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EXCHANGE REACTION BETWEEN DEUTERIUM AND WATER ON NICKEL IN ALKALINE SOLUTIONS: COOPERATION OF RIDEAL-ELEY MECHANISM AND MECHANISM OF HYDROGEN ELECTRODE REACTION

By

Michio Enyo, Masamitsu Hoshi and Hideaki Kita

(Received April 30, 1963)

Abstract

Exchange reactions between pure deuterium and aqueous alkaline solutions were carried out on nickel wire catalyst at various pH's and deuterium pressures at 0~50°C. The exchange rate and the heat of activation were independent of pH (7~13), being approximately 10^{-5} A/cm² at 1 atm in exchange current density and 9 kcal/mole, respectively. The degree of equilibration, \( \varphi = \frac{P_{PD}}{P_{PD,eq}} \), where \( P_{PD} \) is partial pressure of protium deuteride in the sample gas directly after the exchange and \( P_{PD,eq} \) that when the same gas is brought to equilibrium with respect to \( P_2+D_2=2PD \) subsequently, was found at 0.7~0.9 practically independent of pH, hydrogen pressure or temperature.

From these results, conclusions were drawn (a) that from negligible pH-effect upon the exchange rate or upon the heat of activation, the catalytic mechanism is valid on nickel hydrogen electrode in alkaline solutions at least at its equilibrium potential, and (b) that from \( \varphi > 0 \), RIDEAL-ELEY mechanism, \( H_2+H(a)\rightarrow H(a)+H_2 \), is taking place concurrently and in parallel with the rate-determining recombination step, \( 2H(a)\rightarrow H_2 \), of the catalytic mechanism, where \( H(a) \) is the adsorbed hydrogen atom. Individual rates of the RIDEAL-ELEY and the catalytic mechanisms, both of which contribute to the exchange reaction, were determined by analyzing experimental results on \( D \), the deuterium atomic fraction, and \( \varphi \). Importances of concurrent operation of the RIDEAL-ELEY mechanism in studies of reaction kinetics were briefly discussed.

I. Introduction

A number of investigations have been reported on the mechanism of hydrogen electrode reaction on nickel. As this metal provides an important example in this field and also is connected deeply to the studies on catalysis, it is urgently required to establish the mechanism on solid ground. Earlier
works of Bowden and Rideal\textsuperscript{[1]}, Lukowzev, Lewina and Frumkin\textsuperscript{[2]} and Legran and Lewina\textsuperscript{[3]} have shown that Tafel’s relation\textsuperscript{[4]} generally holds on nickel hydrogen electrode in both acidic and alkaline solutions. The $b$-value of the Tafel equation was obtained to be ca. 120 mV in most cases, and the overpotential\textsuperscript{*1}, $\eta$, drifted with time frequently. Bockris et al.\textsuperscript{[5,6]} extended this study and observed that $b=100\sim120$ mV, that the exchange current density, $i_0$, is of the order of $10^{-6}$ A/cm\textsuperscript{2}, in fair agreements with the former works\textsuperscript{[1,3]}, and that pH-dependence of $\eta$ in e.g. alkaline solutions is small $(\partial\eta/\partial(pH))_b \approx -10$ mV, \textit{i.e.}, decrease in $\eta$ with increase of pH, at 20°C and rather complexed. They\textsuperscript{[7]} have also estimated from their results value of the stoichiometric number, $\nu(r)$, of the rate-determining step\textsuperscript{[8]}, $r$, of this reaction to be two. This indicates that the rate-determining step is discharge of hydrogen ion, H$^+$, associated with Brönsted base, H$_2$O or OH$^-$, (slow discharge mechanism) \textit{i.e.},

\[
\text{H}^+ + \text{e} \rightarrow \text{H(a)}.
\]  

Small magnitudes of pH-dependence of $\eta$ at constant reaction rate as cited above and as reported by Ammar and Awad\textsuperscript{[9]} (−26 mV in the same unit at 25°C) on electrodeposited nickel electrode, however, contradict with this conclusion because pH-dependence of this step is expected to be\textsuperscript{[4,10]} much higher (e.g., −120 mV in dilute alkaline solutions). The above value of $\nu(r)$ was also not very decisive as was pointed out by Horiuti et al.\textsuperscript{[10]}, because value of $i_0$, the exchange current density, needed in obtaining $\nu(r)$, was estimated by extrapolating to $\eta=0$ the Tafel equation assuming its strict linearity in sufficiently a wide range of $\eta$ above ca. 60 mV, which is not sufficiently precisely observed experimentally nor expected theoretically\textsuperscript{[11,12]}. Much higher pH-dependence of $\eta$ was obtained by Frumkin et al.\textsuperscript{[2]}, but this also was not firmly established as criticized\textsuperscript{[10]}. The increase of $\eta$ with time at a constant applied current density as mentioned above, and as reported by many other authors\textsuperscript{[5,6,10]}, was generally accepted as due to dissolution of hydrogen into the electrode metal such as nickel. This view appears quite plausible because cathodically polarized nickel electrode is known to contain an appreciable amount of hydrogen\textsuperscript{[13]}, and because the drift becomes very rapid on thin film electrodes prepared by electrodeposition\textsuperscript{[9]} or by vacuum evaporation\textsuperscript{[14,15]}. The effect of hydrogen dissolution into the electrode material upon $\eta$ is, however, unlikely to be expected from the slow discharge mechanism, because such dissolution would not affect

\textsuperscript{*1) Overpotential used here is defined as negative of potential of the test electrode as referred to the reversible hydrogen electrode under the same conditions, \textit{i.e.}, it is positive in cathodic region.
nature of the electrode surface so significantly as to influence the rate of the discharge step.

