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# RATE OF PERMEATION AND DIFFUSION COEFFICIENT OF HYDROGEN THROUGH PALLADIUM

By

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The permeation rate  $V_p$  of hydrogen through palladium wire from hydrogen gas toward vacuum was measured with the result,

$$V_p = 1.41 \times 10^{-2} \sqrt{P} e^{-\frac{3220}{RT}} \text{ c.c. (N.T.P.)}/\text{sec}/\text{cm}^2/\text{mm},$$

where  $P$  is the hydrogen pressure varied from 3.6 to 63 cmHg,  $T$  the absolute temperature ranging from 443° to 563° K; the palladium wire was fused in glass for its 11.5 mm length with both ends projecting into hydrogen or vacuum.

$V_p$  was found not affected by contaminating hydrogen with carbon monoxide or exposing the wire preliminarily to air. It was concluded from these results that the permeation is controlled by diffusion and henceforth the diffusion coefficient was derived as

$$D = 5.18 \times 10^{-3} e^{-\frac{5650}{RT}} \text{ cm}^2/\text{sec},$$

with reference to the known solubility data of hydrogen in palladium.

Diffusion coefficient was determined alternatively by BARRER's "time lag" method with the result in good agreement with the above value as well as with that obtained by JOST and WIDMANN.

## Introduction

LOMBARD<sup>1)</sup> has observed the permeation rate from hydrogen at different pressures through palladium foil toward vacuum on the opposite side. It was thus found that permeation rate varies at a constant temperature linearly with the square root of the hydrogen pressure but the appropriate straight line does not pass through the origin but beneath it as shown in Fig. 1. SMITHELLS and RANSLEY<sup>2)</sup> have discussed the above experimental result suggesting that the permeation is governed by the surface reaction.

BARRER<sup>3)</sup> has observed both the permeation rate by the above

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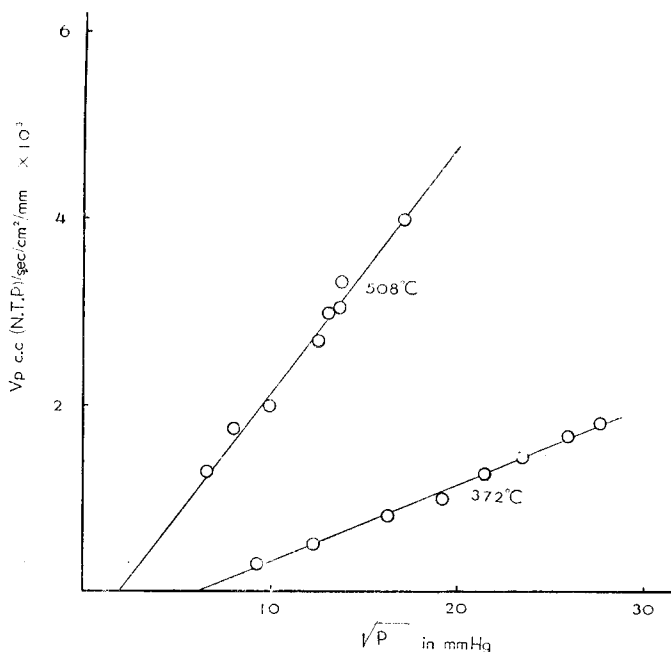


Fig. 1 Permeation rate observed by LOMBARD<sup>1)</sup>.

method and the diffusion coefficient by "time lag" method with the same sample, and calculated the difference between concentrations of hydrogen in metal on both the sides from the observed permeation rate and the diffusion coefficient determined by the "time lag" method on one hand and from the assumption of the dissolution equilibrium on both sides on the other hand. Because of the far smaller value of the concentration difference derived from the former procedure he has concluded that the permeation is governed by the surface reaction.

