Counter-diffusion and counter-permeation of deuterium and hydrogen through palladium

Kaname Kizu [a], Tetsuo Tanabe [b,*]

[a] *Department of Nuclear Engineering, Graduate School of University, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

[b] *Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

Abstract

Experiments for counter-diffusion and counter-permeation of deuterium and hydrogen through a palladium membrane (25 μm thick) were performed. Deuterium permeation rates as a function of upstream D_2 pressure were measured under condition where hydrogen permeated in the opposite direction by supplying H_2 gas at the 'other' side (downstream, corresponding to D permeation) of the membrane. It was found that significant deuterium permeation occurred even when the deuterium upstream pressure was much smaller than the hydrogen downstream pressure. The deuterium permeation rate was gradually reduced by increasing the downstream H_2 pressure and the corresponding counter H permeation. The deuterium permeation rate under counter H permeation can be represented reasonably well by a simple model in which the ratio of the deuterium permeation rates with and without counter H permeation are assumed to be proportional to the fractional concentration of deuterium in the bulk. However, as the hydrogen counter flow increases, the deuterium permeation rate deviates from the model. This implies that adsorption (absorption) of D_2 from the gas phase may be inhibited, and also surface recombination of deuterium may be blocked by hydrogen. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Tritium permeation through the first wall and blanket system is one of the most important safety issues for a fusion reactor. Various efforts have been made to estimate the permeation rate [1], and concepts have been proposed for the reduction of tritium inventory [2], e.g. addition of surface barriers [3,4]. In most cases, only the permeation from the plasma or blanket side to the cooling side has been considered. At the cooling side, however, hydrogen uptake which is accompanied by water corrosion of the wall [3], may lead to the permeation of dissolved hydrogen from the cooling side to the plasma side. Accordingly, tritium and hydrogen may be permeating in opposite directions. Until now, such counter-diffusion and counter-permeation have not been examined.

Before discussing the details of the counter-permeation mechanism of the three hydrogen isotopes (hydrogen, deuterium and tritium), we need reliable data for understanding the two component (H, D) counter-permeation mechanism. In the present work, we have conducted the first counter-permeation experiment (to the author's knowledge) using a new experimental system in which deuterium and hydrogen permeate in opposite directions.

2. Experiment

Fig. 1 shows the permeation apparatus. The system was separated into two vacuum chambers by a palladium membrane. Both chambers were evacuated with rotary pumps and turbo-molecular pumps. The base pressure of the system was maintained below 1×10^{-6} Pa and was measured by an ionization vacuum gauge. For convenience, the chambers are referred to as ''D side'' and ''H side'', corresponding to where the deuterium

