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## FREQUENCY RESPONSE METHOD FOR DETERMINATION OF THE DIFFUSION COEFFICIENT OF HYDROGEN IN METAL

By

K. SEKINE<sup>\*)</sup>

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### Abstract

A new electrochemical method, termed as "the frequency response method", for the determination of the diffusion coefficient  $D$  in metal is proposed. In the bielectrode system, there appears a phase lag in the hydrogen permeation current, when the hydrogen charging constant current is overlapped with a sinusoidal current. The relation between the phase lag and the  $D$  value is given by solving the diffusion equation.

Measurements were carried out for hydrogen and deuterium in the  $\alpha$ -phase systems of Pd/H and Pd/D in the temperature range of 0° to 40°C, and the following values were obtained:

$$D_{\text{H}} = 3.44 \times 10^{-3} \exp(-5.39 \times 10^3 \text{ cal}/RT) \text{ cm}^2/\text{sec},$$

and

$$D_{\text{D}} = 2.46 \times 10^{-3} \exp(-5.08 \times 10^3 \text{ cal}/RT) \text{ cm}^2/\text{sec}.$$

The time lag method based on hydrogen charging by a constant current was also carried out; it was found that by this method the same  $D$  value is obtained as that by the frequency response method.

### § 1. Introduction

Diffusion of hydrogen in metals such as palladium, nickel and steel is of great interest because of the following reasons; a) its practical application to hydrogen purification<sup>1)</sup> or to fuel cell,<sup>2,3)</sup> b) its role in hydrogen embrittlement,<sup>4)</sup> and c) theoretical importance of the solid state interstitial diffusion process.<sup>5)</sup>

Many methods have been devised for the determination of the diffusion coefficient  $D$  of hydrogen in metal,<sup>6~11)</sup> by which the diffusive property of hydrogen in metal is well described.

The author proposes here a new method to determine the  $D$  value,

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<sup>\*)</sup> Department of Chemistry, Faculty of Science, Rikkyo (St. PAUL's) University, Nishi-ikebukuro, Toshima-ku, Tokyo 171, Japan.

*i. e.*, the frequency response method based on hydrogen charging by a constant current overlapped with a sinusoidal current.

The method was applied to determine the  $D$  value of hydrogen in the  $\alpha$ -phase palladium/hydrogen system, and it was found that the method is reliable in this system.

Diffusion study of hydrogen in metal by a constant charging current has not been carried out yet in detail, so that a study of diffusion by the time lag method was also made in the course of this work.

## § 2. Theory of the Frequency Response Method and Theoretical Background of the Time Lag Method

The frequency response method is based on the following principle; if hydrogen is charged by a constant cathodic current overlapped with a sinusoidal current, there appears a phase lag in the sinusoidal component of the hydrogen permeation current in the sinusoidal steady state (see Fig. 1). This phase lag is related to the diffusion velocity of hydrogen in metal; therefore, analysis of the phase lag for various frequencies will give information on the  $D$  value.

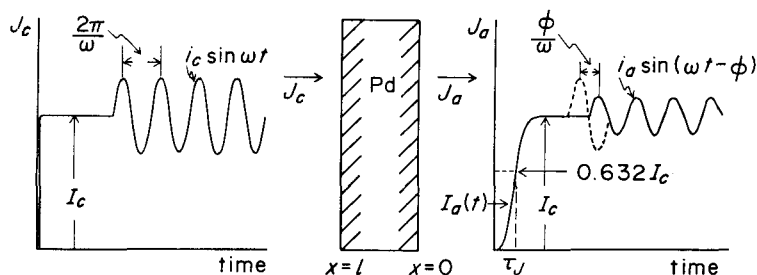


Fig. 1. Principle of the frequency response method for diffusion measurement.

In this section, the relation between the  $D$  value and the phase lag  $\phi$  is deduced by solving the diffusion equation. The theoretical background for the time lag method by a constant charging current is also described.

Analytical procedures for the determination of the  $D$  value will be presented in the experimental section.

### (2-1) Diffusion Equation

The rate of permeation of hydrogen through a metal foil can be well described mathematically by solving the diffusion equation under the assumption that the rate-determining step of hydrogen permeation is the diffusion

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process of hydrogen in the foil. The diffusion equation is given according to FICK's second law as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $C$  is the concentration of hydrogen in the metal,  $D$  the diffusion coefficient of hydrogen in the metal,  $t$  the elapsed time starting from the instant of the hydrogen supply by a cathodic current, and  $x$  the distance from the surface of the permeation side of the foil with the thickness of  $l$  ( $0 \leq x \leq l$ ).

To solve the diffusion equation, the author set initial and boundary conditions as follows;

(a) no hydrogen is present in the foil at first ( $t=0$ ),

(b) at the permeation side ( $x=0$ ) hydrogen concentration in the foil is always zero, and

(c) at the cathodic (hydrogen) charging side ( $x=l$ ) hydrogen enters at the rate  $J_c$  (charging current).

These conditions can be formulated as follows:  
the initial condition

$$C = 0 \quad \text{for } 0 \leq x \leq l \text{ at } t = 0, \quad (2)$$

the boundary conditions

$$C = 0 \quad \text{for } x = 0, t \geq 0 \quad (3)$$

and

$$J_c = DF \left( \frac{\partial C}{\partial x} \right)_{x=l} \quad \text{for } x = l, t \geq 0 \quad (4)$$

where  $F$  is the faraday.

