Electrochemical Measurement of Tritium and Hydrogen Permeation through Iron Membranes*

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Permeation rates of tritium and hydrogen through iron were measured by the electrochemical method in which an aqueous solution containing $3.7 \times 10^{12}$ Bq/m³ tritium was used as a cathodic electrolyte. Tritium and hydrogen were introduced from one side of a specimen by cathodic polarization with a constant current density, while at the other side of the specimen the permeated tritium and hydrogen were extracted by potentiostatical ionization. Nearly all of the potentiostatic current of the extraction side stands for the ionization of hydrogen, because the concentration of tritium in the cathodic electrolyte is very small. The amount of permeated hydrogen was obtained by integrating the anodic current, and that of tritium was determined by measuring the radioactivity of the electrolyte sampled from the extraction side. The separation factor for permeation obtained under steady state conditions (the ratio of permeation rates of hydrogen to tritium divided by the ratio of the concentration of hydrogen to tritium in the charging electrolyte) is 12 at 288 K. This value is independent of cathodic current density. Diffusion coefficients of tritium ($D_T$) and hydrogen ($D_H$) in iron were determined from the time lag of tritium and hydrogen permeation. For annealed specimens at 286 K, $D_T = 9 \times 10^{-10}$ m²/s and $D_H = 4 \times 10^{-9}$ m²/s, and for 9% cold-worked specimens at 284 K, $D_T = 3 \times 10^{-10}$ m²/s and $D_H = 4 \times 10^{-10}$ m²/s.

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I. Introduction

A safety treatment of the solution and gas containing tritium produced in nuclear fission reactors has been an important problem. Storage containers of tritiated solution and gas must be ensured against leakage of tritium. Furthermore, in order to realize a nuclear fusion reactor, it is essential to know the behavior of tritium dissolved in various metals. In few metals the data on diffusion coefficients, permeation rates and solubilities of tritium have been reported(1).

In the present work, the experimental technique of the electrochemical permeation of tritium in steels was established, and the method was applied to determine the diffusion coefficient and permeation rate of tritium in iron.

II. Electrochemical Permeation Method

An electrochemical permeation method has been used extensively for measurements of diffusion coefficients of hydrogen dissolved in iron around room temperature(2)(3). The principle of the method is briefly described below. The electrochemical cell is separated into two compartments by a specimen membrane as shown in Fig. 1(a). One side of the membrane (which is called the cathodic surface) is polarized at a constant cathodic current density $i_c$. Hydrogen ions $H^+$ in the cathodic electrolyte discharge on the surface to be adsorbed atoms $H_{ad}$. Most of the adsorbed atoms change into hydrogen gas $H_2$ and a small amount of them enters the specimen as dissolved hydrogen atoms $H_{ab}$. The dissolved hydrogen atoms diffuse to the other side of the specimen (which is called the anodic surface) according to the concentration gradient. The anodic surface is maintained at a noble electrode potential by a potentiostat and the permeating hydrogen is ionized. The potentiostatic current $i_a$, which is
proportional to the rate of hydrogen permeation, is recorded.

Figure 1(b) shows schematically the charging time dependence of the distribution of the dissolved hydrogen, i.e., the distributions at \( t_1, t_2, \) and \( t_{\infty} \) of charging time \( (t_1 < t_2 < t_{\infty}) \), under the following initial and boundary conditions:

(i) The hydrogen concentration before cathodic polarization is zero everywhere in the specimen.
(ii) The concentration of dissolved hydrogen at the cathodic surface increases to a constant value \( C_0 \) immediately after cathodic polarization.
(iii) The concentration of hydrogen at the anodic surface is maintained at zero. The charging time dependence of hydrogen permeation rate \( i_a \) and amount of permeated hydrogen \( Q \) obtained under those conditions are schematically shown in Fig. 2. The value of \( i_a \) is proportional to the gradient of hydrogen concentration at the anodic surface, and the value of \( Q \) is given by the integration of \( i_a \).

The diffusion coefficient of hydrogen \( D_H \) can be determined by the time-lag method. The value of \( D_H \) is calculated from the lag time \( (t_{\text{lag}} \) in Fig. 2(c)) obtained from the charging time dependence of \( Q \). In the case of the initial and boundary conditions described above, \( D_H \) is given by

\[
D_H = \frac{L^2}{6t_{\text{lag}}},
\]

where \( L \) is the specimen thickness.

