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PERMEABILITIES OF HYDROGEN ISOTOPES  
THROUGH Pd-25wt % Ag ALLOY MEMBRANE  
AT COMPARATIVELY HIGH PRESSURE AND  
TEMPERATURE

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PERMEABILITIES OF HYDROGEN ISOTOPES THROUGH Pd-25wt%Ag ALLOY  
MEMBRANE AT COMPARATIVELY HIGH PRESSURE AND TEMPERATURE

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In order to obtain basic design data for the purification system in a fusion reactor fuel circulation system, permeation characteristics of a commercial palladium-silver alloy membrane for  $H_2$  and  $D_2$  were measured under comparatively high pressure (120-1300kPa) and temperature (653-853K).

Permeabilities for  $H_2$  and  $D_2$  respectively obeyed the Sieverts law, i.e., the permeation flow rates were proportional to square root pressure of hydrogen. The relation was reflected in the Arrhenius formula. Pressure dependence was observed on the diffusion coefficients for  $H_2$  and  $D_2$ . The permeation coefficient ratio was within the range of 1.54 - 1.68. The diffusion coefficient ratio was smaller than that of permeability ratio for these isotopes.

Keywords; fusion Fuel Cycle, Tritium, Hydrogen Isotope, Fuel purification Process, Palladium Alloy Membrane, Permeability, Diffusivity, Solubility, Isotope Effect

比較的高い圧力、温度におけるPd-25wt%Ag  
合金膜の水素透過特性

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トリチウムを含む水素ガス精製プロセスの1つとしてパラジウム膜法をとり上げ、実用装置の設計に必要な基礎データを得るために、市販のパラジウム・銀合金膜の $H_2$ 、 $D_2$ に対する透過特性を測定した。この結果、水素の透過流量は、比較的高い圧力(120~1300 hpa)、温度(653~853 K)においてSieverts則及びAmhenuis則に従うことが確かめられた。拡散係数については圧力依存性が見られた。なお、透過係数の比はH及びDの質量比の平方根 $\sqrt{2}$ より大きな値(1.54~1.68)が得られたが、拡散係数の比は $\sqrt{2}$ より小さな値(約1.1)となることが分かった。

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## 1. Introduction

Purification techniques of hydrogen gases are necessary for a pretreating process of hydrogen isotope separation such as cryogenic distillation and thermal diffusion in a fusion reactor fuel circulation and blanket gas circulation systems [1-5]. Permselective membrane method using palladium-silver alloy is considered to be a useful purification technique because of its very high permeability and reliability for hydrogen at high pressure and temperature [1,3].

A lot of works have been performed on the hydrogen permeation through palladium and its alloys [6-13], and a several permeation data of tritium have been reported [12].

The large permeability of hydrogen in the palladium is possibly attributed to the high solubility and the diffusivity of hydrogen isotopes in the metal systems [8]. As the permeation mechanism, it has been widely accepted Lewis's theory [13] which explains by the following mechanism; (1) dissociation of hydrogen molecules to the hydrogen atoms, (2) adsorption of the hydrogen atoms on the palladium-silver front surface, (3) diffusion through bulk metal, (4) reemergence of hydrogen from solution, (5) recombination and desorption of the molecules from palladium-silver back surface. When there were no poisoning materials such as oxide layer on the metal surface, diffusion through the bulk metal has been confirmed to be the rate-controlling step [14].

Most of the literature data had been obtained using entirely an ideal membrane prepared especially for the permeation

study. Besides, there are only a few limited measurements [8,10] on hydrogen permeation through palladium-silver alloy at high pressure above 100kPa and elevated temperature above 653K. Tube type permeation membrane should be designed as a compact and practical purification device in a fusion reactor circulation systems.

This paper represents permeabilities, diffusion coefficients and isotope effects for hydrogen and deuterium, respectively, through Pd-25wt%Ag alloy tube at the following experimental conditions; driving pressure, 120 - 1300kPa, back pressure, 0 - 100kPa and temperature range, 653 - 853K.



## 2. Experimentals

### 2.1 Apparatus

A conceptual flow sheet of the experimental apparatus, which is composed of permeation cell using commercial Pd-25wt% Ag alloy tube, is shown in Fig.1. Feed gas  $H_2$  or  $D_2$  flowing into the permeation cell is preheated before it reaches to the outer surface of the permeation tube that is made of the palladium-silver alloy. Feed pressure is regulated by control valve CV-1 and measured by Bourdon tube pressure gauge PG-1 (measuring range; 0 - 2000kPa, precision; 0.1% of full scale). Feed flow rate is measured by mass flow meter FIR-1 (measuring range; 0 - 100std.cm<sup>3</sup>- $H_2$ /min, precision; 1% of full scale).

Permeated and unpermeated gas leaving the cell are cooled to room temperature by cooling coils HX-1,2 and their pressures and flow rates are measured by the Bourdon tube pressure gauges PG-2,3 (0 - 1000kPa, 0.1%F.S.) and mass flow meters FIR-2,3, respectively. Control valves CV-2,3 are used to regulate the pressure. In the experiment, unpermeated gas flow line from HX-2 to stop valve SV-5 is only used for activation of the surfaces of the permeation tube.

Two parts of the apparatus are left out from the figure; a nitrogen feed line to keep the pressure of permeated gas flow line at atmospheric pressure after evacuating the apparatus, and a vacuum pump to evacuate down to  $1 \times 10^{-3}$  Torr for cleanup and outgassing of the whole experimental system.

In the design of the apparatus, several precautions were taken to prevent some troubles caused by the contact of the

palladium-silver alloy tube with air, lubricants and other poisoning materials. Swage locks and brazing connections were used to joint all parts of the apparatus to keep the leak rate lower than  $1 \times 10^{-6}$  atm.cm<sup>3</sup>-He/sec. Copper tube (4.35mm inner diameter) was used as the piping material for the convenience of brazing. Valves with bellow and metal seals were employed. Pippings, valves and instruments, which contact with hydrogen gas were washed by volatile organic solvent such as ethyl alcohol to avoid contamination of the permeation cell.

Fig.2 shows some details of the permeation cell and a temperature distribution around the cell heated to 420°C by electric resistance heater. The cell is constructed by an outer shell (16mm outer diameter, 12mm inner diameter, 370mm long, SUS316), an inner shell (6mm outer diameter, 4mm inner diameter, 314mm long, SUS316), palladium-silver alloy tube (1.6mm outer diameter,  $8 \times 10^{-3}$  cm thickness, 96.7mm effective length) and others. The one end of the permeation tube is sealed, and the other end is brazed on nickel tube (2.03mm outer diameter, 103mm long), as indicated in the figure. Feed gas, flowing along the annular space between the outer and the inner shell, enters to the outer surface of permeation tube.

