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ISOTOPE EXCHANGE AND EQUILIBRATION REACTION ON NICKEL IN THE SYSTEM DEUTERIUM-LIGHT WATER

By

Michio Enyo*)

(Received April 10, 1967)

Abstract

Studies are reported, (i) on the exchange reaction between alkaline solution of light water and pure deuterium or deuterium-containing hydrogen on nickel catalysts with and without cathodic polarization and (ii) on the equilibration reaction between hydrogen and deuterium and the parahydrogen conversion reaction in the same system.

From the observed deuterium exchange rates, change in composition of the gaseous hydrogen, and rates of the hydrogen electrode reaction, the following conclusions were drawn: (A) the hydrogen electrode reaction on nickel in alkaline solution obeys the catalytic mechanism; (B) the equilibration reaction between the gaseous hydrogen isotopes as well as parahydrogen conversion reaction take place rapidly, as side reactions, simultaneously with the exchange reaction; and (C) the Langmuir-Hinshelwood mechanism of the equilibration reaction between adsorbed hydrogen molecules best interprete the experimental results obtained on moderately smooth nickel catalysts.

Introduction

The equilibration reaction**) between light hydrogen gas (called protium hereafter) and deuterium gas on various kinds of catalysts has been the subject of a number of investigations. In spite of these efforts, however, one must admit as yet that the mechanism is not fully understood1), even on typical metallic catalysts such as nickel. Three mechanisms have been generally accepted as possible: the Bonhoeffer-Farkas, the Rideal-Eley, and the Langmuir-Hinshelwood mechanisms. Much of the work published has been concerned with the pressure dependence of the rate, which should distinguish these mechanisms1,2). This approach does not appear to be very powerful, however,

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**) The term “equilibration” is used for reactions resulting in the interconversion of hydrogen isotopes in the gas phase, while the term “exchange” is used for reactions taking place between different phases (here gaseous hydrogen and water).
because the differences among the pressure dependences expected for the individual mechanisms are not sufficiently distinct to draw unambiguous conclusions. In this work, the equilibration reaction in presence of aqueous solution is investigated from a rather different angle.

It is well-known that deuterium exchange takes place between gaseous hydrogen and water in the presence of a metallic catalyst along the path of the hydrogen electrode reaction (HER) on the metal surface. In the exchange reaction taking place between deuterium gas and light water, the isotopic composition \( ^* \) (with respect to \( P_2 \), PD and \( D_2 \)) changes in a way that is characteristic for the mechanism of the HER \(^{3,4} \). If, for instance, the HER obeys the catalytic or the electrochemical mechanism, where one of the steps \( 2H(a)\rightarrow H_2 \) and \( H_2^+ (a) + e^- \rightarrow H_2 \) ((a) denotes an adsorbed state), is, respectively, taken as the rate-determining step, then there is equilibrium between the hydrogen intermediate on the electrode, \( H(a) \) or \( H_2^+ (a) \), and the \( H^+ \) ions in water by virtue of the rapid (not rate-determining) step, \( i.e., H(a)\equiv H^+ + e \) or \( H_2^+ (a)\equiv 2H^+ + e \). The deuterium content in the intermediate is governed by the relative rates of two steps, that between \( H^+ \) ions and the intermediate and that between the latter and the deuterium-containing gaseous hydrogen. It must be very low in either mechanism under the present conditions, since light water is the source of \( H^+ \) ions formed as intermediates, and the deuterium content of the aqueous phase does not become appreciable during the runs. Hence, practically only \( P_2 \), but not PD, should be formed in this exchange reaction at the expense of \( D_2 \) or PD initially placed in the gas phase. This means that the hydrogen gas present after the exchange should not be in equilibrium with respect to the reaction between the hydrogen isotopes,

\[
P_2 + D_2 = 2PD. \tag{1}
\]

Consequently, if we start with pure \( D_2 \) gas, the degree of equilibration, \( \rho \), defined as

\[
\rho = X^{PD}/X_{K-4}^{PD} \tag{2}
\]

should be zero; here, \( X^{PD} \) is the mole fraction of PD in hydrogen in the gas phase and \( X_{K-4}^{PD} \) is the value \( X^{PD} \) would assume, were the same gas brought to equilibrium with respect to the reaction of Eq. (1), with an equilibrium constant, \( K \), of four (the value at sufficiently high temperature, at which the isotope effect is negligible).

Conversely, if the slow-discharge mechanism is operative, where a third

* P and D stand, respectively, for protium and deuterium atoms. The term "hydrogen atom" and the symbol H, as used in this article, do not discriminate the two isotopes.
step, $\text{H}(a)\rightarrow\text{H}^+ + e$, is rate-determining, isotopic equilibration of the gas is very rapid because the recombination step, $2\text{H}(a)\rightleftharpoons\text{H}_2$, is now sufficiently fast as compared with the exchange reaction. Hence, we expect $P = P_{eq}$, where $P_{eq}$ is the equilibrium value of $P$ at the experimental temperature; the value of $P_{eq}$ is rather close to unity (e.g., $>0.95$) since $K$ at ordinary temperatures is fairly close to four.

It has been reported previously that on nickel in alkaline solution, $P$ is approximately 0.7, while a value of zero was found on platinum in acidic solution. Such an intermediate value of $P$ on nickel conforms to none of the figures expected above. However, there is no pH effect upon the isotope exchange rate, and it has been concluded on this basis that the catalytic mechanism is operative on nickel. The above intermediate $P$-value has, consequently, been attributed to a side reaction, such as the following reaction obeying the Rideal-Eley (atom-molecule) mechanism,

$$\text{H}_2 + \text{H}(a)\rightarrow \text{H}(a) + \text{H}_2,$$

which can allow equilibration of the isotopes. Recently, the view that the catalytic mechanism is operative on nickel hydrogen electrode has been further supported by findings that the stoichiometric number of the rate-determining step is unity at the equilibrium potential. Also, the lack of pH-dependence of the exchange rate was confirmed in the presence as well as in the absence of a supporting electrolyte.

The present work is aimed at (i) determining the stoichiometric number under cathodic polarization as well as at the equilibrium potential, in order to see whether this will give further support to the catalytic mechanism, and (ii) deducing a plausible mechanism for the side reaction from data on the rate of the equilibration reaction between $\text{P}_2$ and $\text{D}_2$ and of the parahydrogen conversion reaction as compared with that of the exchange reaction.