Electrolytic separation factor, $S$, of deuterium has been studied as one of the criteria of the mechanism. The value of $S$ for nickel is $ca. 7$ as have been reported by various authors$^{19-20}$, and Horiuti et al.$^{19}$ attributed this value from theoretical considerations to the catalytic mechanism, where the rate is governed by the step,

$$2\text{H(a)} \rightarrow \text{H}_2. \quad (2)$$

The greatest opposition$^{5,21-23}$ against the catalytic mechanism on nickel hydrogen electrode was the difficulty in interpreting the Tafel $b$-value ($\sim 120 \text{ mV}$), as was firstly encountered by Tafel$^{9}$, but Horiuti et al.$^{19,13}$ were able to overcome this difficulty on the basis of existence of repulsive interactions among H(a)'s on the electrode surface. The increase in $\eta$ with time as mentioned above can easily be explained on the basis of the catalytic mechanism, because dissolution of hydrogen into the electrode material implies that activity of H(a), which determines the reaction rate in this mechanism, does not attain its steady state value until the diffusion of hydrogen into the electrode is practically ceased after a prolonged time.

Recently, further evidences in favour of the catalytic mechanism have been demonstrated in this Institute. Thus, Matsuda and Ohmori$^{16,17}$ have observed, after careful eliminations of ohmic and concentration overpotentials by a transient method, very small pH-dependence of $\eta$ on evaporated nickel film hydrogen electrode$^{16}$ in alkaline solutions higher than $10^{-1} \text{ N}$ ($\equiv -5 \text{ mV}$), and large values of differential capacity of the electrode$^{10}$, which may undoubtedly be attributed to an accumulation of an appreciable amount of hydrogen intermediate, probably H(a), on the electrode surface with increasing $\eta$, which supports further the catalytic mechanism. Kita$^{10}$ has actually observed saturation current density, $i_s$, predicted by the catalytic mechanism at sufficiently large $\eta$, where the electrode surface is completely covered with H(a). He used the galvanostatic pulse method to eliminate ohmic and concentration overpotentials and to reduce heating effect to an insignificant extent, and found $i_s$ at $ca. 10^2 \text{ A/cm}^2$ in alkaline solutions, which agrees well with the value theoretically predicted$^{19}$ basing on the repulsive interactions among H(a)'s mentioned above.

These investigations rendered it increasingly likely that the catalytic mechanism is valid on nickel hydrogen electrode. Some disagreements may, however, still exist mainly on the experimental results, which were not always in sufficient agreement among various authors. At this position, it seems very desirable to attack the problem from different experimental point of view.
In their former work\textsuperscript{25}, the present authors have conducted exchange reactions between pure deuterium and light water on platinum in acidic solutions. In that work, exchange reaction rates as well as compositions of gaseous hydrogen after the exchange were observed, from which mechanism of the hydrogen electrode reaction was inferred. Thus, if the slow discharge mechanism is operative, \textit{i.e.}, the rate of hydrogen electrode reaction is governed by the step (1), the intermediate, H(a), must be in quasi-equilibrium with gaseous hydrogen throughout the course of exchange, and hence the hydrogen after the exchange must practically be in equilibrium with respect to the reaction,

\[ \text{P}_2 + \text{D}_2 = 2\text{PD}, \]  

where P and D are light hydrogen and deuterium atoms respectively\textsuperscript{*).} Therefore, the degree of equilibration, \( \rho \), defined by,

\[ \rho = \frac{P_{PD}}{P_{PD,eq}}, \]  

where \( P_{PD} \) is the partial pressure of PD in the sample gas directly after the exchange and \( P_{PD,eq} \), that when the same gas (at a definite deuterium concentration in atomic fraction, \( D \)) is brought to equilibrium with respect to reaction (3) subsequently, should be unity. If, on the other hand, either the catalytic or the electrochemical mechanism, respectively with the rate-determining step (2) or,

\[ \text{H}_2(a) + e \rightarrow \text{H}_2, \]  

where \( \text{H}_2^+(a) \) is an adsorbed hydrogen molecule-ion, is operative, the intermediate H(a) or \( \text{H}_2^+(a) \) is in quasi-equilibrium with \( \text{H}^+ \) (associated with the Brönsted base) in the solution, where the deuterium content is kept virtually zero, or the intermediate is composed of protium only, and hence practically only \( \text{P}_2 \), but not PD, replaces \( \text{D}_2 \). The value of \( \rho \) must therefore be zero in these cases. This method, therefore, has an advantage over usual methods such as observations of Tafel lines, in the point that it provides a possibility to distinguish between the slow discharge and the dual mechanisms, without assuming \textit{e.g.} the value of \( \alpha \), the transfer coefficient: the dual mechanism of hydrogen electrode reaction was put forward by Horiuti \textit{et al.}\textsuperscript{18,30} and termed by Walton and Wolfenden\textsuperscript{19} as an alternative operation of the catalytic or the electrochemical mechanism, depending on experimental conditions and electrode material used.

\textsuperscript{*} H is used for hydrogen atom without distinguishing between P and D.

\textsuperscript{**} Step (5) covers here the rate-determining step, \( \text{H}^+ + \text{H}(a) + e \rightarrow \text{H}_2 \), of the ion+atom desorption mechanism.
On platinum catalyst, they could conclude\textsuperscript{25} the electrochemical mechanism to be operative at the equilibrium potential from the experimental facts that $\rho = 0$ and that $i_0$ depends significantly on pH. The present work is concerned with application of this method to nickel, and to elucidate mechanism of the hydrogen electrode reaction directly.

II. Experimental

\textbf{Apparatus:} Reaction vessel with $5\sim 7$ breakable joints was constructed of borosilicate glass “Hario” of Shibata & Co., Tokyo. Nickel wire (0.1 mm diameter) used as the catalyst was obtained from Johnson Matthey & Co., London (99.999\%). Water was obtained by four time distillations of deionized water, with KOH and KMnO$_4$ added in the first still. Solution was prepared from special grade NaOH from Junsei Pure Chemicals Co., Tokyo. The solution (30~50 cc) was previously degassed carefully by vacuum operations. Deuterium (>99.6\% from Stuart Oxygen Co., San Francisco) was purified by filtering through a heated palladium thimble. Further details were similar to those reported previously\textsuperscript{25}.

