, and rewriting as,

\begin{equation}
\overline{V}_e t \approx \frac{V_e t}{N} \approx (X_{q,0} - X_q) + S_q \left( \frac{X_{q,0} - X_q}{X_q} \right)
\end{equation}

we see that the second term on the right-hand side of Eq. (9) can be neglected as compared with the first, provided that $S_q$ is not very much greater than unity\textsuperscript{**}. We have thus with reference to Eqs. (6) and (7),

\textsuperscript{11} As seen in Fig. 3, the variation in the reaction resistance, and hence $V_e$ according to Eqs. (6) and (7), with $X_q$ was of the order of 10\% under the conditions here employed. This approximation, Eq. (8), therefore introduces a possible maximum error of about 5\% (but probably much less than this), which is within the experimental error.

\textsuperscript{**} The value of $S_q$ is usually found to be roughly between one and two. LEWIS and RÜETSCHI\textsuperscript{17} evaluated the value as 1.5~1.8 at 30\(^\circ\)C from the individual ionization rates of both $P_2$ and $D_2$ on a rotating platinized platinum disk electrode at a sufficiently high rotating speed to avoid diffusion control. Roughly the same value was also obtained from the ionization experiments of an equimolar mixture of $P_2$ and $D_2$. (However, the limiting value of ionization current at the highest rotation speed claimed by the authors to be free of diffusion control and used in the estimation of $S_q$ is doubtful as can be demonstrated by plotting their results in the $(\text{current})^{-1}$ vs. $(\text{rotation speed})^{-1/2}$ diagram. As a result of this, the true value of $S_q$ is likely to be smaller than this figure, because

(continued to next page)
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\[ v(r) \approx -\frac{F}{At} \frac{N}{N_A} (X_{p,0} - X_{p}) \frac{2F}{RT} \left( \frac{\partial \eta}{\partial t} \right)_{\eta=0}. \]  

(10)\(^*\)

\( S_g \) is now determined at any deuterium content by Eq. (5) using the \( v(r) \) thus obtained, which is assumed to be independent of the isotopic composition.

It has been demonstrated\(^{20,21} \) that the relation,

\[ S_f/S_g = S, \]  

(11)

holds at low deuterium contents in gaseous hydrogen and water even if the isotopic exchange between the two phases is out of equilibrium; the requirement being that the gaseous hydrogen itself is in equilibrium with respect to the reaction, \( \text{P}_2 + \text{D}_2 = 2\text{PD} \). Here \( S \) is the partition coefficient of deuterium between the two phases defined in terms of \( X_o \) and of the atomic fraction, \( X_z \), of deuterium in water as,

\[ S = \frac{\left\{ \frac{X_z}{1-X_z} \right\}}{\left\{ \frac{X_o}{1-X_o} \right\}}. \]  

(12)

which is about 4 at room temperature\(^{22} \), and \( S_f \) is defined as,

\[ S_f = \frac{\left\{ \frac{V_+(P)}{1-X_f} \right\}}{\left\{ \frac{V_+(D)}{1-X_f} \right\}}. \]  

(13)

which alternatively represents the isotope effect in the hydrogen electrode re-

the maximum current for the deuterium ionization would have been more heavily underestimated than for protium). LAUER and VIELSTICH\(^{23} \) obtained the \( S_f \) value of unity on a rotating Pt or Au electrode.

The \( S_f \) can be alternatively estimated from \( S_f \) by Eq. (11) when the deuterium content is low, assuming that the hydrogen evolved is isotopically in equilibrium as required for Eq. (11) to be valid. On nickel, \( S_f \) was obtained as 6.7 by HORIZUTI and OKAMOTO\(^{24} \) with an atomic fraction, \( X_f \), of deuterium in the solution of 0.06. Hence \( S_g = 1.7 \) according to Eq. (11), taking \( S = 4 \) at the room temperature\(^{22} \). On Pt, \( S_f \) was 4.7 according to FUKUDA and HORIZUTI\(^{25} \) at \( X_f = 0.085 \), and 15°C, from which \( S_g = 1.0 \sim 1.8 \). A similar value, 1~2, can be estimated from the data of LEWIS and RÜETSCHI\(^{26} \) for Ag, Pd, Ag-Pd alloy, Ni-Ag-Pd alloy etc. with \( X_f = 0.02 \), at 30°C. On Hg, \( S_f = 3.1 \)\(^{27} \), hence \( S_g \) is roughly 0.8.