**Experimental**

1. **Apparatus and Technique**

The apparatus, similar to that used previously, consisted of a main compartment (containing the nickel electrode used as catalyst, a small Pt reference electrode, and a Ni-wire pre-electrolysis electrode), a side compartment (containing a Pd-thimble counter electrode), and an all-glass magnet-operated circulation pump. The side compartment was connected to the main compartment through a capillary in order to prevent the Pd-electrode from contributing to the exchange and equilibration. Besides a liquid nitrogen trap, an indium stopcock was inserted between the apparatus and a vacuum line, as described
previously. In part of the work this was replaced by a greaseless magnet-operated glass stopcock, in order to check possible contributions to isotopic equilibration or parahydrogen conversion by the heated glass wall and/or indium introduced by melting the indium during sampling. The contribution, however, turned out to be insignificant (see below, Table 4).

The nickel catalyst (wire, wound in the shape of a cylinder; apparent area, 1320 cm²) was reduced with hydrogen (≈10 cm Hg) at 350°C for 2 hr before use. The solution was prepared from special grade NaOH and conductivity water, thoroughly degassed by vacuum operations, and stored in a closed container equipped with a breakable joint; it was introduced into the apparatus under vacuum⁶. Deuterium gas was purified by filtering through a Pd-thimble. Para-rich hydrogen (55%) was prepared by means of an active charcoal trap cooled with liquid nitrogen under reduced pressure.

During exchange or conversion experiments, the solution was stirred by bubbling through it the hydrogen gas subjected to the reaction, which was circulated by means of the pump mentioned above.

The isotopic gas mixture was analyzed with respect to P₂, PD, and D₂ by means of a gas-chromatograph with an iron oxide-coated alumina column at liquid nitrogen temperature⁶, except in cases of low deuterium contents where a mass-spectrometer was used. Parahydrogen was analysed by a similar technique using an alumina column.

The reaction resistance was determined from the current density-overpotential relation, which was measured by means of a high-sensitivity vacuum-tube voltmeter with a high input resistance (Yokogawa, VM-31; 10⁷ ohm) or a glass electrode pH-meter (Metrohm, E-300; 10¹⁵ ohm). The gas phase volume of the main compartment was determined from the pressure change recorded when a known amount of hydrogen was expanded into the cell.

2. Evaluation of Isotope Exchange Rate and Stoichiometric Number

The isotope effect is neglected throughout the following treatment*). The isotope exchange rate is evaluated as follows. In the case where the exchange experiment is conducted without applying a polarizing current, i.e., without evolving or consuming gaseous hydrogen in the system, the rate of exchange in terms of current density, \( i_{ex} \), is obtained from the atom fraction of deuterium, \( X_0 \), in the gaseous hydrogen at time \( t \) and its initial value, \( X_0^0 \), using the relation

\[
i_{ex} = -\frac{2nF}{At} \ln \left( \frac{X_0}{X_0^0} \right),
\]

(4)

*) See footnote, p. 7
where $A$ is the apparent surface area of the catalyst, $F$ the Faraday, and $n$ the number of moles of total gaseous hydrogen in the system. This quantity $i_{ex}$ is identical with the familiar exchange current density $i_o$ if it is defined at the equilibrium potential (strictly speaking, at the rest potential if the isotope effect is significant$^9$), but $i_{ex}$ is distinguished here from $i_o$ so that $i_{ex}$ can represent the quantity under non-equilibrium conditions as well.

On some occasions in the present experimental work, a constant cathodic polarizing current was applied to the nickel electrode during the exchange experiment. (No hydrogen was then consumed in the system, nor did oxygen evolve at the counter electrode, because a Pd-thimble, which ionized hydrogen permeating its wall, was employed$^6$.) As the hydrogen evolved on nickel by the electrolysis is practically pure $P_2$ originating from light water, it continuously lowers the deuterium concentration of the gas phase. The same situation is also realized if $P_2$ is evolved from a pre-electrolysis electrode enclosed in the main compartment.

The exchange rate is, under such circumstances, evaluated as follows. We may start with the relation

$$Vex = \frac{dN^D}{dt} = -Vex'X^o,$$  \hspace{1cm} (5)

where $Vex$ is the exchange rate at a given pressure and $N^D$ is the total number of deuterium atoms in the gaseous hydrogen, which can be expressed as $N^D=NX_o$, in terms of $X_o$ and the total number of hydrogen atoms in the gaseous hydrogen, $N$. $N$ increases with time due to the electrolysis. We hence write, denoting the initial value of $N$ by $N_0$ and the rate of increase of $N$ by $c$, $N^D = N_0 (1+ct) X^o.$

$Vex$ also changes with time due to the increase in total hydrogen pressure from $P_o$ to $P_o+\Delta P$, viz.,

$$Vex = Vex\cdot \left\{ \left( \frac{P_o+\Delta P}{P_o} \right)^{\beta} = Vex\cdot (1+ct)^{\beta}, \right.$$  \hspace{1cm} (6)

where $Vex_0$ is the initial value of $Vex$ and $\beta$ is a constant representing the pressure dependence of the exchange rate, i.e., the order of the reaction (approximately 0.5 under the present experimental conditions$^3$). Introducing the last two equations into Eq. (5), we obtain

$$\frac{dX^o}{dt} = -\left\{ Vex_0 (1+ct)^{\beta-1} + \frac{c}{1+ct} \right\} X^o,$$  \hspace{1cm} (7)

where $Vex_0 = Vex_0 / N_0$. Integration of Eq. (7) yields, with the boundary con-
The average value of $V_{ex}$ between $t=0$ and $t=t$ is obtained from an equation analogous to Eq. (6) as

$$
\bar{V}_{ex} = \frac{V_{ex,0}}{t} \int_0^t (1 + ct) \, dt = V_{ex,0} \frac{(1 + ct)^{\beta + 1} - 1}{ct(\beta + 1)}. \tag{9}
$$

Hence, eliminating $V_{ex,0}$ from Eqs. (8) and (9) we have,

$$
\bar{V}_{ex} = \frac{1}{t} \frac{\beta}{\beta + 1} \frac{(1 + ct)^{\beta + 1} - 1}{(1 + ct)^\beta - 1} \ln \frac{X_0^g}{X^g(1 + ct)}. \tag{10}
$$

Since $ct$ is considerably smaller than unity ($ct < 0.3$ in the present experiments), we may expand the two power terms in Eq. (10) into series and approximate by retaining only the first three terms in each series. We find that

$$
\bar{V}_{ex} = \frac{1}{t} \frac{ct^2}{2} \ln \frac{X_0^g}{X^g(1 + ct)}, \tag{11}
$$

which is independent of the value of $\beta$. Finally, we convert $\bar{V}_{ex}$ to $\bar{i}_{ex}$, the average value of the exchange rate in terms of current density, by

$$
\bar{i}_{ex} = 2nF \bar{V}_{ex}/A. \tag{12}
$$

Thus, we have

$$
\bar{i}_{ex} = \frac{2nF}{At} \frac{1 + ct}{2} \ln \frac{X_0^g}{X^g(1 + ct)}. \tag{13}
$$

which becomes identical with Eq. (4) if $c=0$, i.e., if no net current is flowing.