\textbf{Procedure:} The reaction vessel (~100 cc) with nickel wire catalyst (apparent area 630 cm$^2$) in it was cleaned with hot 1~2 N NaOH for at least overnight, and rinsed repeatedly with hot water obtained above. This, together with the solution container, was connected to vacuum line via traps in liquid nitrogen baths. After drying the vessel by evacuation, nickel was heated in 5 cmHg D$_2$ at 400°C for 2 hr and then degassed at 450°C for 5~10 hr down to $10^{-5}$ mmHg. The whole system was sealed off from the vacuum line, solution introduced into the reaction vessel by opening the breakable joint of the solution container and then the container removed. Further details and procedures of introduction of D$_2$ and of sampling were similar to those reported\textsuperscript{25}. The exchange reaction was usually conducted at 0~50°C with 20 ± 3 cmHg of total hydrogen pressure (initial deuterium pressure), or at 30.0 ± 0.1°C with 2~80 cmHg in the case of observations of pressure effect. The shaking was 170/min over 5 cm amplitude.

\textbf{Analysis:} Sample gases were analyzed by the thermal conductivity method\textsuperscript{27} for both the atomic fraction of deuterium, $D$, and the degree of equilibration, $\rho$, using standard $P_2 + D_2$ mixture gases and those equilibrated by passing over a hot nickel wire. It is implied in this method that the isotopic effects, or hence variations in the equilibrium constant $K$ of reaction (3) with temperature, were neglected (see Discussion section). Solutions were analyzed after the experiments by titrations or the pH’s determined by a pH-meter.
III. Results

A. Blank Tests

These were made (a) with a similar reaction vessel without nickel catalyst using pure D₂ and solution and (b) with similar arrangements but with 1:1 mixture of P₂ and D₂ instead of pure D₂. In (a), with 37 cc of 0.5 N NaOH and 40 cc of D₂ at 15 cmHg at 0°C, the D-value after the reaction at 47.6°C for 20.5 hr was more than 99%. In (b), with 0.1 N NaOH and the mixture gas pressure 20 cmHg, reaction at 50°C for 16.5 hr did not result in noticeable decrease in \( D (D_0 = 0.53) \), in agreement with (a) above, nor any increase in \( \rho \) from the initial value zero*).

B. Dependence of \( i_o \) on Hydrogen Pressure

Experiments were carried out on observations of exchange rate, given here in terms of exchange current density, \( i_o \), defined by Eq. (6) below, with various initial deuterium pressures, \( P_{D_2,0}'s \), and various pH's (7~13) at 30°C.

\[
D = D_0 \exp \left( -i_o \frac{At}{2nF} \right),
\]

\[ (6) \]

![Graph](image)

Fig. 1. Pressure dependence of exchange current density at 30°C. Solution (NaOH); O; Run 1, pH=13.0, X; Run 2, pH=9.4. \( \beta = \frac{\Delta \log i_o}{\Delta \log P_{H_2}} \). Numbers on Figure indicate order of experiment.

*) A long constriction (3 cm) was used in this case in order to avoid effect on the equilibration of the mixture gas (cf. ref. 28) of hot glass wall during the sealing.
where \( D_0 \) is the initial deuterium concentration in atomic fraction (equal to unity here), \( \Lambda \) the apparent surface area of the catalyst, \( n \) the total number of moles of hydrogen in the gas phase and \( t \) the time. The order of reaction, or the value of \( \beta \) in,

\[
i_0 = c \cdot P_{H_2}^\beta, \tag{7}
\]

where \( c \) is a constant and \( P_{H_2} = P_{v} + P_{vd} + P_{v} \), was found to be ca. 0.4 at pressures above 20 cmHg, practically independent of pH. At lower pressures (2~10 cmHg), \( \beta \) was higher than this, being ca. 0.8. These are shown in Fig. 1 and the data listed in Table 1.

**TABLE 1.** Pressure dependence of exchange current density and value of \( \rho^{(b)} \)

(a) Run 1, \( A = 630 \text{ cm}^2 \), pH = 13.0, 30.0°C

<table>
<thead>
<tr>
<th>No.</th>
<th>( P_{H_2} ) (atm)</th>
<th>( V_{H_2} ) (cc)</th>
<th>( \log P_{H_2} ) (atm)</th>
<th>( n ) (m mol)</th>
<th>( t ) (sec) ( \times 10^{4} )</th>
<th>( D )</th>
<th>( i_{0} ) ( \times 10^{-6} )</th>
<th>( \rho ) ( \times 10^{-4} )</th>
<th>( i_{0,v} ) ( \times 10^{-4} )</th>
<th>( i_{0,c} ) ( \times 10^{-4} )</th>
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<tbody>
<tr>
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<tr>
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<td>0.55</td>
<td>4.6</td>
<td>0.81</td>
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<tr>
<td>4</td>
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<td>0.84</td>
<td></td>
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</table>

(b) Run 2, \( A = 630 \text{ cm}^2 \), pH = 9.4, 30.0°C

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<tr>
<th>No.</th>
<th>( P_{H_2} ) (atm)</th>
<th>( V_{H_2} ) (cc)</th>
<th>( \log P_{H_2} ) (atm)</th>
<th>( n ) (m mol)</th>
<th>( t ) (sec) ( \times 10^{4} )</th>
<th>( D )</th>
<th>( i_{0} ) ( \times 10^{-6} )</th>
<th>( \rho ) ( \times 10^{-4} )</th>
<th>( i_{0,v} ) ( \times 10^{-4} )</th>
<th>( i_{0,c} ) ( \times 10^{-4} )</th>
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<td>0.76</td>
<td>1.3</td>
<td>0.57</td>
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*) \( P_{H_2} \) is total pressure of hydrogen in cmHg at 30°C (corrected for vapour pressure of water), \( V_{H_2} \) the volume in cc and \( n \) the number of moles of hydrogen in gas phase. \( i_{0,v} \) and \( i_{0,c} \) are exchange current densities for RIDEAL-ELEY and catalytic mechanisms in A/cm² (see text and Eqs. (24) and (25)). \( i_{0} (= i_{0,v} + i_{0,c}) \) is the total exchange current density obtained from Eq. (6).