* Corresponding author. Tel.: +81-52 789 5177; fax: +81-52 789 5177; e-mail: tanabe@cirse.nagoya-u.ac.jp.
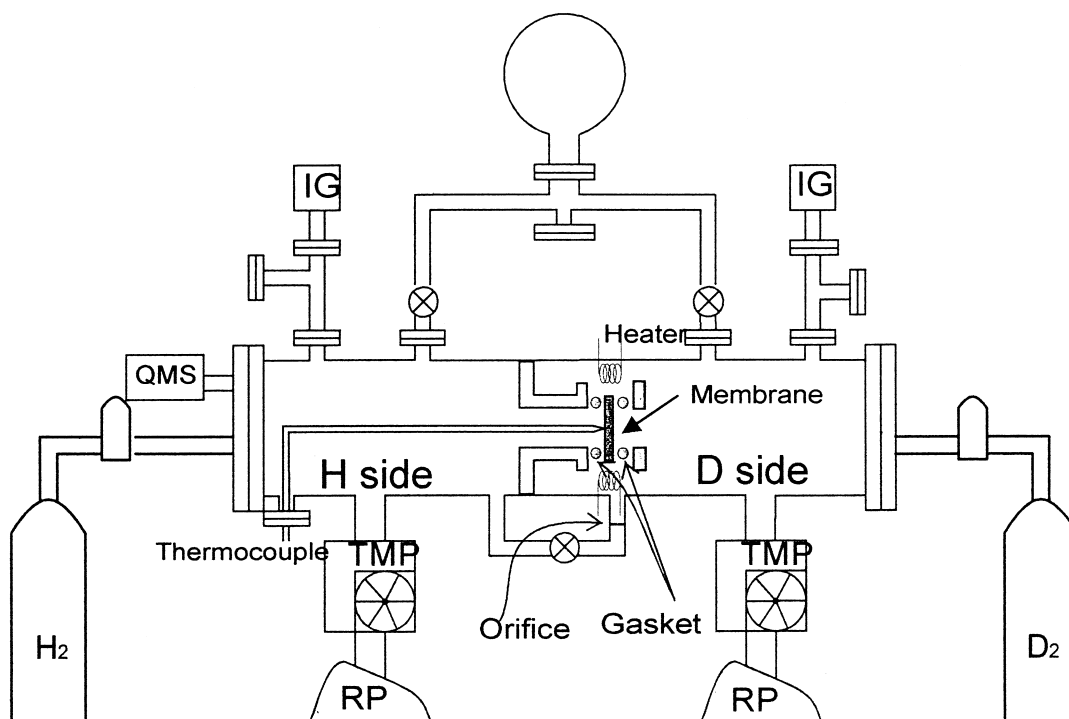
Fig. 1. Schematic diagram of the apparatus for counter-permeation measurements.

gas and the hydrogen gas were injected, respectively. The injected deuterium and hydrogen gas pressure in the chambers was monitored by ionization vacuum gauges (IG) and a quadrupole mass spectrometer (QMS). The relative sensitivity factor of the ionization vacuum gauge for hydrogen was calibrated to be 0.4 and the pumping speed of the system was 1.0×10^{-1} m^3 s^{-1}.

Two types of counter-permeation experiments were carried out. (i) After introducing H$_2$ gas into the H side chamber at a fixed pressure to obtain a steady state permeation of hydrogen to the D side (where initially deuterium pressure was equal to zero), D$_2$ gas was introduced into the D side, and the permeating D$_2$ flux to the H side was measured by QMS. With the H$_2$ pressure kept constant on the H side, the D$_2$ pressure on the D side was raised step-wise, and the resulting permeating D$_2$ flux to the H side was measured. (ii) In another set of experiments, H$_2$ gas was introduced into both sides in addition to the D$_2$ in the D side chamber, in order to measure the steady-state D$_2$ permeation.

The deuterium permeation rate ($Q(t)$) through the membrane was determined from measurements of the partial pressure increment at the H side ($\Delta P D_2(t)$) multiplied by the effective pumping speed of the system (S_{eff}):

$$Q(t) = \frac{\Delta P D_2(t) \times S_{\mathrm{eff}}}{RT}, \tag{1}$$

where R and T are the gas constant and the temperature of the system, respectively. The steady state permeation rate is given by,

$$J(\infty) = \frac{Q(\infty)}{A}, \tag{2}$$

where A is the surface area of the membrane.

In the present work, we could not determine the deuterium partial pressure on the H side directly. The permeated deuterium atoms must be equilibrated with H$_2$ at the Pd membrane surface and are released as D$_2$ ($m/e = 4$) and HD ($m/e = 3$). However, the H$_2$ pressure on the H side was high enough to produce H$_3$ molecules ($m/e = 3$) in the ionizer of the QMS which was several orders of magnitude larger than the observed HD. Therefore, we estimated the partial pressure of deuterium in the H side chamber from the D$_2$ signal ($m/e = 4$) in the QMS which was calibrated using a gas mixture of D$_2$ + H$_2$ in equilibrium in a separate system, assuming that the released D$_2$, HD and H$_2$ molecules were in equilibrium in the H side chamber. This procedure would give rise to a maximum uncertainty of about $\pm 25\%$ when deuterium pressure was the minimum.