The palladium-silver alloy tube was manufactured by Japan Pure Hydrogen Company, Ltd.. The nominal content of silver in the alloy is 25wt%. The purity of gases used in the experiment was ordinary commercial grade; hydrogen, 99.96% up, deuterium, 99.8% up, and nitrogen, 99.99% up, respectively.

## (1) Calibration of temperature and flow rate

Six sets of chromel-alumel thermocouples for measuring the temperature are welded at each interval of 2cm on the outer surface of the permeation cell. A similar thermocouple for the control of the heater is positionned in the middle of the electric resistance heater. The permeation temperature is calculated by averaging the outputs of six thermocouples. Temperature distribution is observed along the longitudinal direction of the permeation cell, as shown in the Fig.2. Consequently, the calculated permeation temperature have an uncertainty of about 30°C considering an accuracy within  $\pm 4^\circ\text{C}$  of the heater controller.

Calibration of the mass flow meters for  $\text{H}_2$  and  $\text{D}_2$  gases at normal pressure and temperature was carried out using a standard soap bubble flow meter. Fig.3, a result of the calibration, shows that linearity of the readings output of the mass flow meter FIR-2 is obtained within whole measuring range and a value 0.9285 as the correction factor of the readings can be used for both gases. Besides, it is well known that the sensitivity of the meter varies with the change of gas pressure flowing through the transducer. To exclude the pressure dependence on the mass flow meter FIR-2 at the initiation of the permeation experiment, the permeated gas flow line is filled with nitrogen gas at about 100kPa. Here, the sensitivity for nitrogen is almost equal to that for hydrogen.

## (2) Activation of palladium-silver alloy tube

Permeation characteristics of hydrogen isotopes through palladium and its alloys are considered to be affected by conditions of the metal surface [14]. In the experiment, following activation treatment was successfully carried out to exclude poisoning materials on the surface of the permeation tube; baking of the tube by air purge at about 700K followed by evacuating down to  $1 \times 10^{-3}$  Torr, and reducing by  $H_2$  or  $D_2$  gas at permeation temperatures for long period until permeation comes to a steady flow rate at each condition. If some decrease of permeability is observed during experiment, above activation is repeated. In addition, while the measurements are rested, the apparatus is filled with  $H_2$  or  $D_2$  at a permeation temperature.

## 2.2 Procedures

Several methods have been reported to study the permeation of hydrogen [12]. In this work, permeation time lag method [8-11] has been employed to measure both permeability and diffusion coefficient. Measurements could be successfully carried out with the present apparatus. Care is taken to evacuate the residual gases in the permeation cell.

Fig.4 shows a typical recording of feed and permeated flow rate of hydrogen against time. The delay time,  $\tau = t_f - t_0$ , are defined by the time elapsed until the first hydrogen appears at the low-pressure side of the permeation tube.

The initial time  $t_0$  is determined by the increase of the feed flow rate, and  $t_T$  is evaluated from the extrapolated time, as indicated in the figure. The  $\tau$  is calculated by averaging the results of three runs carried out under the same conditions. Steady state permeation flow rates are obtained by the recordings of constant values against time, because the constant pressure difference of hydrogen gas is maintained from high to low pressure side in the permeation tube.

### 3. Results and discussions

Diffusion through the bulk metal can be assumed to be the rate-controlling step for the permeation of hydrogen isotopes. Following discussion is carried out by using Fick's theory of diffusion by the assumption that diffusion coefficient is independent of the concentration of hydrogen dissolved in the palladium-silver alloy [7].

Fig.5 shows the steady state permeation fluxes  $J_H$  and  $J_D$  ( $\text{mol}/\text{cm}^2 \cdot \text{min}$ ) for  $H_2$  and  $D_2$  at each constant temperature against the difference of the hydrogen pressures. Here,  $P_H$  and  $P_L$  are the driving pressure and back pressure in the permeation cell, respectively. The fluxes are calculated by effective area  $A$  of the permeation tube.

$$A = \frac{2\pi l(r_2 - r_1)}{\ln\left(\frac{r_2}{r_1}\right)} \quad \text{-----}(1)$$

where  $r_1$  and  $r_2$  are the inner and outer radius, respectively and  $l$  is the effective length.

Assuming that the permeation occurs only perpendicular direction to the surface of permeation tube, and that a linear concentration gradient is formed in the metal, the flux  $j$  ( $\text{mol}/\text{cm}^2 \cdot \text{sec}$ ) can be expressed by Fick's first law;

$$j = -D \frac{dC}{dr} \quad \text{-----}(2)$$

where  $D$  ( $\text{cm}^2/\text{sec}$ ) is diffusion coefficient,  $C$  ( $\text{mol}/\text{cm}^3$ ) is hydrogen concentration and  $r$  (cm) is the coordinate chosen

perpendicular to the reference surface. Integration of equation(2) for cylindrical geometry with the concentration independent D gives;

$$j = D \frac{C_1 - C_2}{r_1 - r_2} \quad \text{-----(3)}$$

where  $C_1$  and  $C_2$  are the concentrations equilibrated with hydrogen pressures  $P_H$  and  $P_L$  at the both sides of the permeation tube. Equation(3) indicates the permeation flux can be evaluated by the product of the diffusion coefficient D and the solubility gradient  $(C_1 - C_2)/(r_1 - r_2)$ .

Now, Sieverts law .i.e. the square-root relationship between solubility and pressure, has been given for hydrogen-metal system in the low hydrogen pressure range. By using this relation, a practical evaluation function related to operating conditions is derived as;

$$\left. \begin{aligned} W &= 60Aj \\ &= K \exp\left[-\frac{E_p}{RT}\right] \cdot \left(\frac{A}{\Delta}\right) \cdot (\sqrt{P_H} - \sqrt{P_L}) \end{aligned} \right\} \quad \text{-----(4)}$$

where W (mol/min) is the permeation flow rate of the permeation cell, K (mol.cm/cm<sup>2</sup>.min.√kPa) is the Sieverts constant,  $E_p$  (cal/mol) is the activation energy for permeation, R (cal/mol.K) is the gas constant, T (K) is the temperature and  $\Delta$  (cm) is the thickness of the permeation tube. The equation means the permeation flow rate is inversely proportional to the thickness

$\Delta$ , and proportional to the square-root pressure difference ( $\sqrt{P_H} - \sqrt{P_L}$ ). Temperature dependence is represented by Arrhenius formula. In the equation(3) and (4), activation energy term includes the energy for both solubility and diffusion coefficient of hydrogen isotopes.