We can obtain the solution of the diffusion equation in terms of the permeation current  $J_a$  by use of the Laplace transformation technique. Derivations of Eqs. (5) to (7) are described in the Appendix.

In the following sections, we describe the solution of the diffusion equation for two cases of  $J_c$ ; one is the case in which  $J_c$  is composed of a constant current and a sinusoidal current, and the other is the case in which  $J_c$  is composed of only a constant current. In determining the  $D$  value, these cases are denoted as the frequency response method and the time lag method, respectively.

## (2-2) Solution of the Diffusion Equation

(a) In the case  $J_c = I_c + i_c \sin \omega t$ 

When  $J_c$  is composed of a constant (direct) current,  $I_c$ , and a sinusoidal current,  $i_c \sin \omega t$ , with an angular frequency,  $\omega$ , and an amplitude,  $i_c$ ,  $J_a$  is given at the sinusoidal steady state as

$$J_a = I_c + i_a \sin(\omega t - \phi), \quad (5)$$

where

$$i_a = i_c (\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl)^{-1/2} \quad (6)$$

and

$$\phi = \sin^{-1} \left\{ \frac{\sinh kl \sin kl}{(\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl)^{1/2}} \right\}. \quad (7)$$

Here,  $\phi$  is the phase lag of the sinusoidal component of  $J_a$  caused by a finite velocity of diffusion of hydrogen in the foil, and  $k$  is defined as

$$k \equiv \sqrt{\omega/2D} = \sqrt{\pi f/D}. \quad (8)$$

When  $kl = n\pi$  ( $n=1, 2, 3, \dots$ ), the value of  $\sin \phi$  becomes zero, and specifically, when  $kl = \pi$  (this means  $\phi = \pi$ ), Eq. (6) results

$$i_a/i_c = 0.0863. \quad (9)$$

And Eq. (8) gives the relation

$$D = l^2 f_\pi / \pi, \quad (10)$$

where  $f_\pi$  is the frequency in which  $\phi$  becomes  $\pi$ .

Equations (6), (7), and (10) are related to the  $D$  value and can be used to determine the  $D$  value.

(b) In the case  $J_c = I_c$ 

When  $J_c$  is composed only of a constant current  $I_c$ , the time dependency of the hydrogen permeation current  $I_a(t)$  is given by FULLENWIDER<sup>12)</sup> as

$$I_a(t) = I_c \left[ 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \{ -D(2n+1)^2 \pi^2 t / 4l^2 \} \right]. \quad (11)$$

By integrating Eq. (11) with respect to time  $t$ , we obtain  $Q_t$ , the total amount of the permeated hydrogen through the foil at time  $t$ , as

$$Q_t = \frac{I_c}{F} \left[ t + \frac{16l^2}{D\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \{ \exp(-D(2n+1)^2 \pi^2 t / 4l^2) - 1 \} \right] \quad (12)$$

which, as  $t$  becomes large, approaches the asymptote

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$$Q_t = \frac{I_c}{F} \left\{ t - \frac{16l^2}{D\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \right\}. \quad (13)$$

This asymptote has an intercept on the  $t$  axis. We define the magnitude of the time lag  $\tau_J$  as the time from the origin to the intercept, so that  $\tau_J$  is given by

$$\tau_J = \frac{16l^2}{D\pi^3} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^3} \approx \frac{l^2}{2D}. \quad (14)$$

Inserting  $t = \tau_J = l^2/2D$  into Eq. (11), we obtain the value  $I_a(t)/I_c = 0.632$  at  $\tau_J$ . Thus, from a transient curve of  $I_a(t)$ , we can decide the  $D$  value on the basis of Eq. (14).

### § 3. Experimental

#### (1) The palladium foils

The Pd foils (99.9%) ranging in thickness from 50 to 200  $\mu\text{m}$ , purchased from Tanaka Kikinzoku Kogyo K. K. (Tokyo), were cut into 30  $\times$  30 mm square pieces and weighed precisely to determine the thickness. The specimen foil was then heated to red in an oxidizing gas flame about 30 seconds to activate the surfaces.<sup>19)</sup> A further, or another, pretreatment of the specimen was made in some cases (see Section (4-3)).

#### (2) The cell

The cell and the electrical circuit are shown in Fig. 2 schematically. The Pyrex glass cell consisted of two compartments separated by a Pd foil specimen; one was the cathodic (hydrogen charging) compartment and the other the anodic (hydrogen permeation) compartment. Each compartment had a flange with a silicone rubber gasket. These compartments were bolted together, holding the Pd foil inbetween, so as to keep them water-tight.

In the cathodic compartment there was a bright Pt counter electrode (anode) in a glass pipe, on which a fritted glass was fused to the end so as

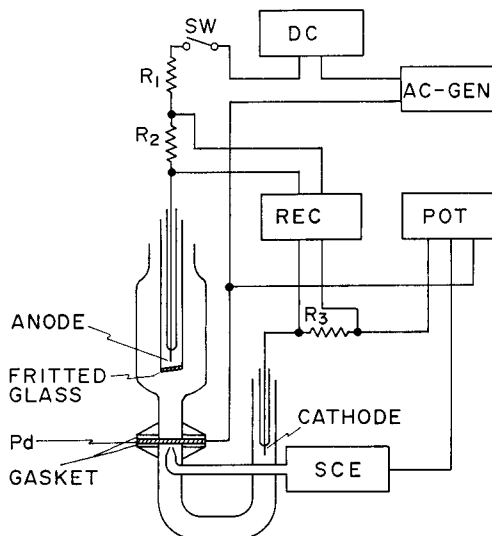


Fig. 2. Measurement circuit and cell.