Incidentally, in the work of WALTON and WOLFENDEN\(^{28} \), \( S_f \) was 3.3 with \( X_f = 0.3 \sim 0.5 \), at 15°C, in that of POST and HISKEY\(^{29} \), \( S_f \) was 3.1 at 20°C which was estimated by comparing reaction rates observed in the electrolyses of pure D\(_2\)O and P\(_2\)O. It seems from these data that neither \( S_f \) nor \( S_f \) on a given metal electrode varies in its order of magnitude with the deuterium concentration in the system. On these grounds, it is assumed that the value of \( S_g \) for \( X_g \approx 1 \) on nickel would not be too far apart from the value 1.7 estimated above for nickel, or 1.5 obtained later in this work at \( X_g = 0.125 \).

\(^*\) The approximation used in deriving Eq. (10) causes a systematic error in the \( v(r) \)\)-determination if \( X_g \) is not sufficiently close to unity. As \( X_g \) at the end of the exchange experiment was roughly 0.8 as in Table 1 below, the value of \( v(r) \) obtained there would be too small roughly by 20\%, for \( S_g \approx 1.5 \) as will be found later.
action. $S_i$ can hence be evaluated from $S_q$ under the above conditions of validity of Eq. (11).

**Experimental**

**Materials.**

1. Hydrogen gas: Deuterium gas was prepared by filtering cylinder deuterium from Stuart Oxygen Co., San Fransisco (purity > 99.5%) through a Pd-thimble heated at about 300°C. Mixture gas of protium and deuterium (12.5% D) was prepared using light hydrogen similarly purified.

2. Distilled water: Water was distilled first from alkaline permanganate solution of deionized water and then twice further under flow of air purified with KOH solution.

3. Aqueous electrolyte: 0.124N aqueous NaOH solution was prepared from Special grade NaOH from KANTO Chem. Co., Tokyo, and distilled water prepared as above. The solution prepared was preliminarily well degassed and introduced into the reaction vessel under vacuum.

**Reaction vessel.**

The reaction vessel was constructed of borosilicate glass “Hario” of SHIBATA & Co., Tokyo, as shown in Fig. 1. C is the nickel electrode used as the catalyst for the exchange reaction, on which the reaction resistance of the reaction (1) was measured at the same time. This was made of nickel wire (0.08 mm diameter, purity 99.99%, JOHNSON and MATTHEY Co., London) wound into a cylinder. The apparent surface area was 1320 cm². P is an electrode of similar nickel wire for pre-electrolysis and designed so as to be raised by means of a magnet from the solution. R is the reference electrode, made of a platinum wire of 10⁻² cm² apparent area, which is small enough to ignore its contribution to the exchange reaction as compared with that of the nickel catalyst. (In an alkaline solution, the catalytic activity of platinum for the exchange reaction is rather comparable with that of nickel.) A is an auxiliary electrode of Pd-thimble with about 10 cm² exterior area and 0.2 mm thick, sealed to glass with a Kovar metal-to-glass seal K. This was used as the counter electrode for polarizing the electrode C and also as the anode in the pre-electrolysis without evolving oxygen but ionizing hydrogen from container H (Fig. 2). The compartment containing A was connected to the main compartment by a capillary of 2 mm inner diameter and 3 cm length in order to prevent contribution of the Pd-thimble to the exchange reaction. No gas phase was left in this compartment in order to arrest the interflow of solution when samples were taken which was accompanied by a sudden change of pressure in the main compartment.
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Fig. 1. Reaction vessel

A: Pd-thimble
B: Breakable joint
C: Ni electrode as catalyst
F: Sintered frit
K: Kovar metal-to-glass seal
L: Solution container
P: Pre-electrolysis electrode
R: Pt reference electrode
S: Constriction
Procedure.