Rewriting the equation(4), permeability  $Q$  (mol.cm/cm<sup>2</sup>.min.  $\sqrt{kPa}$ ) is represented by;

$$Q = \frac{W \cdot \Delta}{A} \cdot \frac{1}{\sqrt{P_H} - \sqrt{P_L}} = K \exp\left[-\frac{E_p}{RT}\right] \quad \text{----- (5)}$$

Fig.6 shows the pressure dependence of the permeation fluxes for  $H_2$  and  $D_2$ . Most of the data at each temperature lie on straight lines which should intersect the origin. This result indicates square-root pressure dependence for the permeation of hydrogen isotopes. The dependence can be adopted at relatively high pressure. Fig.7 shows a typical plot of the fluxes at constant pressure differences against reciprocal temperature. The observed systematic temperature dependence indicates that an approximation of the Arrhenius's relation could be effective within this experimental conditions. Solid and dotted lines in the figure represent a tendency of permeation fluxes to the reciprocal temperature,  $1/T$ .

Fig.8 shows the Arrhenius plot of  $Q_H$  and  $Q_D$  against  $1000/T$  for  $H_2$  and  $D_2$ . Here, plotted values at each temperature are calculated by averaging the data obtained in the pressure range of 120 - 1300kPa. Following experimental equations for



the permeabilities, expressed by two lines in the figure, are determined by least-squares method.

$$Q_H = 7.31 \times 10^{-7} \exp\left[-\frac{1370}{RT}\right] \quad \text{----- (6)}$$

$$Q_D = 4.78 \times 10^{-7} \exp\left[-\frac{1470}{RT}\right] \quad \text{----- (7)}$$

where  $Q_H$  and  $Q_D$  are the permeabilities for  $H_2$  and  $D_2$ , respectively. The activation energy of the permeability for  $H_2$  is smaller than that for  $D_2$ . In order to evaluate the isotope effect on the permeability, the ratio  $Q_H/Q_D$  is plotted. A straight line calculated by equation (6) and (7) are shown in Fig.9. Here, the straight line is given by;

$$\frac{Q_H}{Q_D} = 1.53 \exp\left[\frac{100}{RT}\right] \quad \text{----- (8)}$$

The values obtained at 833K and 853K are little scattered from the straight line. This is considered to be resulted mainly by the uncertainties of temperature distribution in the permeation tube. The values decrease from 1.68 to 1.54 with the increase of the temperature from 653K to 853K. In the figure, the data from earlier investigators are simultaneously shown to compare with our results. The value of Tanaka [15] was obtained by a thin disk of palladium at very low driving pressure. The experimental condition of the data by Ackerman [10] are; permeation membrane, Pd-25wt%Ag tube, driving pressure, 600 - 2200kPa, back pressure, 120 - 700kPa.

Considering the differences of experimental conditions, it can be concluded that the earlier data well agree with our results. Now, note that in the permeability ratio, mass effect is larger than that of classical theoretical value of diffusion coefficient ratio  $\sqrt{2}$ .

Fig.10 shows pressure dependence of diffusion coefficients  $D_H$  and  $D_D$  for  $H_2$  and  $D_2$  at constant temperatures. In our experiment, permeation time lag method is used, therefore, Fick's second law with following initial and boundary conditions can be successfully adopted under the previous assumptions.

$$\frac{\partial C}{\partial t} = D \left( \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad \text{----- (9)}$$

$$\left. \begin{array}{l} C = C_0 = 0, \quad r_1 < r < r_2 \quad \text{at } t = 0 \\ C = C_1 = 0, \quad r = r_1 \\ C = C_2, \quad r = r_2 \end{array} \right\} \text{at } t > 0 \quad \text{----- (10)}$$

where  $t$  is time.

The solution of the above diffusion equation, as given by Crank [7], is represented by;

$$D = \frac{(r_1^2 - r_2^2) + (r_1^2 + r_2^2) \ln \frac{r_2}{r_1}}{4 \tau \ln \frac{r_2}{r_1}} \quad \text{----- (11)}$$

When hydrogen concentration  $C_1$  at  $r = r_1$  is negligibly small and the other two conditions are valid, this equation gives the diffusion coefficient.

A marked increase of the diffusion coefficients  $D_H$  and  $D_D$  with increasing of the driving pressure  $P_H$  is observed. Also, there is a tendency coming to constant value in each temperature. Because, most of the earlier works of the hydrogen permeation had been carried out at low pressure, no discussion of the pressure effect on the diffusion coefficient had been reported. Besides, the dissociation and the adsorption steps of the hydrogen permeation had not been taken into account in the measurement by the permeation time lag method. However, in the case of the experiment for very thin membrane at high pressure, effect on the delay time by these steps can not be negligible. Moreover, it is considered that the exothermic heat of solution may affect the diffusivity. Study by Hickman indicated that Sieverts law and pressure dependence of the diffusion coefficients for  $H_2$  and  $D_2$  are held in the range 0 - 0.2 of hydrogen to metal ratio.

Fig. 11, the temperature dependence of the diffusion coefficient, shows our experimental results and the earlier data. Lines by this work are represented by following experimental equations, which are obtained from data at 800kPa.

$$D_H = 2.82 \times 10^{-5} \exp\left[-\frac{2100}{RT}\right] \quad \text{-----} \quad (12)$$

$$D_D = 2.60 \times 10^{-5} \exp\left[-\frac{2160}{RT}\right] \quad \text{-----} \quad (13)$$

These results indicate that the Arrhenius formula is valid in the range of this study.

Fig. 12, the Arrhenius plot of the diffusion coefficient ratio, shows our experimental result and the earlier data summerized by Alefeld [12]. Data for Nb, V and Ta which have the bcc structure are shown in order to compare the isotope effect on the diffusion coefficient with those for Pd having the fcc structure. Although some difference among the published data obtained for Pd at low hydrogen concentration is observed, Gol'tsov's data [19] agree well with our result.

It is noticed that whole data of the ratio,  $D_H/D_D$ , are smaller than  $\sqrt{2}$ , which has been given by classical relationship [20,21]  $D_1/D_2 = \sqrt{m_2/m_1}$ , where  $D_1, D_2$  and  $m_1, m_2$  are the diffusion coefficients and atomic mass of hydrogen isotopes, respectively. However, a consistent temperature dependence has not been obtained for tritium. In constrast to Pd, the values of  $D_H/D_D$  for the bcc metals are  $\sqrt{2}$  at about 673K and increase with the decrease of the temperature. The similar temperature dependence is shown for the relation between hydrogen and tritium.