DC: dc voltage supply, AC-GEN: sine-wave generator, REC: X-Y and dual-pen recorders, POT: potentiostat, SCE: saturated calomel electrode,  $R_2 = R_3 = 100$  ohm, CATHODE and ANODE: platinum electrodes, Pd: Pd foil, and GASKET: silicone rubber gaskets.

to prevent diffusion of oxygen to the Pd foil surface. The permeation compartment had a bright Pt counter electrode (cathode) and a saturated calomel electrode (SCE) as a reference electrode.

### (3) Solutions

1 N NaOH and 1 N H<sub>2</sub>SO<sub>4</sub> solutions were prepared from analytical grade reagents and re-distilled water. No further purification was done. 1 N D<sub>2</sub>SO<sub>4</sub> solution was prepared from D<sub>2</sub>SO<sub>4</sub> (98%) and D<sub>2</sub>O (99.75%), supplied by Merck Co..

### (4) The electrical circuit

The cathodic current  $J_c$ , with a constant current and a sinusoidal current  $i_c \sin \omega t$ , was supplied from a regulated dc supply (0 to 50 V) and a sine wave generator (0.001 to 10<sup>5</sup> Hz) through the resistance  $R_1$  ranging from 1.5 to 600 K $\Omega$  according to choice of the  $J_c$  value.

The permeation side of the Pd foil was maintained usually at +0.40 V vs. SCE by a potentiostat.

$J_c$  was observed by recording the potential drop across  $R_2$  (100  $\Omega$ ) inserted in series with the cathodic circuit.  $J_a$  was observed in a similar manner as  $J_c$ .  $J_c$  and  $J_a$  were simultaneously measured with the aid of dual-pen type and X-Y type recorders.

### (5) Measuring procedure

After the Pd foil had been mounted on the cell, 50 ml of 1 N NaOH solution was introduced into the permeation compartment and the anodic circuit was switched on. The anodic current was large at first but became smaller and tended to a constant value of about 1  $\mu$ A/1.78 cm<sup>2</sup> in a few minutes, this constant current being termed the residual current hereinafter. Then 50 ml of a solution (1 N H<sub>2</sub>SO<sub>4</sub>, 1 N D<sub>2</sub>SO<sub>4</sub> or 1 N NaOH) was introduced into the cathodic compartment, and the cathodic current was supplied. In the frequency response method, the amplitude of the sinusoidal current was set at one-tenth of the constant current ( $i_a/I_c=0.1$ ).

### (6) Procedures of analysis

$J_c$  and  $J_a$  were observed in the above mentioned manner for a given frequency.

(a) *Frequency Response Method.* After the hydrogen permeation reached the sinusoidal steady state for a given frequency  $f$  ( $f=\omega/2\pi$ ), of which state can be checked by observing the recorder chart on the dual-pen type recorder, the X-Y recorder drew a LISSAJOUS's figure, which was an oval or a straight line.

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The amplitude ratio  $i_a/i_c$  of the sinusoidal currents and the phase lag  $\phi$  were obtained from the figure.

(b) *Time Lag Method.* The time lag  $\tau_J$  was obtained as the time when the permeation current reached 0.632 of the steady permeation current by analysing the recorded  $I_a(t)$ -time curve (transient curve) on the recorded chart when  $J_c$  was a constant current.

#### § 4. Results and Discussion

##### (4-1) Determination of $D_H$ Values\*<sup>1)</sup> by the Frequency Response Method and by the Time Lag Method

(a) *Frequency Response Method.* Measurements of  $\sin \phi$ 's and amplitude ratios ( $i_a/i_c$ )'s for various frequencies were carried out on Pd foil of different thickness. The electrolyte solution used was 1 N  $H_2SO_4$  and the temperature was kept at  $25^\circ \pm 0.03^\circ C$ .

The cathodic current was chosen to give a value of  $C_l$  of about 0.002 (in the atomic ratio H/Pd),  $C_l$  being the concentration of hydrogen in Pd at the cathodic side for the steady state of hydrogen permeation; and it was estimated by inserting the observed steady value of the permeation current  $I_a(st)$  and the preliminarily obtained  $D_H$  value into the equation of FICK's first law:

$$I_a(st) = D_H F (C_l - C_0) / l = D_H F C_l / l.$$

The reason for the choice of the magnitude of the current will be given in Section (4-3).

The current efficiency  $\eta$ , defined by

$$\eta \equiv \int_t^{t+2\pi/\omega} J_a dt / \int_t^{t+2\pi/\omega} J_c dt = I_a(st) / I_c,$$

which indicates how much of the cathodic current was used in charging hydrogen into the foil, was 98% for 71.2  $\mu m$  Pd foil.

The potential of the permeation side of the foil, which was fixed usually at +0.40 V vs. SCE, was changed in some experiments in the range of 0.00 to +0.60 V, but the values of  $\sin \phi$ ,  $i_a/i_c$ , and  $\eta$  (also  $f_x$  and  $\tau_J$  in the later experiments) remained unchanged. Use of 1 N NaOH as the electrolyte solution instead of 1 N  $H_2SO_4$  also did not affect these values.