The reaction vessel was successively cleaned with Special grade ethyl ether, ethyl alcohol, distilled water, dilute HCl to remove oxide on the electrodes, distilled water and 2N aqueous NaOH at 80°C for 10 hr. It was then washed thoroughly with distilled water, filled with it and kept at boiling temperature for more than two days, renewing the water repeatedly in the mean time. After this, the vessel, combined as shown in Fig. 1 with the container L of the electrolytic solution previously degassed, was connected without drying to a vacuum system at J, via a liquid nitrogen trap. The vessel was evacuated, filled with pure hydrogen of 10 cmHg pressure, heated and kept at about 100°C with repeated evacuation and renewal of the hydrogen until the water inside was completely removed. It was then heated to 350°C with hydrogen inside for 2 hr in order to reduce the electrodes, similarly renewing the hydrogen.
After this, it was sealed off together with the solution container at the constrictions S₁ and S₂, the breakable joint B₁ was opened, the solution introduced into the vessel, and finally the container removed by sealing off at the constriction S₃. The reaction vessel thus prepared was mounted as shown in Fig. 2. The magnet-operated circulation pump M (all-glass but springs gold-plated) was joined to the vessel at J₂ and J₃, and the hydrogen container H of about 200 cc volume at J₁. The water thermostat T was kept at 25±0.1°C.

H was filled with purified hydrogen through a U-tube immersed in liquid nitrogen and then the breakable joint B₁ opened. After the considerable decrease of pressure in H due to dissolution of hydrogen into the Pd-thimble had ceased, the pressure in H was adjusted to about 10 cmHg and the greaseless stopcock G kept closed to protect the thimble against mercury or grease vapor.

The exchange reaction was now conducted by introducing hydrogen of known deuterium content into the vessel through a liquid nitrogen trap and the indium stopcock I by opening the breakable joints B₂ and B₃, and circulating the hydrogen by means of the pump in the direction of arrows, through a condenser cooled with tap water and a bubble-breaker lest the pump should be wetted by water vapor or bubbles from the solution. After a recorded time, the hydrogen was sampled and its deuterium content analyzed by means of a gas chromatograph with a Fe₂O₃-coated alumina column²³) (when the exchange was started with pure deuterium) or a mass-spectrometer (HITACHI RMD-3, when started with 12.5% deuterium); both were specially designed for analysis of hydrogen isotopes, P₂, PD and D₂. The exchange run was then repeated in the same way, flushing before the next run several times with the hydrogen gas to be used in the next run.

The reaction resistance of the reaction (1) was measured at the beginning and at the end of each run by applying currents between A and C and measuring the potential difference between C and R by means of a high sensitivity vacuum tube voltmeter of a high input resistance (10⁷ ohm, YOKOGAWA, VM-31) or of a glass electrode pH-meter (∼10⁻⁹ ohm, METROHM, E-300).

The volume of the system was estimated by expanding a known amount of hydrogen into the system and measuring its pressure, correcting for the vapor pressure of water.

The solution was pre-electrolyzed prior to the exchange experiments with the electrode A as anode and P as cathode respectively at 0.47 mA for 17 hr. The potential of P referred to R was about −0.18 V. A similar "pre-electrolysis” was inserted in some cases between the exchange experiments without noticeable effect on the catalytic activity of the electrode. After the
pre-electrolysis, the electrode P was raised from the solution by means of a magnet and enclosed in the small compartment (Fig. 1).

Results

The potential of the nickel electrode C agreed with that of the reference electrode R usually within ca. 1 mV and varied with time. This variation with time was found to be due mainly to the fact that the response of the platinum electrode R to changes in hydrogen pressure is much slower than that of the nickel electrode C, as observed with reference to electrode A. It

Fig. 3. Current-overpotential relation on the Ni electrode in the system of D₂/P₂O near the rest potential.
Curve 1: at the beginning, \(X_p = 1.00\), and curve 2: at the end, \(X_p = 0.80\), of the exchange reaction. Solution: 0.124 N NaOH, gas phase: 278 cc, 11.2 cmHg, apparent surface area of catalyst: 1320 cm², temperature: 25 ± 0.1°C
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took thus several hours for the platinum electrode to settle its electrode potential within about 0.1 mV difference after a pressure change, while the nickel electrode settled in about five minutes.