Following relationship can be easily derived from the equation (3) and Sieverts law, i.e.,  $C = k/P$ ;  $C$  (mol/cm<sup>3</sup>) is solubility,  $P$  (kPa) is the driving pressure and  $k$  (mol/cm<sup>3</sup>· $\sqrt{\text{kPa}}$ ) is the Sieverts constant.

$$\frac{Q_H}{Q_D} = \frac{D_H}{D_D} \cdot \frac{k_H}{k_D} \quad \text{----- (14)}$$

where,  $k_H$  and  $k_D$  are the Sieverts constant for  $H_2$  and  $D_2$ , respectively.

The values of  $k_H/k_D$  determined by equation (8), (12), (13) and (14) are 1.46 - 1.47 in the temperature range of 693-893K. Calculated values from the solubility data by Hickman are 1.4 - 1.5 in the range of 573 - 773K. From these results, it can be concluded that the disagreement of the values between the permeability ratio and the diffusion coefficient ratio is caused by the large isotope effect on the solubility of hydrogen.

#### 4. Conclusion

Permeation of  $H_2$  and  $D_2$  through commercial Pd-25wt%Ag alloy membrane at comparatively high pressure and temperature were proved to obey Sieverts law. Arrhenius formulas were held for permeability and diffusion coefficient. Permeability ratio was larger than the square root of isotopic mass ratio, whereas diffusion coefficient ratio was much smaller than the square root of the isotopic mass ratio. A large isotope effect on the solubility was also estimated.

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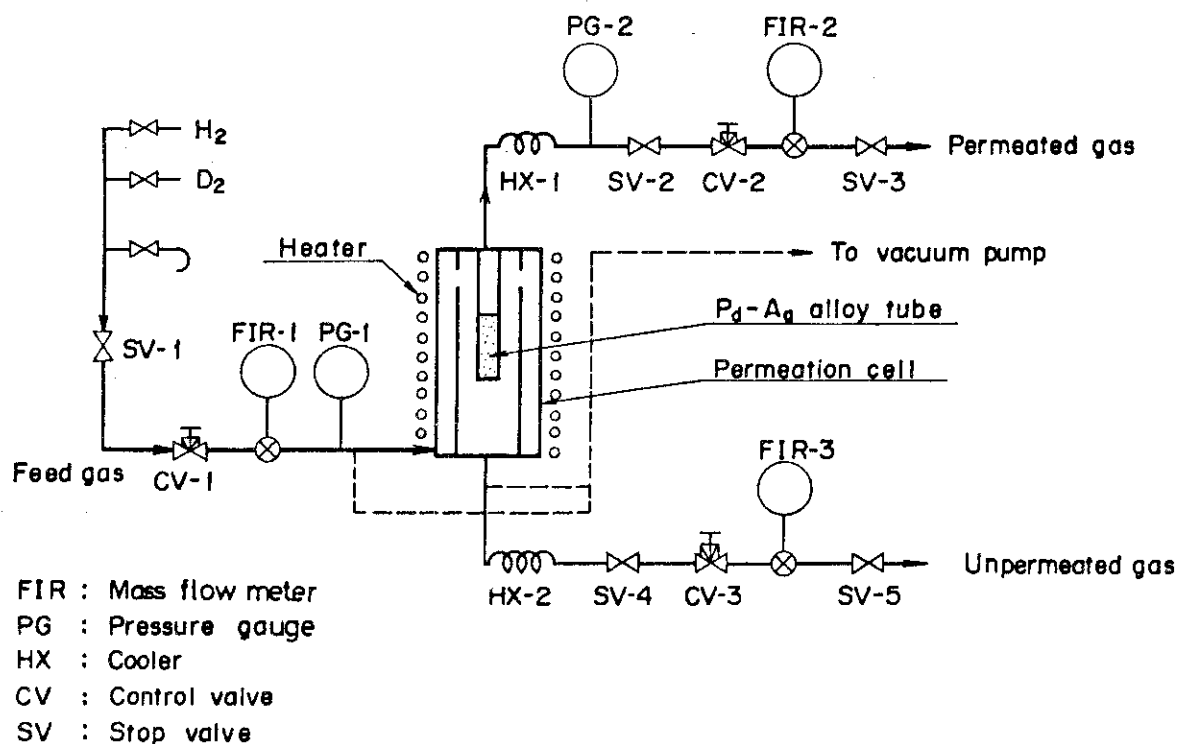


Fig.1 Conceptual flow sheet of experimental apparatus.

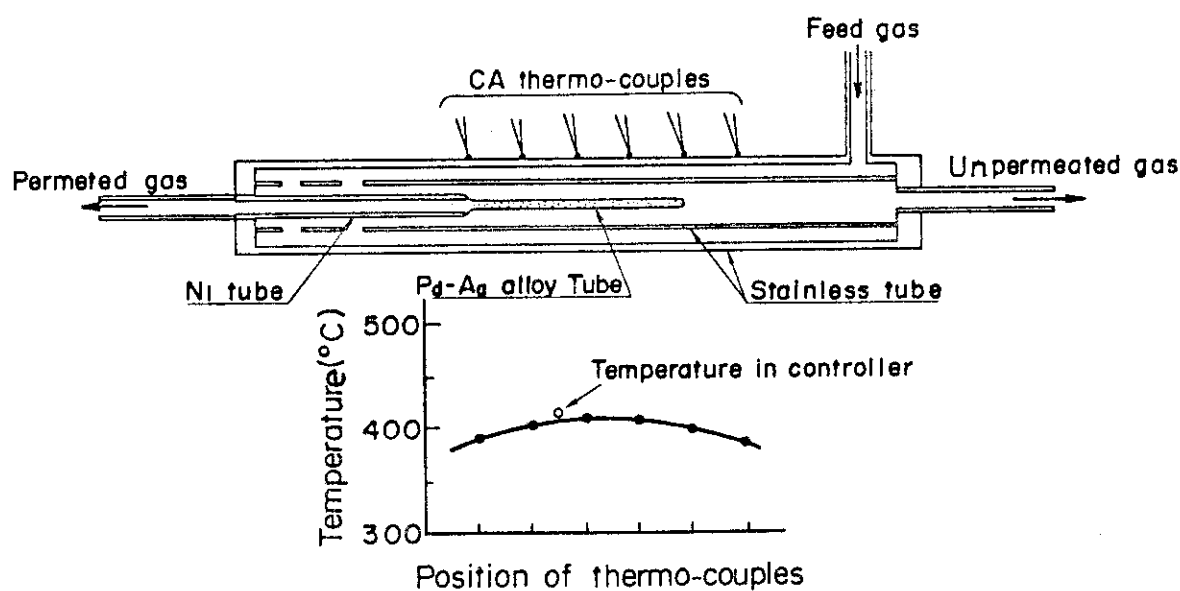


Fig.2 Details of permeation cell and sets of temperature measurement. Temperature distribution was yielded at 420°C on the heater controller.