The Pd membrane (with a purity of 99.95%) was supplied by Nilaco, Japan. The thickness of the membrane was 0.025 mm with a surface area of 1.8×10^{-4} m^2. The membrane was fixed on a stainless steel sample holder using Cu metal gaskets without any vacuum

leaks, and heated to 1000 K using a molybdenum heater. The sample temperature was measured using a K-type thermocouple. Measurements were performed at a temperature of 840 K for D_2 pressures ranging from 7×10^{-4} to 3 Pa on the D side, and the H_2 pressure was set at either: 1.3×10^{-1} or 6.7×10^{-2} or 2.7×10^{-2} Pa.

3. Results and discussion

At first, a normal deuterium gas-driven permeation experiment was conducted without H_2 gas in the H side chamber. For the first permeation experiment, the hydrogen permeation rate was characterized by an initial increase, followed by a quasi-steady state behavior. The quasi-steady state permeation rate, however, continued to increase very slowly and several hours were needed to attain a true steady state [5] where the permeation rate showed no further change. All values of $J_D(\infty)$ in the present work were thus determined after the true steady state was attained. The dependence of the steady-state permeation rate on the deuterium pressure in the D side chamber, with the Pd at 840 K is shown in Fig. 2. The solid line in the figure shows a linear dependence of the pressure. This implies that deuterium permeation in Pd in the present pressure range is a surface rate limited process, and not a diffusion limited process. This is consistent with the results of Andrew and Haasz [6] who found that H_2-driven permeation in Pd was controlled by surface-limited processes for pressures $\lesssim 1$ Pa.

Fig. 3 shows sequential changes of deuterium permeation rates against D_2 pressure with a fixed H_2 pressure in the H side chamber (with no H_2 in the D side chamber). The rates were normalized by the values obtained without H_2 gas on the H side. The deuterium
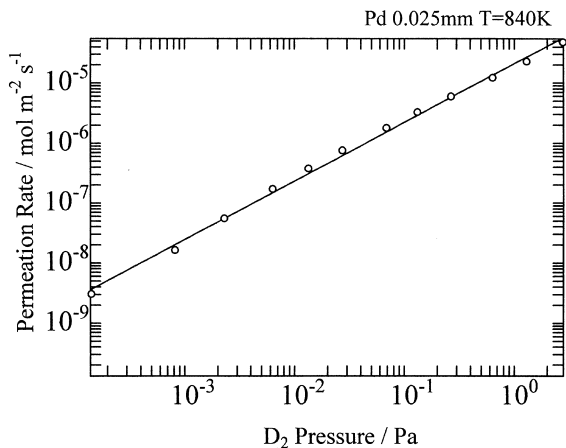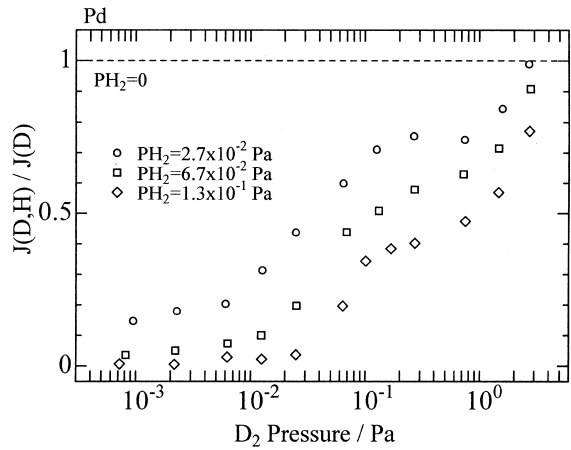

Fig. 3. Normalized deuterium permeation rates as a function of D_2 pressure with counter hydrogen permeation (i.e., D_2 on the D side and H_2 on the H side).

permeation was clearly suppressed by the existence of H_2 in the H side chamber. However, it is noted that a significant amount of deuterium permeated even when the H_2 pressure (on the H side) was higher than the D_2 pressure on the D side ($PD_2 < PH_2$).