A typical $i-\eta$ relation obtained in 0.124 N NaOH solution at 25°C is shown in Fig. 3, where $\eta$ is the potential of the test electrode referred to its rest potential. The slope near the rest potential ($|\eta|<5$ mV) in this isotopically mixed system was, as expected, the same in the anodic and cathodic regions. The curves 1 and 2 were obtained, respectively, at the beginning and the end of the exchange experiment which, in this particular case, was started with light water and pure D$_2$ of 11.2 cmHg pressure and terminated at the time when the deuterium content in the gas phase was 80% (Table 1, Run No. 2). Results of similar exchange reactions are listed in Table 1.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Total hydrogen pressure (25°C)</th>
<th>Reaction time</th>
<th>$X_d$</th>
<th>$-\frac{1}{A}(\frac{\partial \eta}{\partial \bar{n}})_{\bar{n}=0}$</th>
<th>$\nu(\eta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.8 cmHg</td>
<td>26 hr:25 m</td>
<td>0.696</td>
<td>11.8 ohm</td>
<td>1.03</td>
</tr>
<tr>
<td>2</td>
<td>11.2</td>
<td>20:25</td>
<td>0.800</td>
<td>14.1</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>11.7</td>
<td>30:00</td>
<td>0.770</td>
<td>18.1</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>9.2</td>
<td>18:15</td>
<td>0.871</td>
<td>23.6</td>
<td>0.98</td>
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<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
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</table>

(*): The value of $\nu(\eta)$ obtained here must be taken as underestimated by roughly 20%. Nevertheless, it is evident in this Table that the value of $\nu(\eta)$ obtained using Eq. (8) is undoubtedly unity.

Results of exchange reactions started with hydrogen of low deuterium content (12.5%) are given in Table 2. From the values of the exchange rate and the reaction resistance, $S_r$ was calculated by Eq. (5) using the value $\nu(\eta)=1$ as obtained above, and then $S_t$ by the relation, $S_t=S_rS$. In the last column of Table 2 is shown the value of "$\nu(\eta)$" obtained when the isotope effect was neglected, i.e., when $S_r$ was taken to be unity in Eq. (5).

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TABLE 1. Exchange reaction between light water and pure deuterium: Value of $\nu(\eta)$.

Solution: 0.124 N-NaOH, volume of gas phase: 278 cc, apparent surface area of catalyst: 1320 cm$^2$, temperature: 25.0±0.1°C

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*): The value in the system, ($P_2+12.5\%$ D$_2$)/P$_2$O was ca. 0.5 mV more noble than the reversible hydrogen electrode potential in the system, P$_2$/P$_2$O, under otherwise the same conditions, as observed with reference to electrode A.
TABLE 2. Exchange reaction between light water and hydrogen of low deuterium content: Values of $S_g$ and $S_t$ and of $\nu(r)$ from Eq. (5) on the base of $S_g=1$.

$x_{0,0} = 0.125$, otherwise the same conditions as in Table 1.

$S = S_t/S_g = 4$ at $25^\circ C$

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Total hydrogen pressure (25°C)</th>
<th>Reaction time</th>
<th>$X_g$</th>
<th>$-\frac{1}{A} \left( \frac{\partial \nu/\partial t}{} \right)_{t=0}$</th>
<th>$S_g$</th>
<th>$S_t$</th>
<th>$\nu(r)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>12.4 cmHg</td>
<td>18 hr:45m</td>
<td>0.114</td>
<td>18.4 ohm</td>
<td>1.49</td>
<td>6.0</td>
<td>0.70</td>
</tr>
<tr>
<td>6</td>
<td>11.5</td>
<td>39 :35</td>
<td>0.101</td>
<td>18.2</td>
<td>1.47</td>
<td>5.9</td>
<td>0.70</td>
</tr>
<tr>
<td>7</td>
<td>11.8</td>
<td>52:40</td>
<td>0.097</td>
<td>18.4</td>
<td>1.54</td>
<td>6.2</td>
<td>0.68</td>
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<tr>
<td>8</td>
<td>11.5</td>
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<td>1.63</td>
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<td>1.5</td>
<td>6.2</td>
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Discussion

1. The method of determination of $\nu(r)$, $S_g$ and $S_t$

   The method of simultaneous experimental determination of both $\nu(r)$ and $S_g$ has been successfully applied. The $\nu(r)$-determination with the system of light water and pure (≈100%) deuterium is effective in the sense that it is unambiguous particularly with regard to the isotope effect and remarkably insensitive to variations in the catalytic activity of the electrode, e.g., by a factor of two, as seen in Table 1; such a variation occurred in the course of about 15 days.