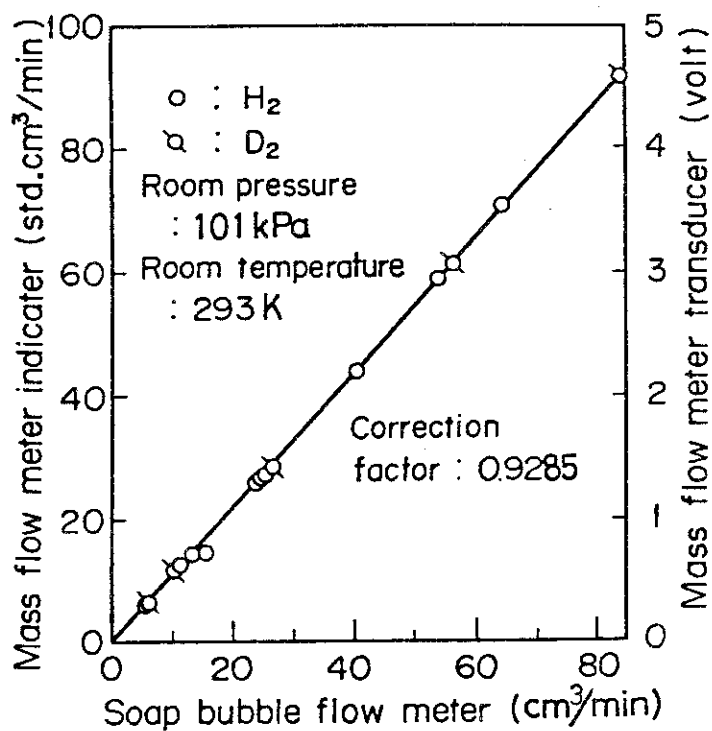


Fig.3 Calibration results of mass flow meter for H<sub>2</sub> and D<sub>2</sub>.

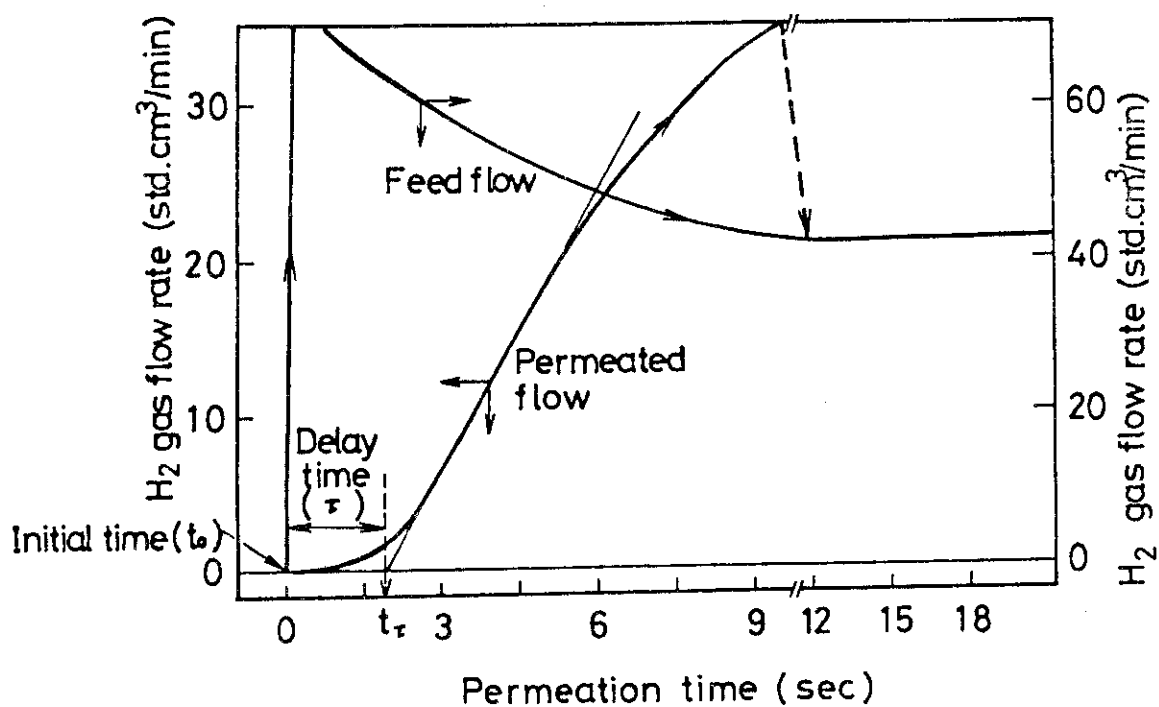


Fig.4 Typical permeation time lag records obtained in this work. driving pressure; 390kPa, back pressure of H<sub>2</sub>; vacuum (at initial), 101kPa (at steady state), permeation temperature; 773K