The $i_{ex}$-values reported below (the bar denoting the average value is omitted for simplicity) were calculated from Eq. (4) or (13), depending on the particular experimental procedure employed. As Eq. (13) is applicable irrespective of the origin of the evolved $P_2$, as stated above, it was also used in cases where an intermediate cathodic "pre-electrolysis" was conducted during the exchange experiment (cf. Table 2A).

Using the value of $i_{ex}$ and the reaction resistance of the electrode, both measured at the equilibrium potential, we can determine the stoichiometric number, $\nu_r$, of the rate-determining step $r$ of the HER in absence of polarization from the relation$^{6,9,10}$,
Hydrogen exchange and equilibration on Ni immersed in water

\( \nu_e = \frac{i_{ex,0}}{(RT/2F)(-\partial \eta / \partial \eta)_{\eta=0}} \equiv \frac{i_{ex,0}}{I_{0,r}}, \quad (\eta=0) \) \hspace{1cm} (14)

where \( i \) is the current density, \( \eta \) is the overpotential, \( i.e., \) the potential of the test electrode as referred to its equilibrium potential in the same system\(^9\), and \( i_{ex,0} \) is the particular value of \( i_{ex} \) at \( \eta=0 \).

If, on the other hand, the exchange reaction is conducted under polarization, \( \nu_e \) is evaluated as follows. We have\(^9,10\)

\( \frac{i_f}{i_b} = \exp \left( -\frac{2F\eta}{\nu_e RT} \right), \)

where \( i_f \) and \( i_b \) are, respectively, the unidirectional rates (without discriminating between the component currents for P and D) of the HER in the forward (cathodic) and in the backward (anodic) direction. Provided that the exchange takes place only through the path of the HER, \( i_b \) is identical with \( i_{ex} \) as derived above (including conditions of polarization). We derive, therefore, using the relation \( i = i_f - i_b \), that

\( \nu_e = -\frac{2F\eta}{RT} \cdot \ln \left( \frac{1 + i_{ex}}{i_{ex}} \right), \quad (\eta \equiv 0) \) \hspace{1cm} (15)

Thus, instead of the exchange rate and the reaction resistance as used in absence of polarization (see Eq. (14)), we now use the exchange rate, the applied current density, and the overpotential, all as observed during polarization.

It is interesting to see the dependence of \( i_{ex} \) upon \( \eta \) in the region of cathodic polarization because it directly gives the anodic Tafel constant of the HER in the cathodic region. However, the procedure requires rather high experimental accuracy since the determination of the \( i_{ex} \)-values becomes increasingly difficult with increase in the cathodic overpotential; this is due to the increased contribution of \( P_2 \) evolution by the cathodic electrolysis, \( i.e., \) \( i (=i_f - i_b) \) tends to be much greater than \( i_{ex} \). Indeed, the actual plot of \( i_{ex} vs. \eta \) became rather erratic on the side of high \( \eta \) partly because the accuracy was not quite sufficient for this purpose, and partly due to slight differences in experimental conditions between the runs. A somewhat better plot was obtained after reducing \( i_{ex} \) to the dimensionless quantity \( j \) defined by

\( j = \frac{i_{ex}}{I_{0,r}}, \)

viz., the quantity representing the exchange rate at \( \eta \equiv 0 \) as referred to the value in the same run at \( \eta=0 \); the value of \( I_{0,r} \) was evaluated from the

\(^9\) Regarding the neglect of the isotope effect in the present work, it can be shown that the values of \( \nu_e \) evaluated from Eqs. (14) and (4) are good approximations to the true value as long as the deuterium contents in the gaseous hydrogen before and after the exchange are sufficiently high\(^6\); \( e.g., \) the error in \( \nu_e \) is 0.05 when \( X^g=1.0, X^p=0.8 \) and the deuterium separation factor in the hydrogen ionization reaction is 1.5 as observed for nickel\(^6\).
reaction resistance (cf. Eq. (14)).

Results

I. Nickel with Heavily Roughened Surface

If nickel is heated during the preparation to high temperatures in presence of water vapor, it is oxidized even in the presence of hydrogen, due to decomposition of water by nickel. In such a case, the surface is heavily roughened and partly covered with nickel black produced, after complete removal of water vapor, by reduction of the oxide with hydrogen. Such a nickel surface has a high catalytic activity for the exchange reaction. Results obtained are given in Table 1. The $\nu_r$-values calculated from Eq. (14) and (15) are roughly four (they are somewhat smaller when the electrode was polarized cathodically).

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$P_0$ (cm Hg)</th>
<th>$t$ (h : m)</th>
<th>$i$</th>
<th>$\Delta P$</th>
<th>$\eta$</th>
<th>$X\theta$</th>
<th>$\rho$</th>
<th>$i_{ex}$</th>
<th>$I_{0,r}$</th>
<th>$\nu_r$</th>
<th>$j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.2</td>
<td>3 : 00</td>
<td>0</td>
<td>0</td>
<td>0.78</td>
<td>0.62</td>
<td>6.26</td>
<td>1.65</td>
<td>3.8</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>34.7</td>
<td>4 : 40</td>
<td>0</td>
<td>0</td>
<td>0.88</td>
<td>0.87</td>
<td>7.11</td>
<td>1.73</td>
<td>4.1</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.2</td>
<td>18: 20</td>
<td>0.61</td>
<td>1.47</td>
<td>-4.1</td>
<td>0.44</td>
<td>0.87</td>
<td>4.72</td>
<td>3.3</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>15.3</td>
<td>7 : 20</td>
<td>1.06</td>
<td>1.03</td>
<td>-7.5</td>
<td>0.70</td>
<td>0.76</td>
<td>4.71</td>
<td>2.9</td>
<td>2.6</td>
<td></td>
</tr>
</tbody>
</table>

II. Smooth Nickel

Reduction of the nickel catalyst after careful removal of water vapor yielded moderately smooth surface; most of the present investigations were concentrated on this type of catalyst.

1. Exchange started with Pure Deuterium

(a) Exchange reaction at the equilibrium potential

Results of exchange experiments on smooth (i.e., not heavily roughened) nickel electrodes without polarization are listed in Table 2A. Values for $\Delta P$,
Hydrogen exchange and equilibration on Ni immersed in water

given in parentheses, show an increase in pressure of gaseous hydrogen due to intermediate cathodic “pre-electrolysis” conducted with the pre-electrolysis electrode during the exchange experiment. The nickel electrode used as catalyst was not polarized during this procedure. The values of \( i_{ex} \) were evaluated by Eq. (4) or (13) and \( \nu_r \) by Eq. (14). The average value of \( \rho \) obtained was roughly 0.9 and \( \nu_r \) was 1.0 ± 0.2.