**C. Dependence of \( i_{0} \) on Temperature**

Experiments at 20 cmHg of \( P_{v} \) were conducted at 0~50°C in various concentrations of NaOH. The **ARRHENIUS** plot of log \( i_{0} \) vs. \( 1/T \),
**Exchange Reaction Between Deuterium and Water on Nickel in Alkaline Solutions**

### TABLE 2. Temperature dependence of exchange current density and value of \( \rho^* \)

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°K)</th>
<th>( P_{\text{H}_2} )</th>
<th>( n ) (m mol)</th>
<th>( t ) (sec) (10^4)</th>
<th>( D )</th>
<th>( i_e^* ) (10^4)</th>
<th>( \rho )</th>
<th>( i_{e,R}^* ) (10^4)</th>
<th>( i_{e,C}^* ) (10^4)</th>
<th>( i_o ) (10^4)</th>
<th>( i_{o,R} ) (10^4)</th>
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<td>5.3^4</td>
<td>3.8^4</td>
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<td>(c) Run 5, pH = 12.9</td>
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<td></td>
<td></td>
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</tr>
<tr>
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<td>284.0</td>
<td>15.8</td>
<td>0.60^4</td>
<td>—</td>
<td>0.75^4</td>
<td>(1.6^4)</td>
<td></td>
<td>0.84</td>
<td>(1.2^7)</td>
<td>(0.36)</td>
<td>(1.4^9)</td>
<td>(0.39)</td>
</tr>
<tr>
<td>2</td>
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<td>20.3</td>
<td>0.68^4</td>
<td>0.738</td>
<td>0.69^4</td>
<td>10.3</td>
<td></td>
<td>0.79</td>
<td>7.8^2</td>
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<td>0.64^4</td>
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<td>0.87</td>
<td>0.89</td>
<td></td>
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<td>0.71</td>
<td>0.18</td>
<td>0.96</td>
<td>0.78</td>
</tr>
</tbody>
</table>

\( \rho^* \) Due to failure of direct determination, average value of the others was used.  
\( **^* \) Approximate value obtained by interpolation from other data in Arrhenius plot. 
\( **^* \) Due to failure of direct determination, average value of the others was used.

\( A = 630 \text{ cm}^2, P_{\text{H}_2} \) is in cmHg at temperature specified (corrected for vapour pressure of water). \( i_{e,R}^* \) and \( i_{e,C}^* \) are exchange current densities in A/cm^2 for RIDDELEYE and catalytic mechanisms obtained directly from experimental results and \( i_e^* \) is the total exchange current density obtained from Eq. (6). \( i_{o,R}, i_{o,C} \) and \( i_o \) are those reduced to \( P_{\text{H}_2} = 20 \text{ cmHg} \) (see text and Eqs. (24) and (25)). For other notations, see Table 1.

where \( T \) is the absolute temperature, generally established its linearity as shown in Fig. 2. The results obtained at pressures with minor shifts from 20 cmHg (±3 cmHg) were reduced to the latter pressure by means of Eq. (7) with \( \beta = 0.4 \), which was observed in this pressure region. Extrapolations to 1 atm* were obtained by multiplying the \( i_e^* \)-value at 20 cmHg with the factor 1.71. At 1 atm and 30°C, it amounts ca. \( 1 \times 10^{-5} \text{ A/cm}^2 \).
The heat of activation, $\Delta H^*$, defined by,

$$\Delta H^* = -R \ln \frac{i_0}{d (1/T)}, \tag{8}$$

where $R$ is the gas constant, was found at ca. 9 kcal/mole, without appreciable dependence on pH. The data used in plotting Eq. (8) are listed in Table 2.

**D. Value of $\rho$**

In contrast to the former works on platinum in acidic solutions, the value of $\rho$ on nickel was always larger than zero, being 0.7–0.9, i.e., the hydrogen gas after the exchange reaction was partially equilibrated with respect to reaction (3). The values of $\rho$ did not show any systematic variations with pH, $P_{H_2}$ or temperature, though they differed somewhat among different series of experiments, as seen in Tables 1 and 2.

Fig. 2. Arrhenius plots of exchange current densities at 20 cmHg in various solutions.

○; Run 3, pH=11, $\Delta H^* = 9.2$ kcal/mole, ●; Run 4, pH=7.4, $\Delta H^* = 8.3$ kcal/mole, △; Run 5, pH=12.9, $\Delta H^* = 9.0$ kcal/mole.

avoided in order to minimize possible systematic errors due to an uncertainty likely to be involved in this $\beta$ -value (see Discussion section).
IV. Discussion

A. Blank Tests

It is well known\(^{29-31}\) that exchange reaction between deuterium and water takes place without intentional addition of catalyst to an appreciable extent in alkaline solutions, but negligibly in neutral and acidic solutions. From known value of specific rate of the exchange\(^{31}\) \((k\approx 3 \times 10^{-2}/\text{hr} \text{ in } 0.5 \text{ N NaOH at } 100^\circ\text{C})\) and the heat of activation \((\approx 25 \text{ kcal/mole})\), \(k\) at 47.6°C in 0.5 N NaOH can be estimated to be ca. 1 \times 10^{-4}/\text{hr}. Using this value and volumes of deuterium and solutions (40 and 37 cc respectively in blank test (a)), the expected \(D\)-value after 20.5 hr is approximately obtained from the equation,

\[
k = \frac{2.3}{\tau} \frac{V_{\text{D,0}}}{V_{\text{oln}}} \log \frac{D_0}{D},
\]

where \(D_0\) is approximated as 100%, to be \(D = 99.8\%\), which confirms the result of blank test (a). According to this result and that of the blank test (b), contributions of alkaline solutions (less than 0.1 N) or also of the glass wall to the exchange reaction or to the equilibration reaction are totally negligible under the experimental conditions here employed, thus confirming that the observed results are purely relevant to heterogeneous reactions on nickel catalyst.