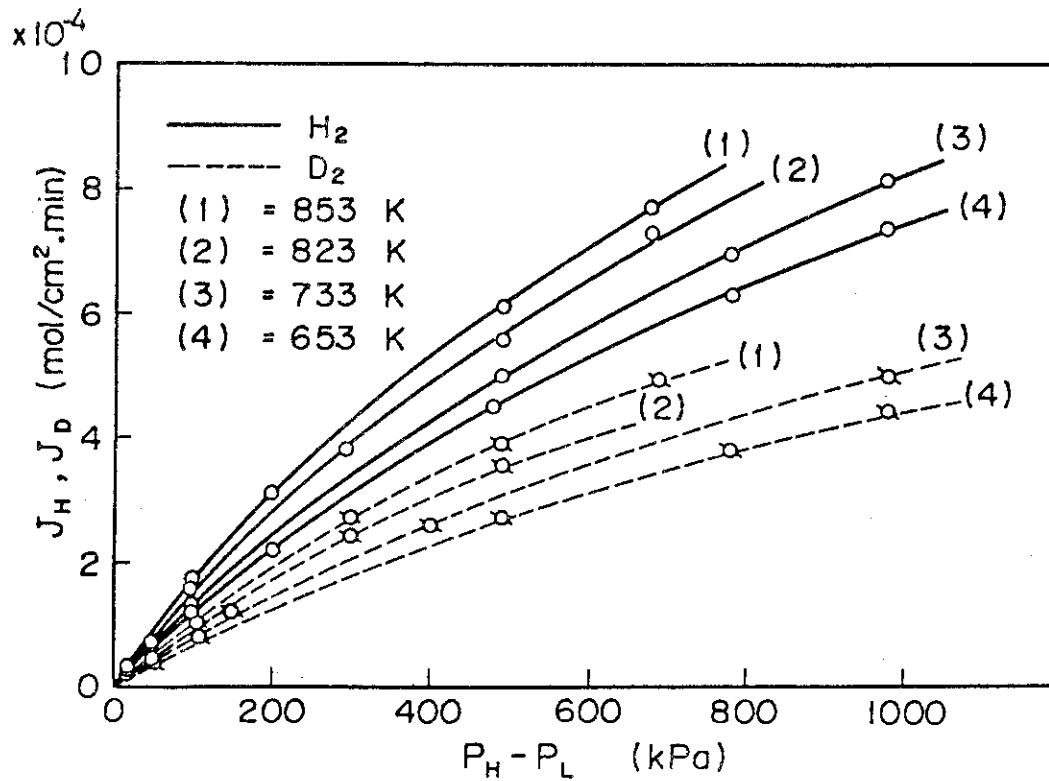


Fig.5 Permeation fluxes of  $H_2$  and  $D_2$  at several temperatures against the pressure differences of the permeation cell.

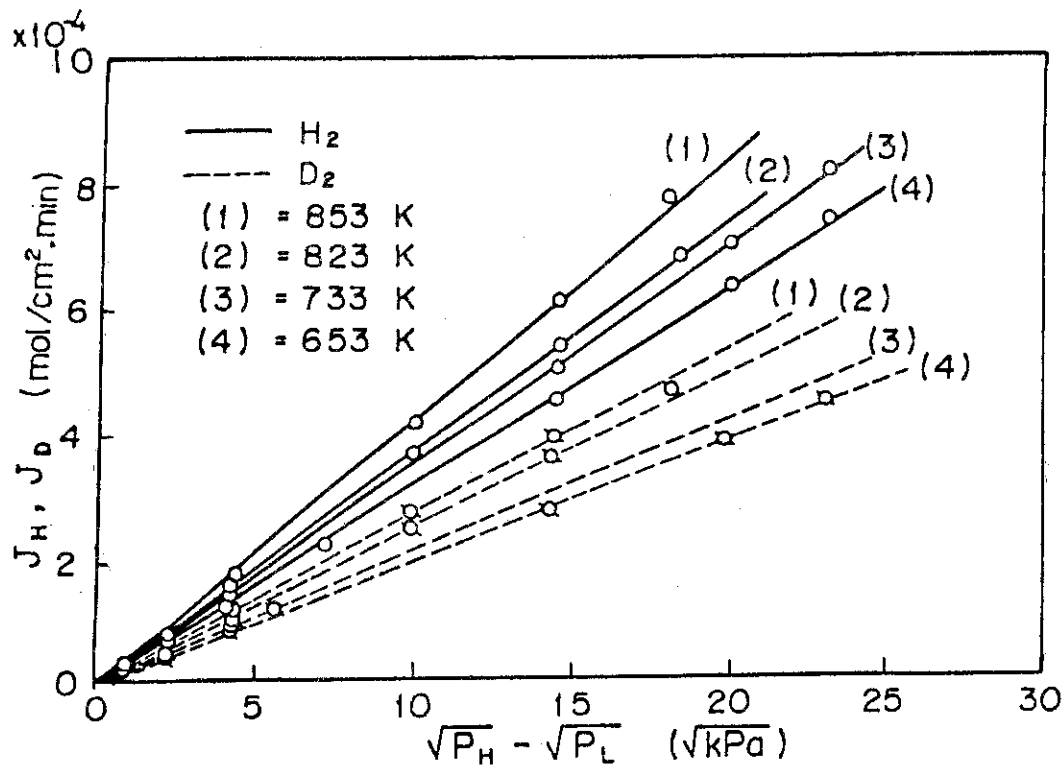


Fig.6 Permeation fluxes of  $H_2$  and  $D_2$  at several temperatures against the square root difference of the pressures of permeation cell.

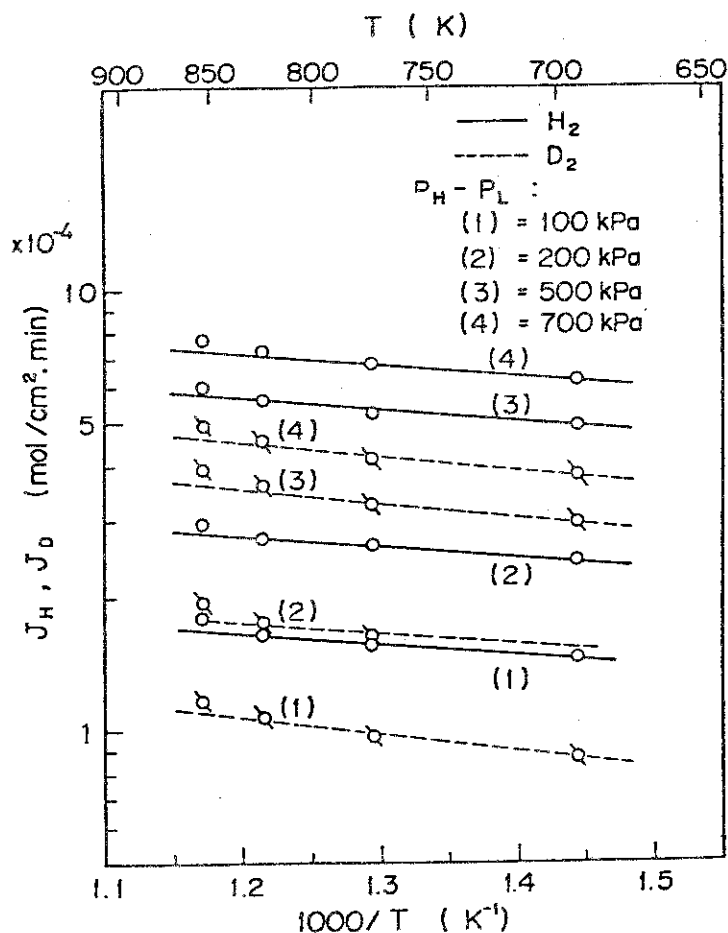


Fig.7 Temperature dependence of permeation fluxes of  $H_2$  and  $D_2$  in different pressures.