### III. Experimental Procedure

#### 1. Specimens

The material used in the experiment is commercially pure iron, of which the chemical composition is shown in Table 1. Two groups of specimens were prepared; (1) annealed in vacuum at 1173 K for 10.8 ks (referred to afterwards as annealed specimens) and (2) 9% cold-worked after annealing (cold-worked specimens). A thin layer of palladium was electrodeposited on the anodic side of the specimen membranes to protect them against anodic dissolution. The specimens were 0.5–1.1 mm thick and the surface area for permeation was 250 mm².

#### 2. Permeation experiment

Table 3 shows schematically the apparatus

| C   | N   | Si  | Mn  | P   | S   | O   |
|-----|-----|-----|-----|-----|-----|-----|
| 0.0033 | 0.0067 | 0.005 | 0.09 | 0.0070 | 0.0022 | 0.0010 |
for electrochemical measurements of tritium and hydrogen permeation. The cell was made of Teflon to prevent failure by an accident. The tritium and hydrogen gases evolved by the electrolysis of the water were collected in a gas bag, and then they were captured with a catalyst and silica-gel. The permeation experiments were done at room temperature.

A galvanostat and a potentiostat shown in Fig. 3 were used for introducing tritium and hydrogen into a specimen and measuring the permeation rate of them, respectively. The electrode potential of the anodic surface was maintained at 0 V against Ag/AgCl reference electrode. Platinum in the anode or cathode cell is a counter electrode.

The cathodic electrolyte was $10^{-4} \text{ m}^3$ aqueous solution of $0.5 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ containing $3.7 \times 10^{12} \text{ Bq/m}^3$ tritium and $10^{-1} \text{ mol/m}^3 \text{ As}_2\text{O}_3$ as a promoter for entry of hydrogen and tritium into a specimen. The anodic electrolyte was an $0.2 \text{ kmol/m}^3 \text{ NaOH}$ aqueous solution (about $10^{-4} \text{ m}^3$).

Polarization in the cathodic electrolyte introduced both tritium and hydrogen into a specimen, and the permeated tritium and hydrogen were extracted at the anodic surface by potentiostatical ionization. Nearly all of the potentiostatic current originated from the ionization of hydrogen, because the concentration of tritium was very small. The amount of permeated tritium was determined by measuring the radioactivity of the electrolyte sampled from the anodic side at intervals of appropriate time. The sampled electrolyte ($10^{-6} \text{ m}^3$) and $1 \text{ kmol/m}^3 \text{ H}_2\text{SO}_4$ aqueous solution ($5 \times 10^{-7} \text{ m}^3$) were added to PCS solution, which was a xylene-surfactant based liquid scintillation cocktail designed for counting of radioactive aqueous samples, ($1.85 \times 10^{-5} \text{ m}^3$), and the radioactivity of the solution was measured with a liquid scintillation counter. The amount of permeated hydrogen was obtained by integrating the potentiostatic current. The diffusion coefficients of tritium and hydrogen were simultaneously determined from the time dependence of the amounts of permeated tritium and hydrogen.

IV. Experimental Results and Discussion

1. Permeation of tritium and hydrogen in iron

Figure 4 shows the change in the permeation rates of tritium and hydrogen by switching the cathodic charging current on and off; notice at the change in the slope of the curves. The permeation rates of them increase and decrease by switching on and off, respectively.

Figure 5 shows an example of charging time dependence of the amounts of tritium and hydrogen permeated through an annealed iron.
specimen polarized with various cathodic current densities ($i_c$). At small $i_c$, the amounts of them increase with $i_c$, and the permeation rates become constant at long charging time. At large $i_c$, however, a steady state of the permeation is not found.

Blisters were observed on the surface of the specimen charged with hydrogen (tritium) at large $i_c$. The occurrence of the blisters is caused by the large pressure of hydrogen gas precipitated from dissolved hydrogen atoms\textsuperscript{(5)(6)}. Namely, the heavy cathodic hydrogen charging with large $i_c$ such as 1000 A/m\textsuperscript{2} produces internal damages by the precipitation of hydrogen, and the diffusion coefficient of hydrogen in the specimen varies during the permeation experiment because of the trapping effects of the damages\textsuperscript{(7)(8)}. The permeation rates of hydrogen (tritium) under such charging conditions do not reach a steady state even at long charging time. Therefore, the permeation experiment at small $i_c$ is necessary for determining the diffusion coefficients of hydrogen and tritium.

The permeation rates of tritium and hydrogen can be measured by the electrochemical permeation method in which tritiated solution is used as a cathodic electrolyte. The proper choice of experimental conditions in the permeation enables us to obtain the diffusion coefficients of tritium and hydrogen from the charging time dependence of the amounts of permeated tritium and hydrogen.