B. Absence of Diffusion Control

The observed value of \(\Delta H^*\) (ca. 9 kcal/mole, which is well comparable with literature values\(^{5,39}\) of \(\Delta H^*\) for the nickel hydrogen electrode reaction) excludes any possibility of rate-determining diffusion of \(H^+\) associated with the Brönsted base or of \(H_2\) dissolved in the solution, as both of these cases should result\(^{5,32}\) in ca. 3.5 kcal/mole for the value. Further, resultant \(\rho\)-value should be unity in the former case or zero in the latter case, both of which disagree with the experimental results.

C. Operation of RIDEAL-ELEY Mechanism

As reported above (Tables 1 and 2, see also Fig. 5 later), the exchange current density, \(i_e\), and consequently also the heat of activation, \(\Delta H^*\), were independent of pH of the solution \((7 \sim 13)\) within the experimental error: the ratio of \(i_e\) at pH=7 to that at pH=13 was about 2 at most. These facts indicate clearly that the discharge step (Eq. (1)) is not controlling, nor the electrochemical step (Eq. (5)) contributing to the exchange rate, i.e., the catalytic mechanism must be operative on nickel.

As has been argued in the Introduction, rapid discharge step followed by rate-determining recombination step (Eq. (2)) should yield \(\rho = 0\), which however contradicts the experimental results, \(0 < \rho < 1\) (Tables 1 and 2). The case where
the rates of the discharge and the recombination steps are comparable, which
seems to interpret the intermediate $\rho$-values in a first glance, is also excluded
since, if then, rate of the discharge step relative to that of the recombination
step should vary with $\mathrm{pH}$, resulting in a significant variation in $\rho$-value with
$\mathrm{pH}$, which contradicts the experimental results.

At this position, it is inevitable to accept an equilibration reaction which
is concurrently taking place independent of, and in parallel with, the rate-
determining recombination step. Many investigations have hitherto been re-
ported in literatures on exchange reaction between $\mathrm{P}_2$ and $\mathrm{D}_2$ or on ortho-para
hydrogen conversion reaction in gas phase. In these works, two mechanisms
have been proposed\textsuperscript{33}; one was the BONHOEFFER-FARKAS mechaism and the other
the RIDEAL-ELEY mechanism. It is not necessary here to take the BONHOEFFER-
FARKAS mechanism\textsuperscript{34}, $\mathrm{H}_2 \rightleftharpoons 2\mathrm{H(a)}$, into consideration, because it is nothing but
the recombination step included in the catalytic mechanism being treated.

The RIDEAL-ELEY mechanism\textsuperscript{35,36},

\[ \mathrm{H}_2 + \mathrm{H(a)} \rightarrow \mathrm{H(a)} + \mathrm{H}_2, \quad (9) \]

is now taken into consideration as the possibility\textsuperscript{*}). This does not provide any
possible path for the hydrogen evolution reaction but contributes to the equili-
bration between $\mathrm{P}_2$ and $\mathrm{D}_2$, and to the isotopic exchange reaction if it operates
in parallel with the rate-determining step. It follows then that the RIDEAL-
ELEY mechanism is operating as a “by-pass” to the rate-determining recombi-
nation step in this exchange reaction on nickel in alkaline solutions, contributing
to the equilibration of gaseous hydrogen as well. Separation of rates of the
RIDEAL-ELEY and the catalytic mechanisms, and interpretation of intermediate

\textsuperscript{*}) It has been tacitly assumed here that the catalyst surface is homogeneous, However,
one might alternatively attribute the experimental aspect in question to the following
possibilliy caused by heterogeneity of the surface. Admitted that the catalytic mechanism
is operative on major portion of the catalyst surface, it is not impossible that a small
fraction of the surface behaves as active centers, which extraordinarily accelerate the
equilibration among hydrogen isotopes in the gas phase through the recombination step,
$\mathrm{H}_2 \rightleftharpoons 2\mathrm{H^*(a)}$, to bring about the observed result $\rho>0$, where $\mathrm{H^*(a)}$ is a special kind of
$\mathrm{H(a)}$ adsorbed on such an active center. The hydrogen electrode reaction on the active
centers should then follow the slow discharge mechanism, since otherwise the recombi-
nation step there could not shift $\rho$ toward unity; $\mathrm{H^*(a)}$ then consisting practically of pro-
tium. The active centers contribute now to the exchange reaction as well through the
slow discharge mechanism. The contribution must however be insignificant inasmuch as
the $\mathrm{pH}$-effect on the exchange reaction, which varies the rate of slow discharge mecha-
nism, is quite imperceptible. This model can, however, be concluded improbable from
the following reasons: (a). It follows from this alternative model that the exchange rate
here observed must be comparable with literature values of exchange current density of
rho-values observed based on this assumption will be treated below.

D. Separation of RIDEAL-ELEY and Catalytic Mechanisms

The reaction scheme to be considered now is,

\[ \text{H}_2 + \text{H(a)} \xrightarrow{v_R} \text{H(a)} + \text{H}_2 , \]  
\[ \text{H}_2 \xrightarrow{v_0} 2\text{H(a)} , \]  
\[ \text{H(a)} \xrightarrow{v_l} \text{H}^+ + e , \]  

where \( v \)'s are unidirectional rates of each specified steps under the experimental conditions. One can assume safely that \( v_l \geq v_R \) or \( v_0 \), based on the above experimental results of no pH-dependence of \( i_o \), and consequently that surface coverage with \( \text{D(a)} \) remains zero, i.e., the intermediate is composed of \( \text{P(a)} \) only, throughout the exchange reaction, which is secured by sufficiently a large number of light water compared with that of deuterium gas under the conditions employed. One can express then, neglecting the isotopic effects,

\[
\frac{dP_{D_i}}{dt} = -(v_R + v_C) P_D, 
\]

or,

\[
P_{D_i} = P_{D_i, 0} \exp \left\{ -(v_R + v_C) t \right\},
\]

\[
\frac{dP_{PD}}{dt} = v_R P_{D_i} \frac{v_R}{2} P_{PD} - v_C P_{PD},
\]

and

\[
\frac{dP_{P_t}}{dt} = \frac{v_R}{2} P_{PD} - v_C P_{P_t} + v_C P_H,
\]