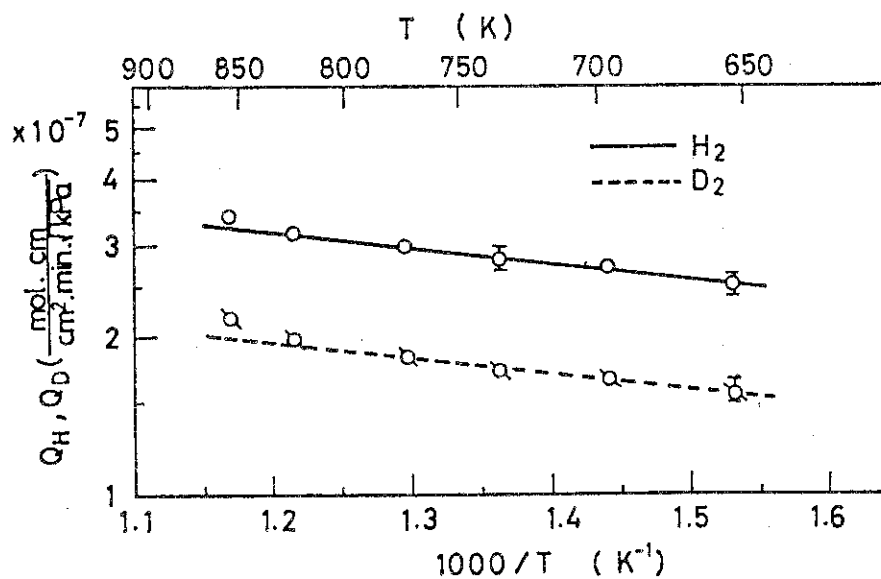


Fig.8 Temperature dependence of permeation coefficients for  $H_2$  and  $D_2$ . driving pressure  $P_H$ ; 100 - 1000kPa, back pressure; 101kPa

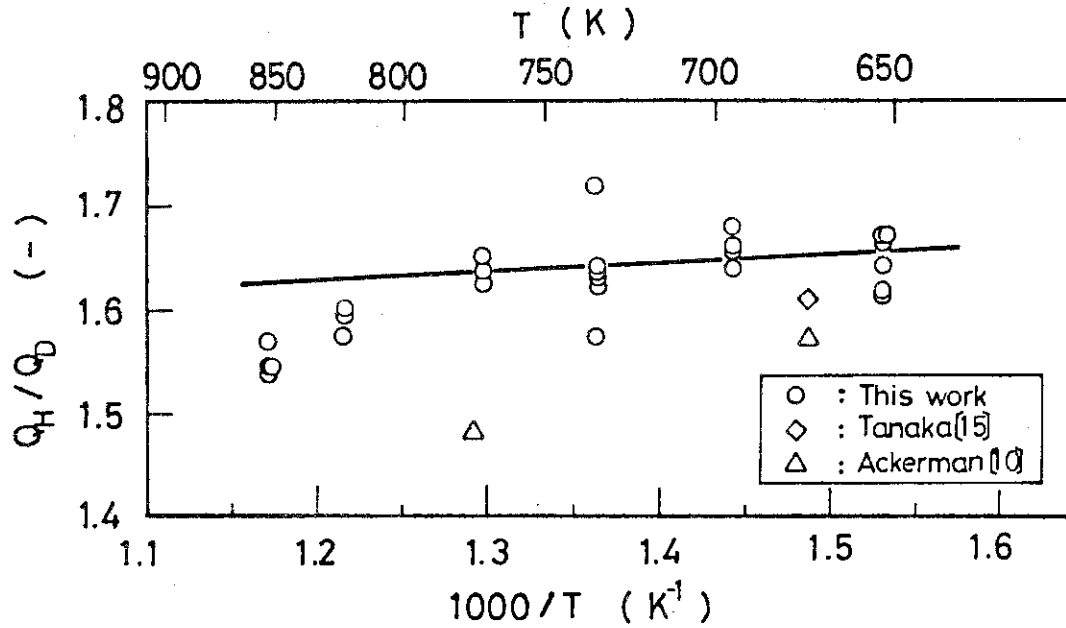


Fig.9 Temperature dependence of permeation coefficient ratio for  $H_2$  and  $D_2$ . Solid line corresponds to the experimental equation obtained by this work.

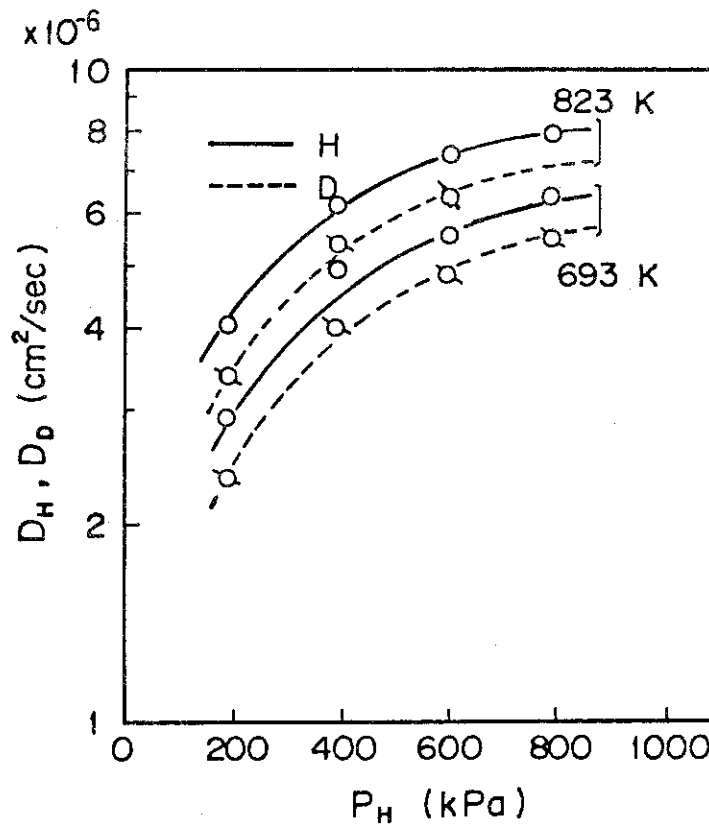


Fig.10 Pressure dependence of diffusion coefficients for  $H_2$  and  $D_2$  obtained by permeation time lag method.