2. Diffusion coefficients of tritium and hydrogen in iron

To obtain reliable data of the diffusion coefficient by the permeation experiment, the experimental results should satisfy the following requirements: (1) The steady state permeation rate should be proportional to the reciprocal of the specimen thickness (1/$L$), and (2) the time lag ($t_{lag}$) should be proportional to the square of the specimen thickness ($L^2$) and independent of the cathodic current density ($i_c$).

Figure 6 shows the relations between the permeation rates and 1/$L$ measured for annealed iron specimens at 10\textsuperscript{3}–10\textsuperscript{4}s of charging time (≈ steady state permeation rates). Though the data on the permeation rates shows large scattering, they are assumed to be proportional to 1/$L$ at each $i_c$. This satisfies the requirement (1).

As described above, the experimental conditions, under which no damages of the specimen occurs by hydrogen precipitation should be chosen. Therefore, the values of $t_{lag}$ were calculated from the charging time dependence of the amounts of permeated tritium and hydrogen measured at small $i_c$ (10–100 A/m\textsuperscript{2}) for short charging time (within 1200 s). The measured time lag ($t_{lag}/L^2$) are shown in Fig. 7. We cannot strictly know whether the values of $t_{lag}/L^2$ depend on $i_c$ and $L$ or not, because they show considerable scatter. Within the experimental accuracy in the present work, however, the time lag $t_{lag}/L^2$ can be said to be independent of $i_c$ and $L$; i.e., the requirement (2) may be satisfied. The diffusion coefficients of tritium ($D_T$) and hydrogen ($D_H$) can be determined from the values of $t_{lag}/L^2$.
given in Fig. 7 by using eq. (1):

Annealed iron specimens at 286 K:

\[
\begin{align*}
D_T &= 9 \times 10^{-10} \text{ m}^2/\text{s} \\
D_H &= 4 \times 10^{-9} \text{ m}^2/\text{s}
\end{align*}
\]

Cold-worked iron specimens at 284 K:

\[
\begin{align*}
D_T &= 3 \times 10^{-10} \text{ m}^2/\text{s} \\
D_H &= 4 \times 10^{-10} \text{ m}^2/\text{s}
\end{align*}
\]

Figure 8 shows the temperature dependence of diffusion coefficients of hydrogen \(D_H\) and deuterium \(D_D\) in annealed and cold-worked specimens\(^7\). The data given in this figure,
which are obtained from analysis of the charging time dependence of the permeation rate in the specimen polarized cathodically in an As$_2$O$_3$-free electrolyte, are higher in accuracy than those obtained in this work. Considering the large experimental error in the values of $D_H$ obtained in this work, the values can be said to be equal to that in the previous work.

The diffusion coefficients of hydrogen isotopes are shown to decrease in the order of H, D and T (i.e., $D_H > D_D > D_T$), and this order corresponds to that known in many metals$^{(1)}$. In cold-worked specimens, however, even if we take account of the experimental error (cf. Fig. 7), $D_D$ is smaller than $D_T$ (i.e., $D_D < D_T$), which differs from the order of the result in annealed specimens. This experimental result may originate from the following causes; (1) quantum effect in diffusion$^{(9)}$, (2) isotope dependence in trapping effect, and (3) peculiarity in the experimental procedure used in the present work for measurement of $D_T$, i.e., coexistence of many hydrogen atoms during tritium permeation experiments. However, it is not possible at present to affirm the cause.

To reduce the experimental error in measurements of $D_T$, the following procedures are desirable; (i) increase in the amount of permeated tritium, (ii) tritium (hydrogen) charging at small $i_c$ in an As$_2$O$_3$ free electrolyte, i.e., under the experimental condition free from hydrogen damage, and (iii) increase in $t_{lag}$ by using thick specimens. And the increase in concentration of tritium in the cathodic electrolyte is the most effective for reducing the error in permeation experiments. However, we cannot use hotter tritium solution as a cathodic electrolyte than that used in the present work because of the restriction on the amount of tritium usable in the laboratory where the experiments have been carried out.

3. Separation factor

It is known that electrolysis condenses the tritium concentration in an aqueous solution, because electrochemical reactions have large separation factors$^{(10)}$. Many investigators have explained this phenomenon on the basis of isotope effects on gas evolution on an electrode surface and evaporation of an electrolyte$^{(11)}$, and few investigators take account of the entry of tritium and hydrogen into electrode metal.