where \( P \)'s are partial pressures of species specified in the gas phase at time nickel hydrogen electrode reaction under similar experimental conditions because of the ignorable contribution from the active centers to the hydrogen electrode reaction. The observed value of \( i_o \) was however considerably larger than the literature value (by 3~10 times). This conclusion rests on the assumption that the catalyst used in the present experiment is nearly identical with the electrodes used for the observations of \( i_o \) in literatures. (b). The recombination on the active centers must be very rapid as compared with that of the catalytic mechanism on major portion of the catalyst, insofar as \( p \) is shifted close to unity as observed. It follows that the activation energy on the active centers is appreciably smaller than that on the major portion of the catalyst. This conclusion is exact, provided that both the active centers and the major portion are well covered by hydrogen atoms as is probably the case. If at all, the rate of equilibration through the recombination on active centers should vary with temperature relative to the rate of the exchange reaction effected by the catalytic mechanism on the major portion of the catalyst, or \( p \) should decrease with increase of temperature in contradiction to the present experimental results (Table 2).
$t$ and $P_{H_2}$ is the total hydrogen pressure. Eqs. (14) and (15) yield,
\begin{equation}
\frac{dP_{PD}}{dt} = v_R P_{n_i,0} \exp \left\{ -(v_R + v_C) \right\} \left\{ \frac{v_R}{2} + v_C \right\} P_{PD} .
\end{equation}
Solution of Eq. (17) with the boundary condition that $P_{PD} = 0$ at $t = 0$ is,
\begin{equation}
P_{PD} = 2 P_{n_i,0} \left[ \exp \left\{ -(\frac{v_R}{2} + v_C) t \right\} - \exp \left\{ -(v_R + v_C) t \right\} \right] ,
\end{equation}
or in words, $P_{PD} = 0$ at $t = 0$ and $t = \infty$, but it remains zero at $t = t$ if $v_R \ll v_C$.

Variation of $D$, $D = (P_{n_i} + \frac{1}{2} P_{PD}) / P_{H_2}$, with time is, on the other hand,
\begin{equation}
\frac{dD}{dt} = \frac{1}{P_{n_i}} \left\{ \frac{dP_{n_i}}{dt} + \frac{1}{2} \frac{dP_{PD}}{dt} \right\} ,
\end{equation}
or substituting Eqs. (13) and (15) and solving,
\begin{equation}
D = D_0 \exp \left\{ -(\frac{v_R}{2} + v_C) t \right\} .
\end{equation}

Using Eq. (20), Eq. (18) yields,
\begin{equation}
P_{PD} = 2 P_{n_i,0} \frac{D}{D_0} \left[ 1 - \exp \left\{ -\frac{v_R}{2} t \right\} \right] ,
\end{equation}
or,
\begin{equation}
P_{PD} = 2 P_{n_i,0} \frac{D}{D_0} \left[ 1 - \frac{D}{D_0} \exp (v_C t) \right] .
\end{equation}

The equilibrium partial pressure of PD, $P_{PD,eq}$, at a definite $D$-value, where the equilibrium constant $K$ of reaction (3) is taken as four in accordance with the neglect of the isotopic effects, is obtained using the relation that $P_{n_i} + P_{PD} + P_{H_2} = P_{H_2}$, and expressions for $D$ and $K$ as,
\begin{equation}
P_{PD,eq} = 2 P_{H_2} D (1 - D) .
\end{equation}
Therefore, the expression for $\rho$ is obtained from Eqs. (21) and (22a) as,
\begin{equation}
\rho = \frac{P_{PD}}{P_{PD,eq}} = \frac{P_{n_i,0}}{D_0} \left[ 1 - \exp \left\{ -\frac{v_R}{2} t \right\} \right] / P_{H_2} (1 - D) ,
\end{equation}
or,
\begin{equation}
\rho = \frac{P_{n_i,0}}{D_0} \left[ 1 - \frac{D}{D_0} \exp (v_C t) \right] / P_{H_2} (1 - D) .
\end{equation}

According to the above boundary condition that $P_{PD} = 0$ at $t = 0$, however, $P_{n_i,0} / P_{H_2} = D_0$. Using this and solving Eqs. (23) for $v_R$ and $v_C$, one obtains finally,
\begin{equation}
P_{PD,eq} = P_{H_2} \frac{K}{4 - K} \left\{ \sqrt{1 + 4 \frac{4 - K}{K} D (1 - D)} - 1 \right\} .
\end{equation}
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\[ v_R = -\frac{4.6}{t} \log \{1 - \rho (1 - D)\} \]  
\[ v_C = \frac{2.3}{t} \log \frac{D}{D} \{1 - \rho (1 - D)\} \]

(24a)

(24b)

i.e., \( \rho = 0 \) if \( v_R = 0 \), and in the case that \( D_R = 1 \), \( \rho = 1 \) if \( v_C = 0 \), both at \( t = t \), or intermediate \( \rho \)-values (near to unity) obtained in this work are explained by considering an appreciable magnitude of \( v_R \) over that of \( v_C \). Thus, Eqs. (24) allow us to evaluate \( v_R \) and \( v_C \) individually from the experimental values of \( D \) and \( \rho \) observed at \( t \).

In actual presentations of the experimental results, \( v_R \) and \( v_C \) were both reduced to their respective exchange current densities, \( i_{o,R} \) and \( i_{o,C} \), assigned from comparison of Eq. (6) with Eq. (20) as,

\[ i_{o,R} = nFv_R/A, \quad \text{and} \quad i_{o,C} = 2nFv_C/A \]

(25a, b)

i.e., the total exchange current density, \( i_o \), which is also obtained from Eq. (6) independent of \( \rho \)-values, is,

\[ i_o = \frac{2nF}{A} \left( \frac{v_R}{2} + v_C \right) = i_{o,R} + i_{o,C} \]

(26)

E. Characters of \( i_{o,R} \) and \( i_{o,C} \), the rates of RIDEAL-ELEY and Catalytic Mechanisms

The results of exchange reactions listed in Tables 1 and 2 were now analyzed by Eqs. (24) and (25). As shown in Fig. 3, both the \( \log i_{o,R} \) and \( \log i_{o,C} \) were not linear functions of \( \log P_R \), ranging from 2 to 80 cmHg. At high pressures, however, they assumed approximate lineairities, and the slopes were roughly 0.5 for \( \beta_R = (\partial \log i_{o,R}/\partial \log P_R) \) and 0.25 for \( \beta_C = (\partial \log i_{o,C}/\partial \log P_R) \). The slopes became higher at lower pressures.