Fig. 4 shows results of another type of experiment where H_2 gas was introduced into both chambers at a fixed pressure. In Fig. 4, some of the data from Fig. 3 are superposed as open symbols. Full circles were obtained under the same H_2 pressure on both sides, whereas full squares represent the data obtained when the H_2 pressure on the D side was higher than on the H side, i.e. D and H permeate in the same direction. We

Fig. 2. The deuterium pressure dependence of the steady-state deuterium permeation rate with D_2 on the D side, and no H_2 on either side.
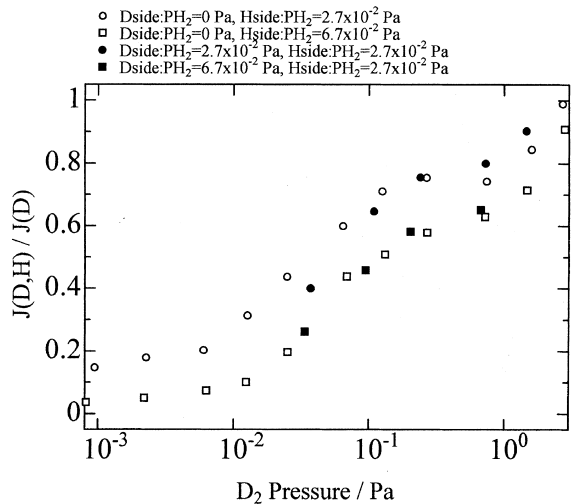

Fig. 4. Normalized deuterium permeation rates with (i) both counter- and co-permeation (full symbols) of H, and (ii) only counter-permeation (open symbols) of H.

note that the open and full symbols are overlapped for D_2 pressure $\gtrsim 10^{-1}$ Pa. We also note that co-diffusion (full squares) where the H_2 pressure on the D side (6.7×10^{-2} Pa) was higher than that on the H side (2.7×10^{-2} Pa) gives the same deuterium permeation that was obtained with 6.7×10^{-2} Pa H_2 on the H side only. This means that the deuterium permeation is not influenced by counter diffusing H, nor by the existence of H on the surface, which is another indication that the permeation is not controlled by diffusion but by surface processes.

All these results can be well explained by a simple model, assuming that the permeation rate is a surface limited process [6,7] and no concentration gradient exists throughout the bulk. The concentration of hydrogen can be expressed as

$$C_H = S_H PH_2^{1/2} \text{ and } C_D = S_D PD_2^{1/2}, \qquad (3)$$

with S being the solubility and PH_2 the hydrogen pressure. Suppose that the surface conditions are the same for both sides and the surface area available for H_2 and D_2 release is blocked by the fractions $C_D/(C_D + C_H)$ and $C_H/(C_D + C_H)$, respectively. Then, the permeating D_2 flux under the existence of H would be suppressed as,

$$J(D,H)/J(D) \propto C_D/(C_D + C_H). \qquad (4)$$

For the same reason hydrogen permeation in the opposite direction should be reduced as,

$$J(H,D) \propto C_H/(C_D + C_H) \times J(H) \qquad (5)$$

but this was not measured in the present work. According to Lacher [8], the solubility ratio of hydrogen to deuterium in Pd is given by,

$$\log \frac{S_H}{S_D} = \frac{161.5}{T} - 0.094. \qquad (6)$$

Substituting Eq. (3) for $T = 840$ K into Eq. (4), yields:

$$\frac{J(D,H)}{J(D)} = \left(\frac{C_D}{C_D + C_H} \right)$$
$$\approx \frac{\sqrt{PD_{2Dside}}}{\sqrt{PD_{2Dside}} + 1.25\sqrt{PH_{2Hside}}} \qquad (7)$$