Table 1-A shows the values of  $\sin \phi$  and  $i_a/i_c$  and the values of  $D_H$ , calculated using Eqs. (6) and (7), and the relation  $kl = \sqrt{\pi f / D_H} l$ , obtained for 71.2  $\mu m$  Pd foil.

\*<sup>1)</sup> Hereinafter, we use  $D_H$  and  $D_D$ , instead of  $D$ , to represent the  $D$  value for hydrogen and deuterium, respectively.



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The frequency 0.0227 Hz in Table 1-B corresponds to  $f_{\pi}$ , which is, as mentioned before, the frequency with which the phase lag  $\phi$  becomes  $\pi$  ( $180^\circ$ ); at this frequency the LISSAJOUS's figure on the X-Y chart gives a straight

TABLE 1. Observed values of  $\sin \phi$ ,  $ia/i_c$ , and  $kl$  and estimated  $D_H$  values for  $71.2 \mu\text{m}$  Pd foil at  $25^\circ\text{C}$

Frequency $f$ Hz	$\sin \phi$	$ia/i_c$	$kl$ from $\sin \phi$	$kl$ from $ia/i_c$	$D_H$ from $\sin \phi$ cm <sup>2</sup> /sec	$D_H$ from $ia/i_c$ cm <sup>2</sup> /sec
0.0401	0.863	0.0309	4.24	4.15	$3.55 \times 10^{-7}$	$3.70 \times 10^{-7}$
0.0600	0.927	0.0123	5.12	5.10	3.64	3.67
0.0150	0.568	0.149	2.55	2.58	3.67	3.58
1-A 0.0100	0.883	0.248	2.08	2.09	3.68	3.64
0.00687	0.990	0.367	1.70	1.70	3.78	3.78
0.00410	0.959	0.558	1.32	1.34	3.74	3.63
0.00127	0.500	0.904	0.750	0.750	3.59	3.59
Mean value for $D_H$ $(3.66 \pm 0.07) \times 10^{-7}$ $(3.66 \pm 0.06) \times 10^{-7}$						
1-B 0.0227	0	0.0861			$3.66 \times 10^{-7}$ (from Eq. (10))	

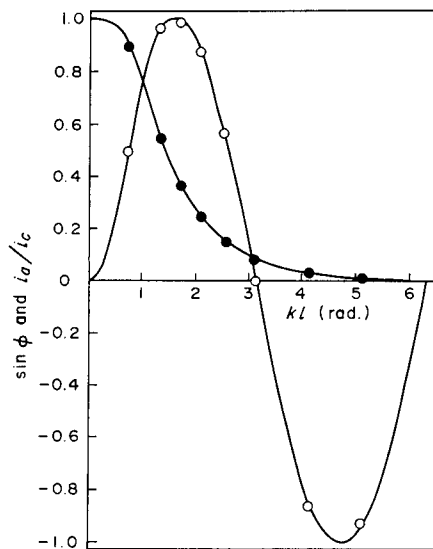


Fig. 3. Relations of  $\sin \phi$  and  $ia/i_c$  against  $kl$ .

—: theoretical curves calculated from Eqs. (6) and (7),  $\circ$  and  $\bullet$ : observed points of  $\sin \phi$  and  $ia/i_c$ , respectively, for  $71.2 \mu\text{m}$  Pd foil at  $25^\circ\text{C}$ .

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TABLE 2. Observed values of  $f_{\pi}$  and estimated  $D_H$  values for Pd foils of various thickness

Thickness of Pd foil $l$ $\mu\text{m}$	Cathodic current $I_c$ mA/1.78 cm <sup>2</sup>	Current efficiency $\eta$ %	Frequency $f_{\pi}$ Hz	$D_H(f_{\pi})$ from Eq. (10) cm <sup>2</sup> /sec
53.4	3.0	99	0.0402	$3.64 \times 10^{-7}$
71.2	2.1	98	0.0227	3.66
97.2	1.5	94	0.0121	3.64
198	1.0	98	0.00293	3.67

Mean value for  $D_H(f_{\pi})$   $(3.65 \pm 0.02) \times 10^{-7}$

line with a negative slope.\*) The  $D_H$  value for this frequency was calculated by using Eq. (10).

The values of  $D_H$  from  $\sin \phi$  and  $i_a/i_c$  give the same constant values independent of the frequencies. This means that the theoretical relation between  $kl$  and  $\sin \phi$  or  $i_a/i_c$ , represented by Eq. (6) or (7), is well satisfied experimentally: plots of  $\sin \phi$  and  $i_a/i_c$  against  $kl$  are shown in Fig. 3.

Measurements of  $f_{\pi}$  for Pd foils of different thickness were also carried out: observed values are listed in Table 2. The electrolyte solution and the temperature were the same as before. The  $D_H(f_{\pi})$  values in Table 2 have a constant value independent of the thickness of the foil. The mean value is almost the same with the mean values in Table 1.

The plot of the reciprocal of the frequency  $f_{\pi}$  against the square of the thickness  $l$  of the foil is given in Fig. 4. The points clearly rest on a straight line starting from the origin, as expected from Eq. (10).

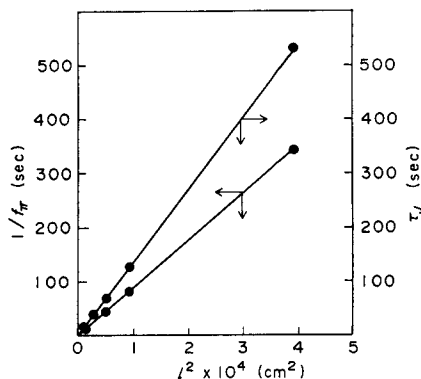


Fig. 4. Plots of the reciprocal of the frequency  $f_{\pi}$  and the time lag  $\tau_J$  against the square of the thickness  $l$  of Pd foil at 25°C.