   It is exemplified by the "$\nu(r)$" values in Table 2 which deviate considerably from unity that neglect of the isotope effect causes a significant error in the $\nu(r)$-determination. One might argue that this value, 0.7, is sufficiently close to unity; but there is no basis to single it out from others, e.g., two, without knowledge of $S_g$.

   The $S_g$ determined in the present work is that of the system (P$_2$ + D$_2$)/P$_2$O at least at the beginning of the exchange reaction but not that of the system (equilibrated mixture of P$_2$, PD and D$_2$)/P$_2$O with the same deuterium content, the latter $S_g$ leading to $S_t$ strictly according to Eq. (11). However, the $S_g$ obtained here would roughly correspond to the latter case since the hydrogen after the exchange experiment was nearly in isotopic equilibrium, indicating a rapid equilibration reaction between P$_2$ and D$_2$ (see later).

2. Values of $\nu(r)$, $S_g$ and $S_t$ and the mechanism of the nickel hydrogen electrode reaction.

   The stoichiometric number, $\nu(r)$, of the rate-determining step of the nickel
Stoichiometric number of nickel hydrogen electrode

hydrogen electrode reaction was first reported by Bockris and Potter\(^2\) as two. This value was one of the bases for their conclusion that the hydrogen electrode reaction on nickel obeys the slow discharge mechanism, \textit{i.e.}, rate-determining neutralization of protons. Horiuti and Sugawara\(^24\) have later criticised this result on the grounds that the determination of \(i_s\) by extrapolation of the Tafel line to \(\eta=0\) could not be sufficiently accurate.

The value \(\nu(r)=1\) obtained here immediately excludes the slow discharge mechanism but does not distinguish between the catalytic and the electrochemical mechanism, as it fits in with both the mechanisms\(^*)\). The latter mechanism is excluded, however, by the experimental evidence that the rate of the exchange reaction on nickel between water and gaseous hydrogen was invariant with pH of the solution\(^{26-27}\). Also, the catalytic mechanism is supported by the agreement of the observed value \(S_I=6.2\) with that theoretically calculated by Okamoto, Horiuti and Hirota\(^2\) for this mechanism.

This demonstration of the catalytic mechanism holds of course in the neighbourhood of the equilibrium potential but not necessarily at higher cathodic polarizations. However, the same mechanism has been verified there on nickel by the observation of a saturation current\(^{29}\), which is theoretically concluded to be characteristic of the mechanism, and of the characteristic value of \(S_I\)\(^4\). It may further be noted that the observed Tafel slope (\(\sim 0.12\) V) which has long been considered as against the catalytic mechanism was theoretically derived on the basis of the catalytic mechanism by allowing for the repulsive interactions between hydrogen atoms involved\(^{30}\).

3. Isotopic equilibration reaction, \(P_2+D_2=2PD\)

It has been previously reported\(^{26}\) and also found in the course of the present work (unpublished results) that on nickel in alkaline solutions the isotopic equilibration reaction between the hydrogen isotopes,

\[
P_2+D_2=2PD, \tag{14}
\]

proceeds rapidly as compared with the exchange reaction between water and hydrogen. It has been there suggested that this equilibration reaction might possibly be due to a side reaction of the Rideal-Eley mechanism,

\[
H_2+H(a)=H(a)+H_2, \tag{15}
\]

where \(H(a)\) denotes an adsorbed hydrogen atom without isotopic discrimination. If \(H(a)\) is exchangeable with hydrogen in water via the step, \(H(a)=H^+ + e^-\),

\(^*)\) Incidentally, this \(\nu(r)\)-value verifies the assumption above that the isotopic exchange is effectuated through the hydrogen electrode reaction alone.
which has to be far more rapid than the recombination step, \( H_2 = 2H(a) \), according to the above-concluded catalytic mechanism, then reaction (15) should contribute at the same time significantly to the exchange reaction as well as to the equilibration, i.e., the exchange rate should be much greater than that expected from Eq. (7). Hence \( \nu(r) \), if calculated formally, should be much greater than a value of the order of unity, which however disagrees with the above experimental results. This indicates, either, that there exists the Rideal-Eley mechanism but \( H(a) \) in the reaction (15) is incapable of being exchanged with \( H^+ \), or, that an equilibration reaction of another type exists in place of the Rideal-Eley mechanism. Further work is needed to clarify this problem.

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