Arrhenius plots of the individual rates satisfied the lineairities acceptably, as shown in Fig. 4. In making these plots, \( i_{o,R} \) and \( i_{o,C} \) at pressures with minor shifts from 20 cmHg were reduced to the latter reference pressure using the above experimental values of \( \beta_R \) and \( \beta_C \). The heats of activation, \( \Delta H_R^* \) and \( \Delta H_C^* \) of the \( i_{o,R} \) and \( i_{o,C} \) were approximately 8.3 and 10.1 kcal/mole respectively. The difference between them was rather small, and hence the Arrhenius plot of the total rate, \( i_o \), roughly satisfied the linearity (Fig. 2).

As can be seen in Tables 1 and 2 or from Figs. 3, 4 and 5, \( i_{o,R} \) was 3~5 times lager than \( i_{o,C} \) at 20 cmHg hydrogen pressure* or somewhat more at 1 atm. This means therefore that a larger portion of the exchange rate is due to combination of the rapid discharge step and the rate-determining

* As is easily seen from Eqs. (25a, b), this means that \( v_R \) is roughly ten times larger than \( v_C \).
RIDAL-ELEY mechanism, and a lesser portion to the catalytic mechanism. No pH-dependence of \( i_{o,R} \) (Fig. 5) is in harmony with the above assumption of the RIDAL-ELEY mechanism, which interprets, besides, why the total exchange current density, \( i_o \), observed (after extrapolating to 1 atm from 20 cmHg, or at 1 atm in Fig. 1, ca. \( 1 \times 10^{-5} \) A/cm\(^2\)) is much higher than literature values\(^1\) of \( i_o \) on nickel hydrogen electrode (\( 1 \sim 3 \times 10^{-6} \) A/cm\(^2\), but \( 1 \times 10^{-5} \) A/cm by MAKRIDES\(^3\)).

**E. Mechanism of Hydrogen Electrode Reaction on Nickel in Alkaline Solutions**

It is evident that the RIDAL-ELEY mechanism does not provide any path for the hydrogen evolution reaction, and consequently the catalytic mechanism must be applicable for this reaction. As is seen in Fig. 5, \( i_{o,c} \) was again practically independent of pH of the solution, which indicates that the above

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**Fig. 3.** Pressure dependences of rates of RIDAL-ELEY \( i_{o,R} \) and catalytic \( i_{o,c} \) mechanisms at 30°C (from analysis of data in Fig. 1 or Table 1 by Eqs. (24) and (25)). Solution (NaOH): ○ Run 1, pH=13.0, △ Run 2, pH=9.4. Empty symbols for RIDAL-ELEY and filled symbols for catalytic mechanism. \( \beta_R = (\partial \log i_{o,R} / \partial \log P_{H_2})T \) and \( \beta_c = (\partial \log i_{o,c} / \partial \log P_{H_2})T \)

---
assumption of the catalytic mechanism was correct. The value of \( i_{o,c} \) at 1 atm and 30°C \((2 \times 10^{-6} \text{ A/cm}^2\), cf. Fig. 3) is in good agreement with the literature values on nickel hydrogen electrode mentioned above.

Pressure dependence of exchange current density when the reaction obeys the catalytic mechanism has been treated theoretically by HORIUTI and SUZUKI as summarized briefly below. The pressure dependence, \( \beta_c \), of rate of the catalytic mechanism is given by e.g., that of the forward unidirectional rate, \( i \), of the rate-determining recombination step, Eq. (2), at equilibrium. Rewriting this,

\[
\beta_c = \left( \frac{\partial \ln i}{\partial \ln P_H} \right)_{T,eq} = \left( \frac{\partial \ln \tilde{i}}{\partial \mu^H_{eq}} \right)_{T,eq} \left( \frac{\partial \mu^H_{eq}}{\partial \ln P_H} \right)_{T,eq}
\]

where \( \mu^H_{eq} \) is the chemical potential of H(a). The first differential coefficient is obtained using the relation which holds generally for the catalytic mechanism.

**Fig. 4.** ARRHENIUS plots of rates of RIDEAL-ELEY \((i_{o,k})\) and catalytic \((i_{o,c})\) mechanisms at 20 cmHg (from analysis of data in Fig. 2 or Table 2 by Eqs. (24) and (25)).
Solution (NaOH); ○ ●; Run 3, pH=11, △ △; Run 4, pH=7.4, □ ■; Run 5, pH=12.9
Empty symbols for RIDEAL-ELEY and filled symbols for catalytic mechanism.
because of quasi-equilibrium of the step (1),

$$\mu_{H^+}^{(a)} = \mu_{H^+}^e + \mu_{e^+}^e,$$

where \( \mu \)'s are chemical potentials of each species specified. \( \mu^e \) is expressed by its value at equilibrium, \( \mu_{e^+}^{eq} \), and the overpotential, \( \eta \), as \( \mu^e = \mu_{e^+}^{eq} + F \eta^e \). It follows then,

$$\mu_{H^+}^{(a)} = \mu_{H^+}^e + \mu_{e^+}^{eq} + F \eta,$$

where \( F \) is FARADAY, or in a given solution,

$$\left( \frac{\partial \mu_{H^+}^{(a)}}{\partial \eta} \right) \mu_{H^+}^e = F,$$

and hence,

---

**Fig. 5.** Dependences on pH of rates of total \( (i_{0, tot}, \text{total}) \), RIDEAL-ELEY \( (i_{0, R}) \) or catalytic \( (i_{0, C}) \) mechanism at 30°C, and respective heats of activation, \( \Delta H_{\text{total}}^a, \Delta H_{R}^a \) and \( \Delta H_{C}^a \) at 20 cmHg \( P_{H^+} \).