\*) According to Eq. (7), when  $n$  (in  $kl=n\pi$ ) becomes 3, 5, 7..., LISSAJOUS's figures also give straight lines with negative slopes. However, the values of  $i_a/i_c$  are estimated from Eq. (6) as  $1.61 \times 10^{-4}$  ( $n=3$ ),  $3.01 \times 10^{-7}$  ( $n=5$ ),  $5.63 \times 10^{-10}$  ( $n=7$ )... These values are too low to observe. Hence an observed negative straight line can be regarded as corresponding only to  $n=1$  ( $\phi=\pi$ ). This was also confirmed by observing  $i_a/i_c$  for this frequency: its value was found to be in good agreement with the theoretical value 0.0863 for  $n=1$  (see Table 1-B).

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(b) *Time Lag Method.* Measurements of the time lag  $\tau_J$  were carried out just before every measurement by the frequency response method. Observed  $\tau_J$  values and calculated  $D_H(\tau_J)$  values are listed in Table 3. The  $D_H(\tau_J)$  values are almost the same with the  $D_H(f_s)$  values for each Pd foil.

The plot of the time lag  $\tau_J$  against the square of the thickness  $l$  of the foil is given in Fig. 4. The points also rest on a straight line starting from the origin, as expected from Eq. (14).

A typical transient curve, observed for 97.2  $\mu\text{m}$  Pd foil, is shown in Fig. 5, together with the theoretical curve. The hydrogen permeation current is given in the relative current and the time scale of the theoretical curve was adjusted at the time lag  $\tau_J$ . The observed curve coincides well with the theoretical curve.

TABLE 3. Observed values of  $\tau_J$  and estimated  $D_H$  values for Pd foils of various thickness at 25°C

Thickness of Pd foil $\mu\text{m}$	Cathodic current $I_c$ mA/1.78 cm <sup>2</sup>	Current efficiency $\eta$ %	Time lag $\tau_J$ sec	$D_H(\tau_J)$ from Eq. (14) cm <sup>2</sup> /sec
53.4	3.0	99	39.0	$3.65 \times 10^{-7}$
71.2	2.1	98	70.4	3.59
97.2	1.5	94	129	3.65
198	1.0	98	530	3.70

Mean value for  $D_H(\tau_J)$   $(3.65 \pm 0.04) \times 10^{-7}$

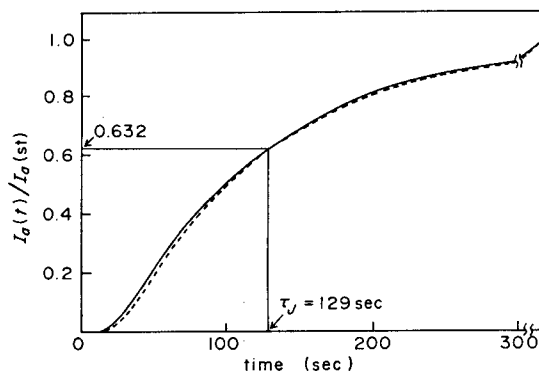


Fig. 5. Theoretical and observed curves for 97.3  $\mu\text{m}$  Pd foil at 25°C.

— : theoretical curve calculated from Eq. (11), - - - : observed curve.

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(c) *Examination of Diffusion Controlled Permeation of Hydrogen.*

We discuss here two items (A) and (B): (A). whether the initial and boundary conditions postulated in the theoretical section are satisfied experimentally or not; and (B). whether permeation of hydrogen through Pd foil is controlled solely by the diffusion process of hydrogen in the foil or not, since the reliability of the obtained  $D_H$  values depends exclusively on them.

The discussion is based on a comparison of each observed result with the theoretical one.\*)

Experimentally observed results are summarized below from (i) to (vi).

(A): (i) The residual current which appeared at the permeation side of the foil was very low (about  $1 \mu\text{A}/1.78 \text{ cm}^2$ ) for hydrogen free foil and also held the same value before starting each successive hydrogen charging.

(ii) Change in the potential of the permeation side of the foil (from 0.00 to  $+0.60 \text{ V vs. SCE}$ ) did not have any appreciable effect on  $f_x$ ,  $\eta$ , and  $\tau_J$ .

(iii) The observed current efficiencies  $\eta$ 's ranged from 94 to 99%.

Case (i) shows that the initial concentration of hydrogen in the foil can be considered zero and case (ii) shows that the hydrogen concentration at the permeation side is constant and the value may be put zero independent of the potential of the permeation side; from the observed potential values it may be deduced that practically no hydrogen is present at the surface. Case (iii) shows some deviations of observed  $\eta$ 's from the expected value (100%). To confirm this value, some experiments were carried out over a wide range of cathodic current: the results and discussion are described in Section (4-3). It might be concluded that such a small deviation of  $\eta$  from the value of 100% does not affect the conclusion of the discussion in this section.

(B): (iv) As shown in Table 1, the  $D_H$  values from  $\sin \phi$  and  $i_a/i_c$  were the same at a given frequency, and also at several frequencies the values had a constant value within experimental error: the theoretical relations between  $\sin \phi$  and  $kl$  and between  $i_a/i_c$  and  $kl$  expressed in Eqs. (6) and (7) are well satisfied experimentally, as seen in Fig. 3.