On the other hand, tritium enrichment may be made possible by utilizing permeation of hydrogen isotopes through metal membranes, because the permeation rate is isotope dependent$^{(1)(12)}$. Several investigations on the basis of this technique have been reported, but in few works the electrochemical reactions on the electrode surface have been discussed$^{(13)}$. And the experimental result using an iron electrode has not been reported. Therefore, considering the entry of tritium and hydrogen into iron, the electrochemical reactions are inspected as follows: Figure 9 indicates the electrochemical permeation process$^{(14)}$ of tritium and hydrogen. The cathodic electrolyte used in this work contains As$_2$O$_3$ as a promoter for hydrogen (tritium) entry into a specimen. Though cathodic polarization induces deposition of metallic As$^{(4)}$, cathodic current for precipitation of As is negligibly small, and it is not illustrated in Fig. 9. Furthermore, assuming that arsenic has the same effects for hydrogen and tritium on the rates of the electrochemical reactions, gas evolution and entry of adsorbed atoms into iron electrodes, we discuss the experimental results obtained in this work.

The concentrations of tritium, hydrogen, tritium ion, and hydrogen ion in the electrolyte are $C_T$, $C_H$, $C_{T^+}$, and $C_{H^+}$. When an iron ele-

\[
\begin{align*}
T & \quad T^+ \quad T_{ad} \\
C_T & \quad C_T^+ \quad C_{T_{ad}} \\
\hline
H & \quad H^+ \quad H_{ad} \\
C_H & \quad C_{H^+} \quad C_{H_{ad}}
\end{align*}
\]

Fig. 9 Electrochemical permeation process of tritium (T) and hydrogen (H). $C_T$, $C_H$, $C_{T^+}$, and $C_{H^+}$: concentrations of T, H, T$^+$ and H$^+$ in a cathodic electrolyte; $C_{T_{ad}}$ and $C_{H_{ad}}$: coverages of T and H adsorbed on the cathodic surface; $i_{c,T}$ and $i_{c,H}$: cathodic currents for discharge of T$^+$ and H$^+$; $i_{a,T}$ and $i_{a,H}$: permeation rates of T and H; $P_T$ and $P_H$: concentrations of T and H in the gas evolved by cathodic polarization.
trode is polarized in the electrolyte, cathodic current density \( (i_c) \) is nearly equal to the sum of the discharge rates of tritium ion \( (i_{c,T}) \) and hydrogen ion \( (i_{c,H}) \); the discharge rate of arsenic is negligibly small. The following equation is obtained:

\[
i_c = i_{c,T} + i_{c,H}.
\]  

Some parts of tritium \( (T_{ad}) \) and hydrogen \( (H_{ad}) \) adsorbed on the cathodic surface enter the iron electrode, and the others change into gas. The evolution of arsine gas is neglected here. In Fig. 9, the concentrations of \( T_{ad} \) and \( H_{ad} \) are denoted by \( C_{T_{ad}} \) and \( C_{H_{ad}} \), and the concentrations of tritium and hydrogen in the gas evolved by cathodic polarization are denoted by \( P_T \) and \( P_H \). Tritium \( (T_{ab}) \) and hydrogen \( (H_{ab}) \) atoms dissolved in the iron membrane diffuse in the specimen and the permeated atoms are extracted by potentiostatic ionization. The potentiostatic current \( (i_a) \) is the sum of the ionization currents of tritium \( (i_{a,T}) \) and hydrogen \( (i_{a,H}) \):

\[
i_a = i_{a,T} + i_{a,H}.
\]  

In the case of such a permeation process, three kinds of separation factors are defined; for gas evolution on the cathodic surface \( (\alpha_G) \), permeation through iron \( (\alpha_P) \), and solution into iron \( (\alpha_S) \):

\[
\alpha_G = \frac{P_H}{P_T} \left( \frac{C_H}{C_T} \right), \\
\alpha_P = \frac{i_{a,T}}{i_a} \left( \frac{i_{a,T}}{i_{c,T}} \right) \left( \frac{C_H}{C_T} \right), \\
\alpha_S = \frac{C_{H_{ab}}/C_{T_{ab}}}{C_{H_{ad}}/C_{T_{ad}}},
\]  

where \( C_{H_{ab}} \) and \( C_{T_{ab}} \) are the concentrations of dissolved tritium and hydrogen at the cathodic surface. \( C_{T_{ab}} \) and \( C_{H_{ab}} \) are proportional to \( C_{T_{ad}} \) and \( C_{H_{ad}} \) respectively:

\[
C_{T_{ab}} = k_T C_{T_{ad}}, \\
C_{H_{ab}} = k_H C_{H_{ad}}.
\]  

where \( k_T \) and \( k_H \) are constants. At a steady state permeation, the permeation currents are

\[
i_{a,T} = FC_{T_{ab}} D_T / L, \\
i_{a,H} = FC_{H_{ab}} D_H / L,
\]  

where \( F \) is the Faraday constant. Consequently, the ratio of the permeation currents is

\[
\frac{i_{a,H}}{i_{a,T}} = \left( \frac{C_{H_{ad}}}{C_{T_{ad}}} \right) \left( \frac{D_H}{D_T} \right) \\
= \left( \frac{k_H}{k_T} \right) \left( \frac{C_{H_{ad}}}{C_{T_{ad}}} \right) \left( \frac{D_H}{D_T} \right).
\]  

Now, the kinetics of evolution of hydrogen (tritium) gas on the cathodic surface is assumed to be a discharge-recombination\(^{14}\). Then the gas evolution reactions are

\[
H^+ + e \rightarrow H_{ad}, \\
T^+ + e \rightarrow T_{ad},
\]  

and

\[
2H_{ad} \rightarrow H_2, \\
T_{ad} + H_{ad} \rightarrow HT, \\
2T_{ad} \rightarrow T_2,
\]  

where \( k_{1-5} \) are the rate constants. In this case, \( \alpha_G \) is given by

\[
\alpha_G = \left( \frac{C_T}{C_H} \right) \left( \frac{k_3 C_{H_{ad}} + (k_4/2) C_{H_{ad}} C_{T_{ad}}}{(k_4/2) C_{H_{ad}} C_{T_{ad}} + k_3 C_{T_{ad}}} \right).
\]  

On the basis of these relations, the experimental results are discussed. The value of \( i_c \) is given in the experiments, and \( C_T \) and \( C_H \) are determined from the composition of the cathodic electrolyte, which are shown in Table 2. The values of \( i_a \) and \( i_{a,T} \) for each \( i_c \) are obtained from the potentiostatic current and the

| Table 2 | The values of the concentrations of tritium and hydrogen in the cathodic electrolyte \( (C_T, C_H) \), the ratio of permeation rate of tritium to that of hydrogen \( (i_{a,T} / i_{a,H}) \), the diffusion coefficients of tritium and hydrogen \( (D_T, D_H) \), and the separation factors for permeation, solution and gas evolution \( (\alpha_P, \alpha_S \text{ and } \alpha_G) \). |
| --- | --- | --- |
| \( C_T \) | 3.3 \times 10^{-3} \text{ mol/m}^3 |
| \( C_H \) | 1.1 \times 10^5 \text{ mol/m}^3 |

| annealed iron (at 286 K) | 9% cold-worked iron (at 284 K) |
| --- | --- |
| \( i_{a,T} / i_{a,H} \) | 2.6 \times 10^{-9} | 2.6 \times 10^{-9} |
| \( D_T \) | 9 \times 10^{-10} \text{ m}^2/\text{s} | 3 \times 10^{-10} \text{ m}^2/\text{s} |
| \( D_H \) | 4 \times 10^{-9} \text{ m}^2/\text{s} | 4 \times 10^{-9} \text{ m}^2/\text{s} |
| \( \alpha_P \) | 12 | 12 |
| \( \alpha_S \) | 3 | 9 |
| \( \alpha_G \) | 5 | 18 |
radioactivity of the sampled anodic electrolyte. Furthermore, under the experimental condition of this work \((C_T < C_H)\), the following relations hold:

\[
\begin{align*}
  i_c &= i_{c, H} \quad (15) \\
  i_a &= i_{a, H} \quad (16) \\
  P_T &< P_H \quad (17)
\end{align*}
\]

The value of \(i_a/i_c\) depends on the experimental conditions such as \(i_c\) and \(L\). In the case of the annealed specimen of \(L=0.994 \text{ mm} \) charged at \(i_c=10 \text{ A/m}^2\) in the steady state region (cf. Fig. 5), \(i_a/i_c\) (\(= i_{a, H}/i_{c, H}\)) \(= 0.1\). Namely, in this condition, the large part of hydrogen ions discharged at the cathodic surface change into hydrogen gas, and nearly 10\% of the hydrogen enter the specimen.