\( \times \); for total, empty symbols for RIDEAL-ELEY and filled symbols for catalytic mechanism.

\( ^o \) Cf. footnote of p. 35

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\[
\left( \frac{\partial \ln i}{\partial \mu_{H(a)}} \right)_{T, \text{eq}} = \frac{1}{F} \left( \frac{\partial \ln i}{\partial \eta} \right)_{T},
\]
or using the definition of the TAFEL constant \( \alpha \),

\[
\alpha = \frac{RT}{F} \left( \frac{\partial \ln i}{\partial \eta} \right)_{T},
\]

\[
\left( \frac{\partial \ln i}{\partial \mu_{H(a)}} \right)_{T, \text{eq}} = \frac{\alpha}{RT},
\]

(28)

Secondly, using the following relation which holds at overall equilibrium,

\[
2\mu_{H(a)} = \mu_{H^2} = \mu_{D^2} + RT \ln P_{H^2},
\]

where \( \mu_{H^2} \) is the chemical potential of \( H_2 \) at the standard state \( (P_{H^2} = 1) \), or \( (\partial \mu_{H(a)}/\partial \ln P_{H})_{\text{eq}} = RT/2 \) which is the second differential coefficient in Eq. (27).

From this and Eqs. (27) and (28) one has \( \beta_0 = \alpha/2 \).

The value of \( \alpha \) can be taken as \( 1/2 \) from experimental results\(^{6,9,10} \) and from theoretical calculations\(^{12,13} \) under ordinary conditions. Thus, one can expect \( 1/4 \) approximately for \( \beta_0 \). The observed value of \( \beta_0 \) is in agreement with this, supporting the above conclusion that the catalytic mechanism is applicable on nickel hydrogen electrode reaction.

\( \beta_0 \) became much higher at lower pressures, however (Fig. 3). This increase is in harmony qualitatively with theoretical expectations\(^{12,13} \), that \( \alpha \) should increase with decrease of the surface coverage with \( H(a) \) at lower hydrogen pressures.

G. Isotopic Effects

Throughout the analysis in this paper, the isotopic difference between P and D was at all neglected. Though it is difficult to estimate possible errors due to this neglect, the followings might be argued. It has been derived by Horiiuti and Fukuda\(^{39} \) that the following relation generally holds with good accuracy,

\[
\frac{S(s \rightarrow g)}{S(g \rightarrow s)} = K_p,
\]

(29)

where \( S(s \rightarrow g) \) is the separation factor between P and D in the direction from solution to gas (i.e., the electrolytic separation factor in usual sense), \( S(g \rightarrow s) \) that of the reverse direction and \( K_p \) the partition coefficient between the two phases. On nickel, \( S(s \rightarrow g) \approx 7 \) as cited before and \( K_p \) is approximately four\(^{39} \).

The value of \( S(g \rightarrow s) \) is hence two. This indicates that the exchange current density here obtained experimentally with wide range of mixtures of \( P_2 + PD + D_2 \) would represent the actual value to be obtained with protium only with
the ambiguity factor of two, if the exchange reaction is totally controlled by
the catalytic mechanism. However, as the exchange reaction is proceeding to
a large extent through the RIDEAL-ELEY mechanism as concluded above, the
actual figure should be rather different from this value.

In actuality, the isotopic effect seems much smaller than this. If the
effect is significant, the exchange current density through e.g., the catalytic
mechanism must appreciably be different for different D-values, because when
the D-value decreased from unity, larger portions of the unidirectional current
density, \( i_e \), than that expected without taking the isotopic difference into con­
sideration, should be carried by P which has a higher reactivity than D in this
exchange reaction as can be said from the above value of \( S(s \rightarrow g) \) or \( S(g \rightarrow s) \).
Thus, the rate of decrease of D in the gas phase should become smaller than
that expected from a simple exponential decay curve (Eq. (20)) as the exchange
proceeds. In the experiments here reported, the extent of exchange was
chosen randomly, being 90\textendash}10\% in the final D-value, but still no noticable
variations in e.g., \( i_{v,0} \) were observed in plotting log \( i_{v,0} \) vs. log \( P_H \) or \( 1/T \).
According to these results, the isotopic effect seems to be less than the experi­
mental errors (0.1 in log \( i \) unit).

In the evaluation of \( \rho \), the resistance vs. D curve\textsuperscript{31} for \( K=4 \) was used
instead of \( K<4 \) obtainable from Eq. (22b). This was done because \( K=3.3 \)
(the value at room temperature) gives larger values of \( \rho \) and hence larger
values of \( i_{v,R} \) than with \( K=4 \) by roughly 6\% under the experimental con­
ditions. Then, by use of Eq. (22b) for \( P_{V,D,eq} \) in Eqs. (23), it is numerically
shown that the value \( K=3.3 \) results in smaller values of \( i_{v,R} \) by about 10\%,
cancelling the former effect in part. Other amendments which should also be
made with respect to the isotopic effects are those in the starting equations,
(13), (15) and (16), but the following derivation to Eqs. (21) is then too much
involved and is almost impossible to assign appropriate values for factors
representing the individual behaviours of P, PD and Dv.

H. Addition Remark

According to the above analysis, the concurrent occurrence of the RIDEAL-
ELEY mechanism is established on reasonable bases, and in the authors’ opinion,
this is about the first evidence which made a critical distinction between the
BONHOEFFER-FARKAS and the RIDEAL-ELEY mechanism. Further, it is evident
now that in the system here concerned, the rate of the exchange reaction was
determined by combination of both the contributions from the RIDEAL-ELEY and
the catalytic mechanisms. In this system, therefore, determination of exchange
current density of the rate-determining step, which is one of the most important
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parameters in establishing the mechanism, e.g. in the determination of \( \nu(r) \), encounters a serious difficulty, which must be overcome by means of special experimental methods such as developed in this paper. There might be many other reactions, e.g., similar exchange reactions on platinum in pure water\(^{25}\), where a similar difficulty due to side reactions would arise, and at least due considerations must be paid in such cases.

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