(v) The  $D_H$  values had almost the same independent of the foil thickness. This relation is also in Fig. 4 in the form of  $1/f_x - l^2$  or  $\tau_J - l^2$  plots: it gives a straight line starting from the origin, as expected theoretically from Eq. (10) or (14).

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\*) Examinations for the frequency response method and for the time lag method are made together in the following, because the initial and the boundary conditions are common for both methods. They differ from each other only in the form of  $J_c$ -function.

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(vi) The transient curve observed in the time lag measurement is in good agreement with the theoretically expected curve from Eq. (11).

The results (iv) to (vi) suggest that the rate determining step of hydrogen permeation is the diffusion process of hydrogen in Pd foil: the assumption, set in the beginning, that permeation of hydrogen through Pd foil is controlled by the diffusion process of hydrogen in Pd, is thus proved to be the case.

(d)  $D_H$  Values from  $f_x$ ,  $\sin \phi$ , and  $i_a/i_c$ . The standard deviation of the  $D_H$  values obtained from  $f_x$  values was smaller than from  $\sin \phi$  and  $i_a/i_c$  values, in spite of the mean  $D_H$  values being the same within experimental error (see Tables 1 and 2). The smaller deviation was due to the following reasons; in determining  $f_x$ , change in frequency of 0.5% from  $f_x$ , LISSAJOUS's figure clearly deviates from a straight line, *i. e.*, the  $f_x$  value can be determined within an accuracy of 0.5%. But in calculating these values from the figures on the X-Y chart, large deviations in  $\sin \phi$  and  $i_a/i_c$  values sometimes resulted depending on the inclination of the oval figure.

In addition to the above statement, it can be said that the searching method for  $f_x$  is most simple and easy, so that, this method was used principally in the frequency response method.

(e)  $D_H$  Values from the Time Lag Method. The  $D_H$  values from the time lag method were almost the same with those from the frequency response method for all foils, but the standard deviation of the  $D_H$  values by the latter method was smaller than by the former method.

In addition to the above results, it may be said that the  $D_H$  values by the  $f_x$  searching method have better reproducibility than those by the time lag method;  $\tau_J$  values seem to be sensitive to the interruption period of cathodic charging, but in the frequency response method such phenomena were not observed.

In view of these results, it may further be said that the frequency response method is more adequate than the time lag method.

#### (4-2) Temperature Dependency of the Diffusion Coefficients of Hydrogen and Deuterium in the $\alpha$ -phase Pd/H and Pd/D Systems

Fig. 6 shows the Arrhenius plots of the diffusion coefficients of hydrogen and deuterium observed for Pd foil of 72.4  $\mu\text{m}$  thickness in the temperature range of 0° to 40°C. The  $D$  values were calculated with observed  $f_x$  values according to Eq. (10).

From the least squares calculation, we obtained the pre-exponential term  $D_0$  and the activation energy  $E$  for hydrogen and deuterium as

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$$D_H = D_{0,H} \exp(-E_H/RT)$$

$$= 3.44 \times 10^{-3} \exp(-5.39$$

$$\times 10^3 \text{ cal}/RT) \text{ cm}^2/\text{sec},$$

and

$$D_D = 2.46 \times 10^{-3} \exp(-5.08$$

$$\times 10^3 \text{ cal}/RT) \text{ cm}^2/\text{sec},$$

respectively.

Another measurement for a Pd foil of similar thickness (70.3  $\mu\text{m}$ ) gave the same results as above.

The values of  $D_0$  and  $E$  for hydrogen and deuterium in the  $\alpha$ -phase Pd/H and Pd/D systems have been reported by many authors, as listed in Table 4.

According to the theory developed by TODA, the ratio  $D_{0,H}/D_{0,D}$  should be 1.41, which is the reciprocal of the root of the ratio of masses of hydrogen and deuterium<sup>14)</sup>; our value  $3.44/2.46 = 1.40$  is in good agreement with this theoretical value. The difference  $E_H - E_D$  was observed as  $310 \text{ cal mol}^{-1}$  which also agrees well with the

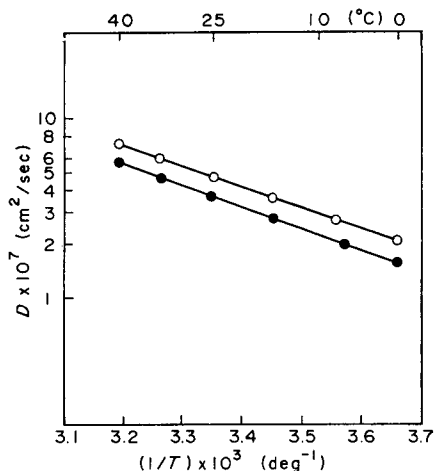


Fig. 6. Arrhenius plots of the diffusion coefficient  $D$  of hydrogen and of deuterium, observed for 72.4  $\mu\text{m}$  Pd foil.

○: deuterium, ●: hydrogen.