TABLE 2 A Results of exchange reaction between light water and pure deuterium on smooth nickel electrode without applied polarization

0.124 N NaOH; 25 ± 0.1°C; \( A = 1320 \text{ cm}^2 \); gas phase volume, 278 cc; \( X_i = 0.996 \).

\( P_0 \) and \( \Delta P \), initial deuterium pressure and pressure increase (cm Hg), respectively, both at 25°C. For other symbols, see Table 1.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( P_0 )</th>
<th>( t )</th>
<th>( \Delta P )</th>
<th>( X_i )</th>
<th>( \rho )</th>
<th>( i_{ex} )</th>
<th>( I_{0,r} )</th>
<th>( \nu_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.1</td>
<td>17:20</td>
<td>(0.96)</td>
<td>0.81</td>
<td>0.77</td>
<td>0.45</td>
<td>0.61</td>
<td>0.73</td>
</tr>
<tr>
<td>2*)</td>
<td>11.8</td>
<td>26:35</td>
<td>0</td>
<td>0.70</td>
<td>0.99</td>
<td>0.79</td>
<td>0.67</td>
<td>1.18</td>
</tr>
<tr>
<td>4*)</td>
<td>11.2</td>
<td>20:25</td>
<td>0</td>
<td>0.80</td>
<td>0.94</td>
<td>0.61</td>
<td>0.56</td>
<td>1.09</td>
</tr>
<tr>
<td>5</td>
<td>11.9</td>
<td>43:10</td>
<td>(2.41)</td>
<td>0.63</td>
<td>0.84</td>
<td>0.46</td>
<td>0.51</td>
<td>0.91</td>
</tr>
<tr>
<td>7*)</td>
<td>11.7</td>
<td>30:00</td>
<td>0</td>
<td>0.77</td>
<td>0.95</td>
<td>0.50</td>
<td>0.43</td>
<td>1.16</td>
</tr>
<tr>
<td>9*)</td>
<td>9.2</td>
<td>18:15</td>
<td>0</td>
<td>0.87</td>
<td>0.92</td>
<td>0.34</td>
<td>0.34</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Average | 0.90 | 0.52 | 0.52 | 1.0 ± 0.2 |

*) Data used in a previous paper6) for the determination of \( \nu_r \). The values presented here differ from those reported before by about 10% because of different approximations used in the calculation.

(b) Exchange reaction under cathodic polarization

Similar results obtained on the same electrode under cathodic polarization are listed in Table 2 B. The values of \( i_{ex} \) were evaluated by Eq. (13) and \( \nu_r \).

TABLE 2 B. Results of exchange between light water and pure deuterium on smooth nickel electrode under cathodic polarization

For experimental conditions, see Table 2 A.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( P_0 )</th>
<th>( t )</th>
<th>( i )</th>
<th>( \Delta P )</th>
<th>( \eta )</th>
<th>( X_i )</th>
<th>( \rho )</th>
<th>( i_{ex} )</th>
<th>( I_{0,r} )</th>
<th>( \nu_r )</th>
<th>( j )</th>
</tr>
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<tbody>
<tr>
<td>3</td>
<td>10.9</td>
<td>24:10</td>
<td>0.34</td>
<td>1.35</td>
<td>- 5</td>
<td>0.68</td>
<td>0.93</td>
<td>0.75</td>
<td>0.81</td>
<td>1.05</td>
<td>0.88</td>
</tr>
<tr>
<td>6</td>
<td>11.7</td>
<td>29:25</td>
<td>0.77</td>
<td>3.70</td>
<td>-14</td>
<td>0.62</td>
<td>0.89</td>
<td>0.59</td>
<td>0.79</td>
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<tr>
<td>8</td>
<td>11.5</td>
<td>13:25</td>
<td>1.50</td>
<td>3.29</td>
<td>-26</td>
<td>0.76</td>
<td>0.79</td>
<td>0.12</td>
<td>0.62</td>
<td>0.78</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Average | 0.74 | 1.1 ± 0.3 |
by Eq. (15). The latter was again found to be approximately unity. As shown in Fig. 1 B, the value of \( j \) decreased with increase in the cathodic overpotential. \( \partial \log j / \partial \eta \) (which is equal to \( \partial \log i_{ex} / \partial \eta \)) was roughly \((90 \text{ mV})^{-1}\). The values of \( \rho \) do not differ significantly from those obtained at the equilibrium potential.

\[
\frac{\partial \log j}{\partial \eta} \bigg|_{\eta=0} = (45 \text{ mV})^{-1}
\]

\[
\frac{\partial \log j}{\partial \eta} \bigg|_{\eta=0} = (90 \text{ mV})^{-1}
\]

Fig. 1. Dependence upon cathodic overpotential of deuterium exchange rate on nickel

\[ j = i_{ex} / (-RT/2F) (\partial i / \partial \eta)_{\eta=0} \] (\( \nu_r \) is taken as unity in both cases)

(A) 0.026 N NaOH; 20 ± 1°C; nickel with heavily roughened surface; total hydrogen pressure, 10~15 cm Hg.

(B) 0.124 N NaOH; 25 ± 0.1°C; smooth nickel; total hydrogen pressure, 10~12 cm Hg.

2. Equilibration Reaction between Hydrogen Isotopes

The rather high values of \( \rho \) in Tables 2 A and 2B indicate either that isotopically nearly equilibrated hydrogen is produced by the exchange reaction, or that only \( P_2 \) is produced but there exists a side reaction which equilibrates the gas subsequently\(^*\). In order to clarify this, further experiments have been carried out starting with a mixed hydrogen gas of \( P_2 \) and \( D_2 \) (but no PD and hence \( \rho \)-value of the gas is zero).

From Table 3, it is clear that the equilibration reaction proceeds much more rapidly than does the exchange reaction, as seen from the quite significant increase in \( \rho \) from its initial value, zero, as compared to the minor changes in \( X^o \). (Even if the decrease in \( X^o \) is supposed to be due exclusively to formation of PD in exchange of \( D_2 \), the amount could account at most for half of the \( \rho \)-value observed.) This result indicates that high values of \( \rho \) in Tables

\(^*\) It has been shown previously\(^3\) from blank tests that this equilibration reaction does not proceed in the absence of nickel \( i.e., \) it is not brought about by glass walls of the vessel, alkaline solutions (less than a few tenth of a normal), etc.
Hydrogen exchange and equilibration on Ni immersed in water

2A and 2B are to be attributed to a rapid equilibration reaction but not to production of the equilibrated mixture of hydrogen isotopes by the exchange reaction.