Experimental values were compared with the simple model Eq. (7) in Fig. 5. It is evident that Eq. (7) predicts the experimental data quite well when the H_2 pressure on the H side is 2.7×10^{-2} Pa. With increasing hydrogen pressure, the experimental data tend to fall below the model prediction. This can be attributed to either (or both) a suppression of deuterium concentration in the Pd bulk by the hydrogen in solution, or surface blocking by H atoms. Of course, if the hydrogen pressure is large, the assumption of the surface-limited permeation breaks down and the observed deviation may be attributed to H–D interaction in the bulk and/or in the diffusion process. This however, is unlikely for pressure $\lesssim 1$ Pa [6].
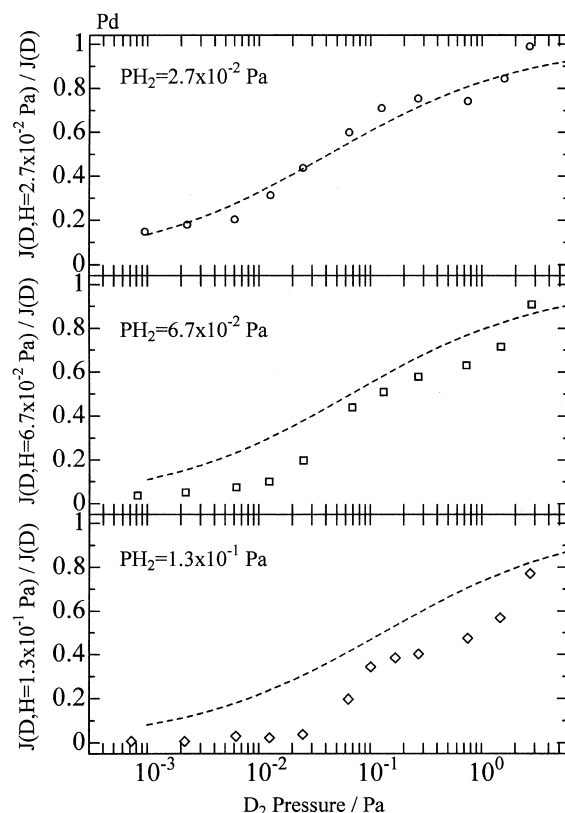

Fig. 5. The comparison of experimental deuterium permeation rates as a function of D_2 pressure with simple model prediction.

To investigate the surface blocking effect, argon gas (7.7×10^{-3} Pa) was injected instead of H_2 in the H side chamber and deuterium permeation in the D to H side direction was measured. This resulted in a reduction of the permeation rate by a factor of 0.2 compared to that of pure D_2 permeation irrespective of the D_2 pressure. Thus Ar appears to have blocked some of the surface recombination sites without changing the permeation mechanism. In the case of H_2, it is possible that the hydrogen not only blocks surface recombination sites but also inhibits adsorption (absorption) of D_2 from the gas phase. This might be the reason for the down side deviation in Fig. 5.

4. Conclusion

The first counter-diffusion and counter-permeation experiment through a palladium membrane was conducted using a new experimental system in which deuterium (D_2) and hydrogen (H_2) permeate in opposite directions. In the present experimental conditions, deuterium permeation through Pd was found to be a surface

rate limited process but not controlled by the diffusion process.

The deuterium permeation rate decreased with increasing hydrogen counter flow (increase of H_2 pressure at the H side). However, the counter deuterium permeation was retained, even if the deuterium pressure in the D side was much smaller than hydrogen pressure on the H side. The dependence of the deuterium permeation rate on the H_2 pressure, as well as the D_2 pressure, were well reproduced by a simple model where the ratio of the deuterium permeation rates with and without the counter H permeation is proportional to the fractional concentration of deuterium ($C_D/(C_H + C_D)$) in the bulk. With increasing hydrogen counter flow, however, the observed permeation rate deviates from the model probably because the surface recombination of deuteri-um is blocked and adsorption (absorption) of D_2 from gas phase is inhibited by hydrogen.

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