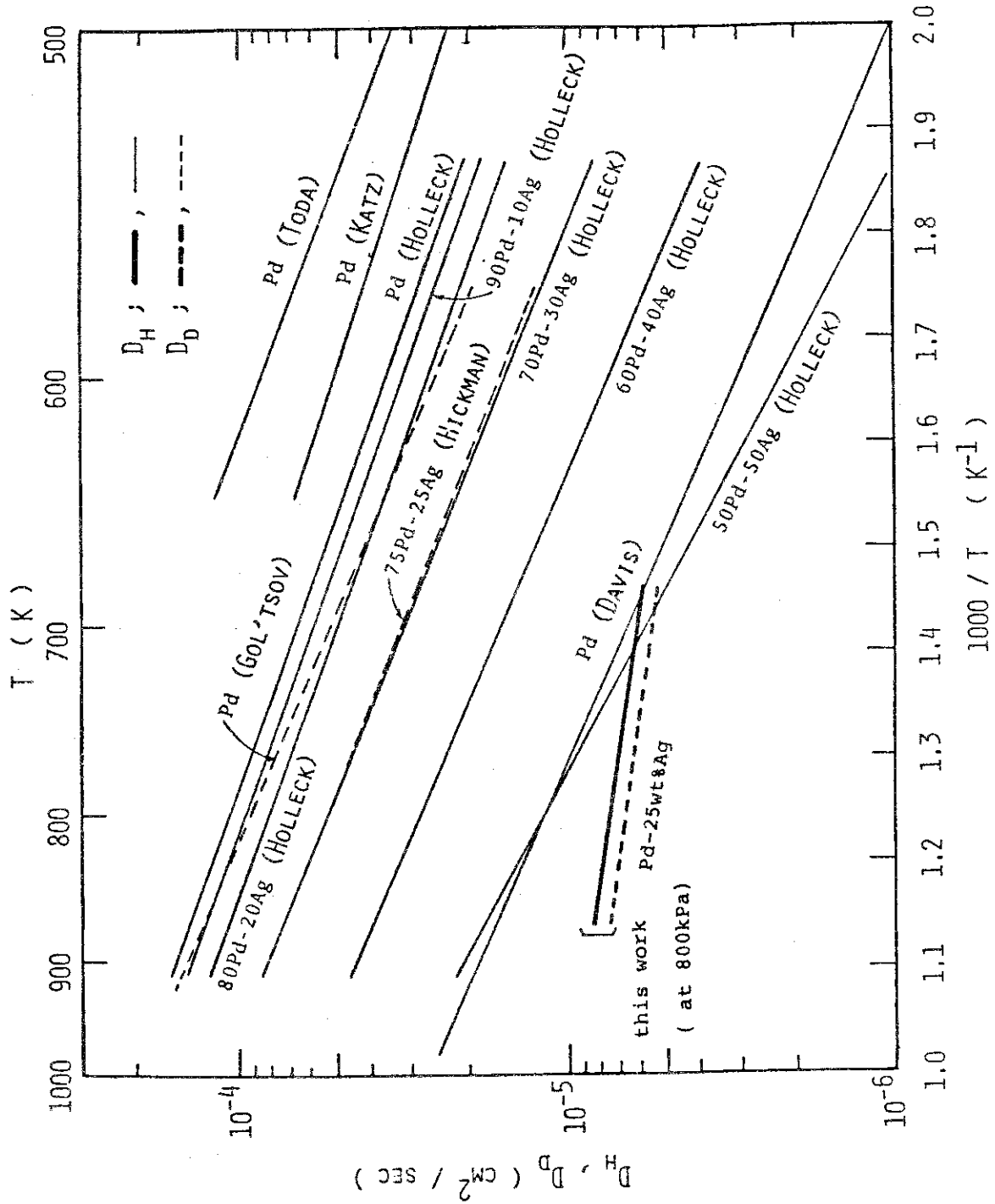


Fig.11 Temperature dependence of diffusion coefficients for  $H_2$  and  $D_2$ .

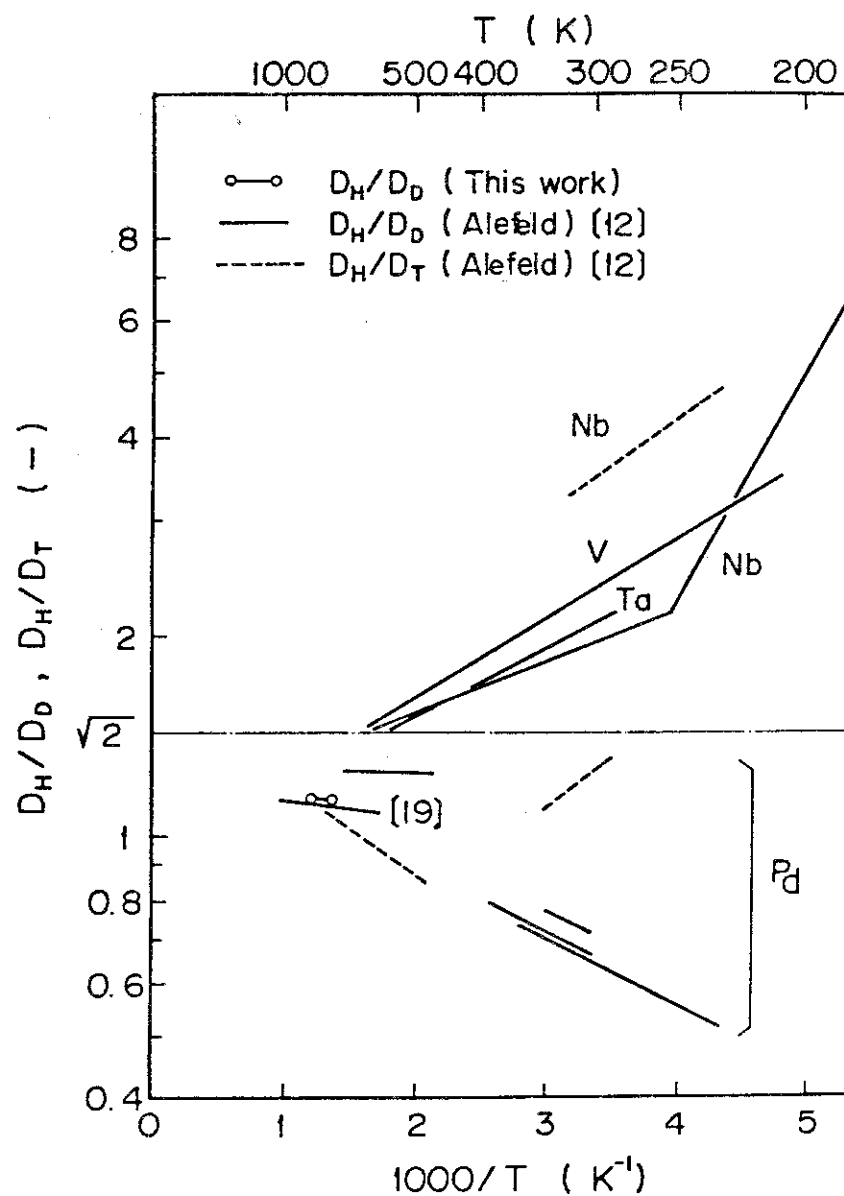


Fig.12 Temperature dependence of diffusion coefficient ratio for hydrogen isotopes in various metals [12].