TABLE 3. Results of equilibration between \( \text{P}_2 \) and \( \text{D}_2 \) on smooth nickel immersed in alkaline solution of light water

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( P_m ) (atm)</th>
<th>( t ) (h: m)</th>
<th>( X_2^0/X_2^o )</th>
<th>( \rho )</th>
<th>( i_{ex} )</th>
<th>( I_{0,r} )</th>
<th>( V_h )</th>
<th>( V_o )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.4</td>
<td>23:20</td>
<td>0.437/0.512</td>
<td>0.70</td>
<td>0.460</td>
<td>0.571</td>
<td>1.89</td>
<td>16.3</td>
<td>8.6</td>
</tr>
<tr>
<td>2</td>
<td>10.3</td>
<td>31:00</td>
<td>0.423/0.512</td>
<td>0.76</td>
<td>0.387</td>
<td>0.498</td>
<td>1.70</td>
<td>14.4</td>
<td>8.5</td>
</tr>
<tr>
<td>3*</td>
<td>12.4</td>
<td>18:45</td>
<td>0.114/0.125</td>
<td>0.53</td>
<td>0.369</td>
<td>0.528</td>
<td>1.35</td>
<td>11.3</td>
<td>8.4</td>
</tr>
<tr>
<td>4*</td>
<td>11.5</td>
<td>39:55</td>
<td>0.101/0.125</td>
<td>0.77</td>
<td>0.377</td>
<td>0.533</td>
<td>1.51</td>
<td>10.7</td>
<td>7.1</td>
</tr>
<tr>
<td>5*</td>
<td>11.8</td>
<td>52:40</td>
<td>0.097/0.125</td>
<td>0.85</td>
<td>0.359</td>
<td>0.528</td>
<td>1.37</td>
<td>10.4</td>
<td>7.6</td>
</tr>
<tr>
<td>6*</td>
<td>11.5</td>
<td>46:00</td>
<td>0.102/0.125</td>
<td>0.78</td>
<td>0.325</td>
<td>0.506</td>
<td>1.28</td>
<td>9.2</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Average: 0.38, 0.53, 1.52, 12.0, 7.9

*) Data obtained from mass-spectrometric analysis.

TABLE 4. Results of parahydrogen conversion on nickel immersed in alkaline solution

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( P ) (atm)</th>
<th>( t ) (h: m)</th>
<th>( X_P/X_P^0 )</th>
<th>( X_P^0 - X_P ) ( X_P^0 - X_P^0 )</th>
<th>( V_h + fV_o )</th>
<th>( i_{conv} )</th>
<th>( I_{0,r} )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \frac{X_P}{X_P^0} )</td>
<td>( \frac{X_P^0 - X_P}{X_P^0 - X_P^0} )</td>
<td>( V_h + fV_o )</td>
<td>( i_{conv} )</td>
<td>( I_{0,r} )</td>
<td>( m )</td>
</tr>
<tr>
<td>(A)</td>
<td></td>
<td></td>
<td>( X_P/X_P^0 )</td>
<td>( X_P^0 - X_P ) ( X_P^0 - X_P^0 )</td>
<td>( V_h + fV_o )</td>
<td>( i_{conv} )</td>
<td>( I_{0,r} )</td>
<td>( m )</td>
</tr>
<tr>
<td>1</td>
<td>12.8</td>
<td>7:05</td>
<td>0.43/0.55</td>
<td>1.66</td>
<td>19.8</td>
<td>5.58</td>
<td>0.61</td>
<td>8.1</td>
</tr>
<tr>
<td>2</td>
<td>11.1</td>
<td>13:05</td>
<td>0.37/0.55</td>
<td>2.50</td>
<td>19.0</td>
<td>4.60</td>
<td>0.59</td>
<td>6.8</td>
</tr>
</tbody>
</table>

(B) With greaseless glass stopcock; 0.05 N NaOH; gas phase volume, 268 cc.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>( P ) (atm)</th>
<th>( t ) (h: m)</th>
<th>( X_P/X_P^0 )</th>
<th>( X_P^0 - X_P ) ( X_P^0 - X_P^0 )</th>
<th>( V_h + fV_o )</th>
<th>( i_{conv} )</th>
<th>( I_{0,r} )</th>
<th>( m )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( X_P/X_P^0 )</td>
<td>( X_P^0 - X_P ) ( X_P^0 - X_P^0 )</td>
<td>( V_h + fV_o )</td>
<td>( i_{conv} )</td>
<td>( I_{0,r} )</td>
<td>( m )</td>
</tr>
<tr>
<td>1</td>
<td>11.2</td>
<td>23:40</td>
<td>0.36/0.45</td>
<td>1.82</td>
<td>7.0</td>
<td>1.65</td>
<td>0.23</td>
<td>6.2</td>
</tr>
<tr>
<td>2</td>
<td>11.7</td>
<td>19:00</td>
<td>0.36/0.45</td>
<td>1.82</td>
<td>8.7</td>
<td>2.16</td>
<td>0.23</td>
<td>8.4</td>
</tr>
<tr>
<td>3</td>
<td>11.3</td>
<td>22:55</td>
<td>0.38/0.45</td>
<td>1.54</td>
<td>5.2</td>
<td>1.24</td>
<td>0.22</td>
<td>4.6</td>
</tr>
<tr>
<td>4*</td>
<td>11.9</td>
<td>53:00</td>
<td>0.43/0.45</td>
<td>1.1</td>
<td>0.5</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*) Blank test carried out without circulating hydrogen in the system.
3. Parahydrogen Conversion Reaction

The results of parahydrogen conversion conducted in the same apparatus are given in Table 4. In order to test the possibility of contributions of heated glass wall and/or indium of the indium stopcock (during melting of the indium) to the catalysis of the conversion reaction during their short period of contact with the sample gas in the sampling procedure (Table 4A), an all-glass greaseless stopcock was used instead (Table 4B). The approximate constancy of \( m \) (which stands for the ratio between the rates of the conversion and the exchange reaction, see later) indicates that such contributions are negligible*).

Discussion

1. Mechanism of HER on Nickel in Alkaline Solution

It is essential to know the mechanism of the HER on nickel in alkaline solution before considering details of the equilibration and conversion reactions studied above. It has been concluded previously\(^6\) that on nickel the former reaction obeys the catalytic mechanism. This conclusion has been based mainly on the following facts: (i) \( \nu_r = 1 \) at the equilibrium potential\(^6\) (cf. also Table 2A), (ii) no effect of solution pH (dilute NaOH) upon \( i_{ct} \) was observed\(^3,5\), and (iii) a cathodic saturation current density exists\(^11\), as predicted for this mechanism, at the point of saturation of the electrode surface with H(a).