TABLE 4. Values of  $D_0$  and  $E$  for hydrogen and deuterium in Pd (in the  $\alpha$ -phase)

Source	Hydrogen		Deuterium		Temperature range °C	Reference
	$D_{0,H}$ cm <sup>2</sup> /sec	$E_H$ cal/mol	$D_{0,D}$ cm <sup>2</sup> /sec	$E_D$ cal/mol		
TODA	$5.96 \times 10^{-3}$	5650	$2.46 \times 10^{-3}$	4800	170-290	14)
HOLLECK	2.94	5260			260-640	15)
ZÜCHNER	3.95	5760			0-60	16)
HOLLECK and WICKE	4.5	5800			0-80	9)
BOHMHOLDT and WICKE	3.65	5600	2.5	5150	20-100	17)
SIMONS and FLANAGAN	6.1	5990			0-50	18)
VÖLKL <i>et al.</i>	2.5	5200	1.7	4750		19)
GOL'TZOV <i>et al.</i>	5.25	6200	4.46	6150		20)
KATZ and GULBRASEN	4.1	5450				21)
Present work	3.44	5390	2.46	5080	0-40	

theoretical value, estimated by the same author.

#### (4-3) Constancy of the Values of $f_{\pi}$ and $\eta$ against Cathodic Currents

Measurements of  $f_{\pi}$  and  $\eta$  for various cathodic currents were made. Observed results for Pd foil of thickness  $73.4 \mu\text{m}$  at  $25^{\circ}\text{C}$  are shown in Fig. 7. Cathodic current  $I_c$  in the figure is given in logarithmic scale. There is a fairly wide region of  $I_c$  which gives constant values of  $f_{\pi}$  and  $\eta$ . But at lower  $I_c$ ,  $\eta$  decreases with decrease in  $I_c$ . The value of  $f_{\pi}$  also showed a similar behavior as  $\eta$ . These phenomena were also observed for the foils which were pretreated in another way, in which in addition to the regular pretreatment (heating to red in a gas flame), a small quantity of Pd black was deposited on the cathodic side of the foil; but  $f_{\pi}$  and  $\eta$  in this case showed the same behavior with the foil pretreated in the regular way. The foil, heated in vacuum ( $10^{-5}$  mmHg) at  $1000^{\circ}\text{C}$  for 2 hours, showed some improvement for the relations between  $I_c \sim f_{\pi}$  and  $I_c \sim \eta$ , *i. e.*, the constancy of  $I_c \sim f_{\pi}$  and  $I_c \sim \eta$  relations extended to lower  $I_c$  region.

The range of the cathodic currents which give constant values of  $f_{\pi}$  and  $\eta$ , in Fig. 7, is about 0.5 to 5 mA/1.78 cm<sup>2</sup>, where the corresponding values of  $C_l$  are from 0.0006 to 0.006 (H/Pd), the latter value being near the upper limit value of concentration of hydrogen in the  $\alpha$ -phase. The value of 0.002 in  $C_l$  is about the center of this concentration region; this is the reason for the choice of the cathodic current, mentioned in Section (4-1). Measurements at another temperature and for foils of another thickness gave also the results that  $f_{\pi}$  and  $\eta$  are constant in the range of  $C_l$  from the upper limit value of concentration of hydrogen in the  $\alpha$ -phase<sup>22</sup> (this value varies with temperature), down to 0.002 or less than 0.002.

The decrease of  $\eta$  at lower  $I_c$  can be interpreted as having possibly

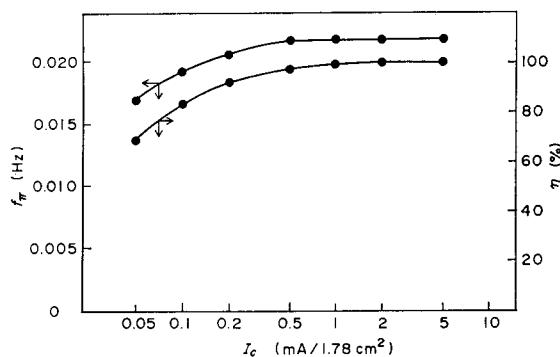


Fig. 7. Relations of frequency  $f_{\pi}$  and permeation efficiency  $\eta$  against cathodic current  $I_c$ , observed for  $73.4 \mu\text{m}$  Pd foil at  $25^{\circ}\text{C}$ .

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been caused by a partial escape of charging hydrogen into the solution at the cathodic side.

The following experiment was carried out to make clear the above effect: a small Pt electrode was placed at several millimeters upwards from the Pd foil specimen in the cathodic compartment, and the open circuit potential of this electrode referred to SCE was measured during hydrogen permeation. The potential was found to shift to the cathodic direction: this indicates that some portion of the hydrogen evolved at the foil migrates to the Pt electrode.

The cause of the decrease in  $f_c$  at lower  $I_c$  is not clear now: it can only be said that it might be caused by the deviation of the diffusion controlled permeation of hydrogen and/or by the deviation of the boundary condition at the cathodic side from the postulated condition.

### § 5. Conclusion

In the present experiments it was confirmed that the rate of permeation of hydrogen through Pd foil is determined by the diffusion process of hydrogen in Pd. Thus, it can be said that frequency response method developed in this report is a reliable method for the determination of the diffusion coefficient of hydrogen in the  $\alpha$ -phase Pd/H (or Pd/D) system.

The time lag method by a constant cathodic current of hydrogen charging was also found to be applicable to the determination of the  $D$  value, but the frequency response method gave a  $D$  value with smaller deviation than that by the time lag method.

The author expects that this frequency response method (or a developed form of this method) may be applied to diffusion studies for many other metal/hydrogen systems in the future.