The value of \(\alpha_p\) has been reported to depend on \(i_c\) for a nickel electrode\(^{(11)}\). So that we consider here the dependence of \(\alpha_p\) on \(i_c\). The permeation rates of tritium and hydrogen at 1500 s of charging time were measured for various \(i_c\). The dependence of the permeation rates on \(i_c\) is shown in Figs. 10 and 11 for annealed and cold-worked specimens, respectively. The permeation rates are divided by \(L\), assuming that they are proportional to \(L^{-1}\) (cf. Fig. 6). When the permeation rate of tritium at \(i_c=0\), i.e., the background for the measurement, is taken into consideration, the ratio of the permeation rates of tritium to hydrogen \(i_{a,T}/i_{a,H}\) is not observed to depend on \(i_c\). The values of the ratio thus obtained are nearly equal for annealed and cold-worked specimens. Calculation of \(\alpha_p\) by using the values of \(C_T\), \(C_H\) and \(i_{a,T}/i_{a,H}\) in Table 2 gives

\[
\alpha_p = 12. \quad (18)
\]

Substitution of eqs. (7) and (11) into eq. (8) gives

\[
\alpha_S = \frac{\alpha_p}{(D_H/D_T)}. \quad (19)
\]

Though the distinct value of \(D_H/D_T\) is unknown because of the large experimental error in determination of \(D_T\), this value seems to depend on the deformation degree of the specimen (cf. Fig. 8). If this is true, the value of \(\alpha_S\) also depends on the deformation degree of the specimen. Substitution of the values of

![Fig. 10 Variation of permeation rates of tritium (a) and hydrogen (b) with cathodic current density for annealed iron specimens.](image)

\(D_T, D_H\) and \(\alpha_p\) (which are given in Table 2) into eq. (19) gives

\[
\alpha_S = \begin{cases} 
3 \text{ (for annealed specimens)} \\
9 \text{ (for cold-worked specimens)}
\end{cases} \quad (20)
\]

When eqs. (7), (9) and (11) are substituted into eq. (14) using the condition \(C_{Tad} < C_{Had}\), \(\alpha_G\) can be expressed as

\[
\alpha_G = 2\alpha_p \left( \frac{k_3}{k_4} \right) \left( \frac{k_T}{k_H} \right) \left( \frac{D_T}{D_H} \right). \quad (21)
\]

In this equation, only the values of \(\alpha_p, D_T\) and \(D_H\) are known, and so the value of \(\alpha_G\) cannot be explicitly determined from the results obtained in this work. Though we have no ex-
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Experimental evidence, if we just assume that \((k_3/k_4)(k_T/k_H)=1\), then the value of \(\alpha_G\) is given by

\[
\alpha_G = \begin{cases} 
5 & \text{(for annealed specimens)} \\
18 & \text{(for cold-worked specimens)} 
\end{cases} \tag{22}
\]

Many data on \(\alpha_G\) have been reported on the basis of the relation between the magnitude of tritium enrichment by cathodic polarization and the tritium concentration in an electrolyte, but they show considerable scatter\(^{(11)}\):

\[
\alpha_G = 6-29. \quad (288 \text{ K}) \tag{23}
\]

The value of \(\alpha_G\) obtained for annealed specimens under the above-mentioned assump-

tion (eq. (22)) is nearly the lower limit in the previous data (eq. (23)) and the value of \(\alpha_G\) for cold-worked specimens is in the region given by eq. (23), but this result must be reexamined in future.

V. Conclusion

(1) The permeation rates and diffusion coefficients of tritium and hydrogen can be measured by the electrochemical permeation method, in which sulfuric acid solution containing tritium is used as a cathodic electrolyte.

(2) The diffusion coefficients of tritium \((D_T)\) and hydrogen \((D_H)\) are given by \(D_T = 9 \times 10^{-10} \text{m}^2/\text{s}\) and \(D_H = 4 \times 10^{-9} \text{m}^2/\text{s}\) for annealed iron specimens at 286 K, and \(D_T = 3 \times 10^{-10} \text{m}^2/\text{s}\) and \(D_H = 4 \times 10^{-10} \text{m}^2/\text{s}\) for 9% cold-worked iron specimens at 284 K, though the experimental error in the measurements of \(D_T\) and \(D_H\) is large.

(3) The separation factor for permeation of tritium and hydrogen through iron is 12 for annealed and 9% cold-worked specimens at room temperature. This value is independent of cathodic current density.

(4) The separation factor for solution of tritium and hydrogen into iron by cathodic polarization is 3 for annealed specimens, and 9 for 9% cold-worked specimens.

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