As briefly mentioned in the Introduction, \( i_{ct} \) has later been found to be independent of the solution pH also in the presence of a supporting electrolyte (KCl, NaClO\(_3\) and K\(_2\)SO\(_4\))\(^7\), which in general affects the structure of the electric double layer at the electrode-solution interface and in turn the pH-dependence of any charge transfer reaction present. The last fact excludes the possibility of the slow-discharge mechanism\(^12\) and at the same time also that of the electrochemical mechanism.

The value of \( \nu_r \) under (i) above is reproduced in the present work even under cathodic polarization (Table 2B). As shown in Fig 1B, \( j \) and hence \( i_{ct} \) decreased with increase in the cathodic overpotential by roughly \( (\partial \log i_{ct}/\partial \eta)^{-1} \approx 90 \text{ mV} \), from which the Tafel “constant” \( \alpha_a \) in the hydrogen ionization reaction (the anodic Tafel constant) is determined to be approximately 0.7 near the equilibrium potential. Now, on the basis of the above result that \( \nu_r = 1 \) and of the relation\(^\text{13}\)

\[
\alpha_a + \alpha_e = 2/\nu_r, \tag{17}
\]

* Additional data concerning the ratio between the rates of equilibration and exchange reaction, obtained in the author’s laboratory but not presented here, also substantiate this conclusion.
the cathodic Tafel constant, \( \alpha_c \), is determined to be roughly 1.3. This means that \( \alpha_c \) increases from a value around 0.5, as obtained on nickel in alkaline solution at high cathodic overpotentials\(^{11,14}\), towards this higher value with decrease in the cathodic overpotential. (A similar behavior of \( \alpha_c \) can be demonstrated from a detailed analysis of the \( i-\eta \) relation\(^{15}\)). This behavior is in harmony with the theory of the catalytic mechanism, because the concentration of the hydrogen intermediates H(a) decreases with decrease in the cathodic overpotential; the decrease should result in an increase of \( \alpha_c \) towards its classical (i.e., non-interaction) value, two\(^{16}\).

Based on the above arguments, the catalytic mechanism is assumed to be operative on nickel in alkaline solution throughout the following treatment.

2. Analysis based on the Assumption of the Rideal-Eley Mechanism

(a) Nickel with heavily roughened surface

In a previous paper\(^3\), the intermediate \( \rho \)-value observed on nickel has been interpreted by assuming the existence of a rapid side reaction obeying the Rideal-Eley mechanism, Eq. (3), and hence contributing to the equilibration between hydrogen isotopes. It is implied in this reaction scheme, composed of the HER and the Rideal-Eley mechanism, that this side reaction, combined with the very fast ionization step, \( \text{H}(a) \rightarrow \text{H}^+ + e^- \), should contribute to the isotope exchange reaction as well. Consequently, the rate of isotope exchange should be much greater than that expected from the activity of the electrode for the HER which can be independently evaluated from the reaction resistance. Hence, the values of \( \nu_r \) calculated formally from Eq. (14) or (15) should become much greater than the values expected for the HER itself (one or two depending on the mechanism).

As seen in Table 1, \( \nu_r \) was found to be \( 3 \sim 4 \) on nickel with a heavily roughened surface, in fair agreement with this expectation. However, there exists a further possibility, \( \text{viz.} \), that some portion of the nickel black, which was present in this case, was detached from the nickel electrode and resulted in high \( \nu_r \)-values; such detached nickel black would contribute to the exchange but not to the reaction resistance. Hence, without having further evidence, it seems difficult to decide for or against the scheme at the present stage.

(b) Smooth nickel

Contrary to the above, \( \nu_r \) is found to be unity on a smooth nickel electrode. This means not only that the discharge step in the HER is sufficiently rapid as compared with the recombination step but also that there exist no side reactions contributing to the isotope exchange. Consequently, the above scheme is not applicable (unless one admitted quite a peculiar character for the reaction,
e.g., that H(a) in the Rideal-Eley mechanism has nothing to do with H(a) in the HER). Hence, further possibilities are sought to interpret the rapid equilibration reaction, as discussed next.

3. Results on Smooth Nickel. Possibility of the Langmuir-Hinshelwood Mechanism

The rather large values of ρ obtained on the smooth nickel electrode (Table 2) indicate that there exists a side reaction which contributes to the equilibration between hydrogen isotopes, but not to the exchange reaction. The same conclusion is drawn from the results in Table 3, where a mixed gas of P₂ and D₂ is much more rapidly equilibrated than one expects from the exchange rate.

Three mechanisms have been discussed in the literature for the equilibration reaction between hydrogen isotopes taking place at a gas-solid interface; they are the Bonhoeffer-Farkas (atom-atom) mechanism in which the reaction proceeds through the step H₂→2 H(a), the Rideal-Eley (atom-molecule) mechanism represented by Eq. (3), and the Langmuir-Hinshelwood (molecule-molecule) mechanism17) in which the reaction proceeds between two hydrogen molecules adsorbed on the catalyst surface*). The last mechanism gives rise to equilibration without forming the intermediate H(a), and is unlikely, therefore, to contribute to the exchange reaction; thus it satisfies the requirements for a side reaction which can account for the present results**.

The results obtained above on the smooth nickel electrode will be analyzed next in order to evaluate the rate of the side reaction. However, it should be emphasized that the analysis holds for any one of the above-mentioned three mechanisms of the equilibration reaction and it is not necessary to assume any particular mechanism.

4. Analysis allowing for an Independent Equilibration Reaction

The results obtained on the smooth nickel electrode are now analyzed in order to evaluate the rates of the exchange and the equilibration reactions individually on the basis of the assumptions (i) that the HER which brings

*) This classification is used by SCHWAB17). A slightly different classification is also used in the literature3).

**) The result that the equilibration reaction is taking place along with the exchange reaction could also be accounted for if one arbitrarily assumed "heterogeneity" of the electrode surface such that there exist two kinds of catalytic sites, one contributing to the exchange reaction through the HER where the catalytic mechanism is operative, and the other independently to the equilibration reaction where the slow-discharge mechanism is operative. No definite arguments are available to test this model at present, except an indirect one against it3).
Hydrogen exchange and equilibration on Ni immersed in water

about the exchange obeys the catalytic mechanism (hence only $P_2$ is produced by the exchange reaction) and (ii) that there is a concurrent side reaction which contributes only to the equilibration. The reaction scheme is

$$H_2 \rightarrow 2H^+ + 2e \quad (18)$$

and

$$H_2 + H_2 \rightarrow 2H_2 \quad (e.g., \quad P_2 + D_2 \rightarrow 2PD) \quad (19)$$

where $V_\alpha$ is the unidirectional rate (number of times the reaction as written by Eqs. (18) and (19) occurs per unit time) of the HER (and hence that of the recombination step, according to the above premise of the catalytic mechanism) and $V_\epsilon$, in the same units, that of the side reaction contributing to the equilibration reaction.