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**Appendix****Solution of the Diffusion Equation by the Laplace Transformation**

The Laplace transform equation corresponding to Eq. (1) is

$$p\bar{C} - C_{t=0} = D \frac{d^2\bar{C}}{dx^2}, \quad (\text{A-1})$$

where  $\bar{C}$  is the Laplace transform of  $C$  ( $\bar{C} = \int_0^\infty C e^{-pt} dt$ ). From the initial condition (Eq. (2)),  $C_{t=0}$  is zero, and therefore Eq. (A-1) reduces to

$$\bar{C} = \frac{D}{p} \frac{d^2\bar{C}}{dx^2}. \quad (\text{A-2})$$

Eq. (A-2) is an ordinary differential equation and the solution satisfying the Laplace transform of the boundary condition (Eq. (3)), *i. e.*,  $\bar{C}=0$  for  $x=0$ , is

$$\bar{C} = R(e^{qx} - e^{-qx}), \quad (\text{A-3})$$

where  $q \equiv \sqrt{p/D}$  and  $R$  is the integral constant. Differentiating Eq. (A-3) with respect to  $x$  and replacing  $x$  by  $l$ , we have

$$\left( \frac{d\bar{C}}{dx} \right)_{x=l} = Rq(e^{ql} + e^{-ql}). \quad (\text{A-4})$$

The Laplace transform of Eq. (4) is

$$\bar{J}_c = DF \left( \frac{d\bar{C}}{dx} \right)_{x=l}, \quad (\text{A-5})$$

where  $\bar{J}_c$  is the Laplace transform of  $J_c$ . Inserting Eq. (A-4) into Eq. (A-5), we obtain

$$R = \frac{1}{DFq(e^{ql} + e^{-ql})} \bar{J}_c. \quad (\text{A-6})$$

Thus Eq. (A-3) reduces to

$$\bar{C} = \frac{e^{qx} - e^{-qx}}{DFq(e^{ql} + e^{-ql})} \bar{J}_c. \quad (\text{A-7})$$

On the other hand,  $J_a$  on the permeation side ( $x=0$ ), can be expressed as  $DF (\partial C/\partial x)_{x=0}$  and the transform is

$$\bar{J}_a = DF \left( \frac{d\bar{C}}{dx} \right)_{x=0}. \quad (\text{A-8})$$

Therefore, differentiating Eq. (A-7) with respect to  $x$  and setting  $x=0$ , we obtain

$$\bar{J}_a = \frac{2}{e^{ql} + e^{-ql}} \bar{J}_c = \frac{1}{\cosh ql} \bar{J}_c = G(p) \bar{J}_c. \quad (\text{A-9})$$

This equation shows that  $\bar{J}_a$  is given by a simple product of  $\bar{J}_c$  and  $1/\cosh ql$ , the "transfer function  $G(p)$ " of this particular diffusion system.

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In general, when a system has a transfer function  $G(p)$ , the complex response  $\varepsilon_0(j\omega)$  for the complex input  $\varepsilon_i(j\omega) = K e^{j\omega t}$  is given in the sinusoidal steady state as

$$\varepsilon_0(j\omega) = G(j\omega) K e^{j\omega t}, \quad (\text{A-10})$$

where  $G(j\omega)$  is obtained by replacing  $p$  in  $G(p)$  by  $j\omega$ .

Therefore, the sinusoidal steady state response  $\varepsilon_0(j\omega)$  for the sinusoidal input  $\varepsilon_i = i_c \sin \omega t$  is the imaginary part of  $\varepsilon_0(j\omega)$  (the real part corresponds to the response for  $\varepsilon_i = i_c \cos \omega t$ ).<sup>23,24)</sup>

By treating Eq. (A-9) in the same way, we obtain

$$\begin{aligned} G(j\omega) &= (1/\cosh ql)_{p=j\omega} \\ &= (\cosh kl \cos kl + j \sinh kl \sin kl)^{-1}, \end{aligned} \quad (\text{A-11})$$

where  $k \equiv \sqrt{\omega/2D}$  and  $q \equiv \sqrt{p/D}$  (defined as before).

Thus,

$$\begin{aligned} J_a(j\omega) &= G(j\omega) i_c e^{j\omega t} \\ &= \frac{i_c}{\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl} (A + jB), \end{aligned} \quad (\text{A-12})$$

where

$$A \equiv \cosh kl \cos kl \cos \omega t + \sinh kl \sin kl \sin \omega t$$

and

$$B \equiv \cosh kl \cos kl \sin \omega t - \sinh kl \sin kl \cos \omega t.$$

The imaginary part of Eq. (A-12) reduces to

$$J_a = \frac{i_c}{(\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl)^{1/2}} \sin(\omega t - \phi), \quad (\text{A-13})$$

where

$$\phi = \tan^{-1} (\sinh kl \sin kl / \cosh kl \cos kl), \quad (\text{A-14})$$

or

$$\phi = \sin^{-1} \left\{ \frac{\sinh kl \sin kl}{(\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl)^{1/2}} \right\}. \quad (7)$$

The diffusion equation is a linear one and in the sinusoidal steady state ( $t \rightarrow \infty$ ) the response of the constant component  $I_a(t \rightarrow \infty)/I_c$  reduces to unity as is seen in Eq. (11). Therefore, the final form of the solution is

$$J_a = I_c + i_a \sin(\omega t - \phi), \quad (5)$$

where

$$i_a = i_c (\cosh^2 kl \cos^2 kl + \sinh^2 kl \sin^2 kl)^{-1/2}. \quad (6)$$

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