At first, we investigate the kinetic expressions for the side reaction alone. In the Langmuir-Hinshelwood (molecule-molecule) mechanism, the sum of constituent rates, as given below, must again give the unit rate $V_\epsilon$, i.e., ($X$ denotes mole fraction of the species specified by its superscript)

$$2X^pX^pV_\epsilon + 2X^pX^{PD}V_\epsilon + 2X^{PD}X^pV_\epsilon + (X^p)^2V_\epsilon + (X^{PD})^2V_\epsilon = V_\epsilon.$$  

On the left-hand side of this equation, only the first and last terms are responsible for the consumption and production of $D_2$. Hence we have

$$-\frac{dX^{PD}}{dt} = 2V_\epsilon X^pX^{PD} - \frac{1}{2} V_\epsilon (X^{PD})^2, \quad (20.\ a)^*$$

where the factor 1/2 is introduced because the probability that $2PD$ actually yield $P_2$ and $D_2$ is half that of the same reaction in the reverse direction.

In the Rideal-Eley (atom-molecule) mechanism, we similarly have

$$X^dX^a + X^{PD}X^a + X^pX^a + X^{PD}(1-X^a) + X^{PD}(1-X^a) + X^{PD}(1-X^a) = 1$$

and

$$-\frac{dX^{PD}}{dt} = V_\epsilon X^d(1-X^a) - \frac{1}{2} V_\epsilon X^{PD}X^a$$

where $X^a$ is the atom fraction of deuterium in the adsorbed atomic hydrogen. In absence of the isotope effect, we may equate $X^a$ to $X^p$. Hence

$$X^a = X^p = X^{PD}/2, \quad \text{and} \quad 1-X^a = X^{PD}/2.$$

*) At the equilibrium of the equilibration reaction, the left-hand side of Eq. (20. a) vanishes and the equation reduces, as it should; to $(X^{PD})^2/X^pX^{PD} = 4$, i.e., the equilibrium constant with no isotope effect present.
Therefore,
\[
- \frac{dX_{D_1}}{dt} = V_s X_{D_1} \left( X_{P_2} + \frac{1}{2} X_{P_D} \right) - \frac{1}{2} V_s X_{P_D} \left( X_{D_1} + \frac{1}{2} X_{P_D} \right)
\]
\[
= V_s X_{P_2} X_{D_1} - \frac{V_s}{4} (X_{P_D})^2 .
\]  

(20. b)

The Bonhoeffer-Farkas (atom-atom) mechanism is but one of the steps comprising the HER. However, we can include the case in the present treatment if we suppose its rapid occurrence on, e.g., a part of the catalyst surface. Thus, we can write

\[
- \frac{dX_{D_1}}{dt} = V_s X_{D_1} - V_s (X^2) = V_s \left[ X_{D_1} - \left( X_{D_1} + \frac{1}{2} X_{P_D} \right)^2 \right]
\]
\[
= V_s \left[ X_{D_1} (1 - X_{D_1} - X_{P_D}) - (X_{P_D})^2/4 \right],
\]

which is identical with Eq. (20. b) above.

In general, Eqs. (20) can be written, irrespective of the mechanism, in the form

\[
- \frac{dX_{D_1}}{dt} = f V_s \left\{ X_{P_2} X_{D_1} - (X_{P_D})^2/4 \right\},
\]

(22)

where \( f \) takes the value of two in the Langmuir-Hinshelwood mechanism and unity in the Rideal-Eley and the Bonhoeffer-Farkas mechanisms.

For the complete scheme composed of the HER and the side reaction, we have now

\[
\frac{dX_{D_1}}{dt} = - V_h X_{D_1} - f V_s X_{P_2} X_{D_1} + \frac{1}{4} f V_s (X_{P_D})^2,
\]

(23. D)

\[
\frac{dX_{P_D}}{dt} = - V_h X_{P_D} - \frac{1}{2} f V_s (X_{P_D})^2 + 2 f V_s X_{P_2} X_{D_1},
\]

(23. PD)

and

\[
\frac{dX_{P_2}}{dt} = (1 - X_{P_2}) V_h - f V_s X_{P_2} X_{D_1} + \frac{1}{4} f V_s (X_{P_D})^2.
\]

(23. P)

Further, from Eqs. (23. D), (23. PD), and (21), we have

\[
\frac{dX^o}{dt} = - V_h X^o
\]

(24. a)

or, with the boundary condition \( X^o = X_{g}^o \) at \( t = 0 \),

\[
X^o = X_{g}^o \exp (- V_h t).
\]

(24. b)

The solution of the simultaneous differential equations (23) is found in
Hydrogen exchange and equilibration on Ni immersed in water

the following way. Using the parameter $\rho$ in Eq. (2), and the relation

$$X_{K=4}^{PD} = 2X^\circ (1 - X^\circ),$$

at the equilibrium of reaction (1) with $K=4$, we have

$$X_{PD}^{K=4} = 2\rho X^\circ (1 - X^\circ),$$

and combining this with Eq. (21),

$$X_{PD}^{K=4} = (1 - X^\circ)(1 - \rho X^\circ)$$

and

$$X_{PD}^{K=4} = X^\circ (1 - \rho + \rho X^\circ).$$

From Eq. (25. PD), we have

$$\frac{dX_{PD}^{K=4}}{dt} = 2X^\circ (1 - X^\circ) \frac{d\rho}{dt} + 2\rho (1 - 2X^\circ) \frac{dX^\circ}{dt},$$

and substituting Eqs. (25. PD) and (26) into (23. PD),

$$X^\circ (1 - X^\circ) \frac{d\rho}{dt} + \rho (1 - 2X^\circ) \frac{dX^\circ}{dt} = -V_h \rho X^\circ (1 - X^\circ)$$

Using Eq. (24. a), this reduces to

$$\frac{d\rho}{dX^\circ} = \frac{\rho}{1 - X^\circ} + m \frac{1 - \rho}{X^\circ} = 0,$$

where

$$m = fV_s / V_h.$$  \hspace{1cm} (27. b)

The solution of Eq. (27. a) at constant $m$ with the boundary condition

$$X_{PD}^{K=4} = 0$$

and hence $\rho = 0$ at $t=0$ is*)

$$\rho (1 - X^\circ) = 1 - \frac{mX^\circ}{m-1} - \left(\frac{X^\circ}{X_0^\circ}\right)^m \left(1 - \frac{mX_0^\circ}{m-1}\right) \hspace{1cm} (m \neq 1),$$

or, using Eq. (25. PD), we alternatively have

$$X_{PD}^{K=4} = 2X^\circ \left\{ 1 - \frac{mX^\circ}{m-1} - \left(\frac{X^\circ}{X_0^\circ}\right)^m \left(1 - \frac{mX_0^\circ}{m-1}\right) \right\} \hspace{1cm} (m \neq 1),$$

*) For the special case that $m=1$, the solution is

$$\rho (1 - X^\circ) = 1 - X^\circ / X_0^\circ + X^\circ \ln X^\circ / X_0^\circ, \hspace{1cm} (m=1),$$

However, this is unimportant since the mathematical condition, $m=1$, will hardly be realized in practical cases.
Now one can, utilizing Eq. (28.a), evaluate $m$ from experimental values of $\rho$ and $X^o$, and further, by determining $V_\alpha$ independently from $X^o$ at $t$ according to Eq. (24.b), both rates individually.

As Eq. (28.a) is transcendental, $m$ has been calculated numerically by the method of successive approximations. Table 3 gives the values of $m$ thus obtained, together with the values of $V_\alpha$ and $V_\beta$. The average value of $m$ is found to be approximately eight and does not significantly depend on the deuterium concentration of the initial gas or on the progress of the equilibration\textsuperscript{*)}. This value of $m$ means that the initial rate of consumption of D$_2$ molecule by the equilibration reaction yielding PD molecules is four times higher than that by the exchange reaction yielding PDO (which enters the aqueous phase), when a gas mixture of $X^{D_2}=X^{PD}=\frac{1}{2}$ at $t=0$ is used to start with.

5. Parahydrogen Conversion Reaction

Not only the HER, but also the side reactions discussed above contribute to parahydrogen conversion reaction. Changes in the mole fraction of parahydrogen $X^p$ with time are similarly formulated in terms of the quantities $V_\alpha$ and $fV_\gamma$ used above as follows.

In the case that the side reaction obeys the Langmuir-Hinshelwood mechanism, the kinetic expression for the reaction scheme composed of the HER and the side reaction (Eqs. (18) and (19)) is

$$
\frac{dX^p}{dt} = -V_\alpha(X^p - X^o) - 2V_\gamma(X^p)^2 - 2V_\gamma X^p(1 - X^p) \\
+ 2V_\gamma(X^p)^2 X^o + 4V_\gamma X^p(1 - X^p)X^o + 2V_\gamma(1 - X^p)^2 X^o
$$

where the terms appearing on the right-hand side are as follows: the first term is the net rate by which parahydrogen is lost by the HER, where $X^o$ is the value of $X^p$ at $t=\infty$ (i.e., at the conversion equilibrium); the second is that lost unidirectionally by the side reaction due to parahydrogen-parahydrogen ($p-p$) combination (two hydrogen molecules are involved); the third is similarly, that for $p-0$ and $0-p$; the fourth is that produced unidirectionally by the reaction for $p-p$ combination; the fifth, similarly, that for $p-0$ and $0-p$; and the last, that for $0-0$. We can rewrite

$$
\frac{dX^p}{dt} = -(V_\alpha + 2V_\gamma)(X^p - X^o).
$$

It can also be shown that we can introduce again the factor $f$ as used above,\textsuperscript{*)} This constancy of $m$ under various conditions of gas phase composition indicates the validity of Eq. (22) in the present system. This is another piece of evidence that the equilibration or the conversion reaction proceed independently of (the rate-determining step of) the HER.

\textsuperscript{*)} This constancy of $m$ under various conditions of gas phase composition indicates the validity of Eq. (22) in the present system. This is another piece of evidence that the equilibration or the conversion reaction proceed independently of (the rate-determining step of) the HER.
and hence we have generally

\[ \frac{dX_p}{dt} = - (V_a + fV_s) (X_p - X_f^p). \]  

Integration of Eq. (30) yields

\[ V_a + fV_s = \frac{1}{t} \ln \frac{X_p^f - X_f^p}{X_p - X_f^p}, \]  

where \( X_f^p \) is the value of \( X_p \) at \( t=0 \). The value of \( m \) defined in Eq. (27.b) can also be estimated in this case by evaluating \( V_a \) independently from data of the reaction resistance and the known value of \( \nu_r \) (identifying \( i_{e\alpha} \) in Eq. (14) with \( V_a \), except for the appropriate conversion factor). The values of \( m \) obtained (Table 4) were rather erratic, but still the value obtained above from the isotope equilibration reaction was in essence reproduced satisfactorily. This agreement indicates that the conversion reaction proceeds through the same mechanism as does the equilibration reaction.

**Conclusions**

A previously reported value of unity for the stoichiometric number \( \nu_r \) of the rate-determining step of the HER on nickel in alkaline solution at the equilibrium potential was reproduced in the present expriments under cathodic polarization; this supports the view that the catalytic mechanism is operative.

The degree of isotopic equilibration of the gaseous hydrogen after the exchange, \( \rho = X_p^{PD}/X_p^{PP} \), with respect to the reaction, \( P_2 + D_2 = 2PD \), is found to be approximately 0.9; the value is not congruent with the catalytic mechanism where a value of zero is expected.

It is demonstrated from simultaneous studies of exchange and equilibration reactions started with a system composed of light water and a gas mixture of \( P_2 \) and \( D_2 \), that an independent equilibration reaction between the hydrogen isotopes proceeds as a side reaction along with the exchange reaction; thus the high \( \rho \)-values mentioned above are brought about by this side reaction.

The Rideal-Eley mechanism that was assumed previously for the equilibration reaction has been found consistent with the results only when the nickel surface is heavily roughened; the value of \( \nu_r \) as formally calculated was roughly four, \( i.e., \) much larger than the value expected for the HER, which is one or two.

On moderately smooth nickel, however, the exchange reaction is brought about only by the HER, \( i.e., \) \( \nu_r \) is found to be unity. The Langmuir-Hinshelwood mechanism which gives rise to the equilibration reaction without splitting hydrogen molecules into atoms is considered as the most likely model.
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of the equilibration reaction. Without assumptions about the operative mechanism of the equilibration reaction, however, the experimental results have been analyzed in order to evaluate separately the rates of the exchange and the equilibration reactions. The equilibration reaction proceeds roughly eight times quicker than the exchange reaction. Essentially the same figure is obtained from a parahydrogen conversion reaction conducted similarly; the conversion reaction takes place through the same mechanism as does the equilibration reaction.

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