The present author has observed the permeation of hydrogen at different pressures through palladium wire of 0.3 mm diameter along *ca.* 1 cm of its length toward vacuum at different temperatures and analysed the result for the governing process of the permeation. Diffusion coefficient of hydrogen in palladium has also been determined by "time lag" method for controlling the above analysis.

### Experimental

The palladium wire of 0.3 mm diameter and about 3 cm length was spot-welded at its both ends to platin wires of 0.3 mm diameter

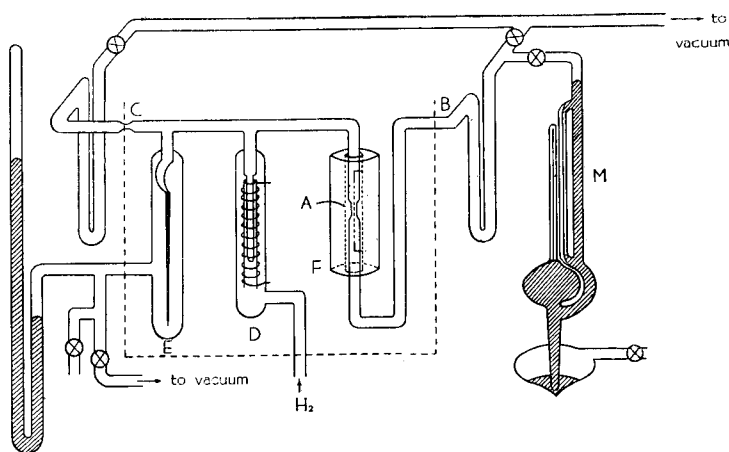


Fig. 2 Apparatus.

joined respectively with two lead wires sealed in the glass tube constricted about 2 cm long over the palladium wire. The glass tube was evacuated, the portion between B and C in Fig. 2 baked out for one day at 350°C by electric furnace, the palladium wire flashed at 1000°–1050°C for half an hour and then fused 11.5 mm long in glass by heating the constriction with hand burner as shown in Fig. 3.

The cell thus constructed was sealed off from vacuum at the constriction C for protection against contamination. Hydrogen was introduced through the palladium thimble D to the cell, and its pressure was measured by Bourdon gauge E. The palladium wire was heated by an electric furnace F, and the amount of permeated hydrogen was measured by the McLEOD gauge M.

With the same permeation cell the diffusion coefficient of hydrogen in palladium was measured by the "time lag" method as follows. After gas was exhausted from the permeation cell by evacuation at 260°C, hydrogen was admitted to the space at one end of the palladium wire and the amount of hydrogen permeated into the other space was measured with time, to determine the "time lag"  $L$ . The diffusion coefficient was deter-

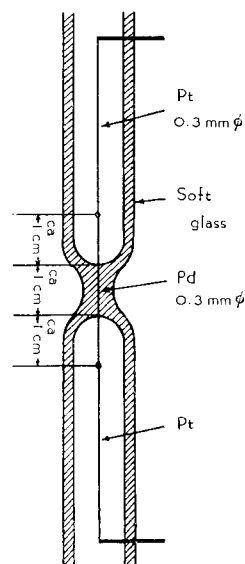


Fig. 3  
Permeation cell.

mined by the equation<sup>3)4)</sup>

$$L = \frac{l^2}{6D} ,$$

where  $l$  is the distance of permeation, *i.e.* the length of the wire fused in glass in this case.

### Result

The steady permeation rates of hydrogen through palladium wire of 11.5 mm length were measured at temperatures from 170° to 290°C and hydrogen pressures from 3.6 to 63 cm Hg. Fig. 4 shows the plot of the rate of permeation *vs.* the square root of the pressure in mm Hg at 260°C. The isobar at 55.3 cm Hg is shown in Fig. 5, where the logarithm of the ratio of the permeation rate to that at 170°C is plotted against the reciprocal absolute temperature, from which the activation energy for permeation was determined at 3220 cal/gram atom H.

The above results were adequately summarised by an empirical equation

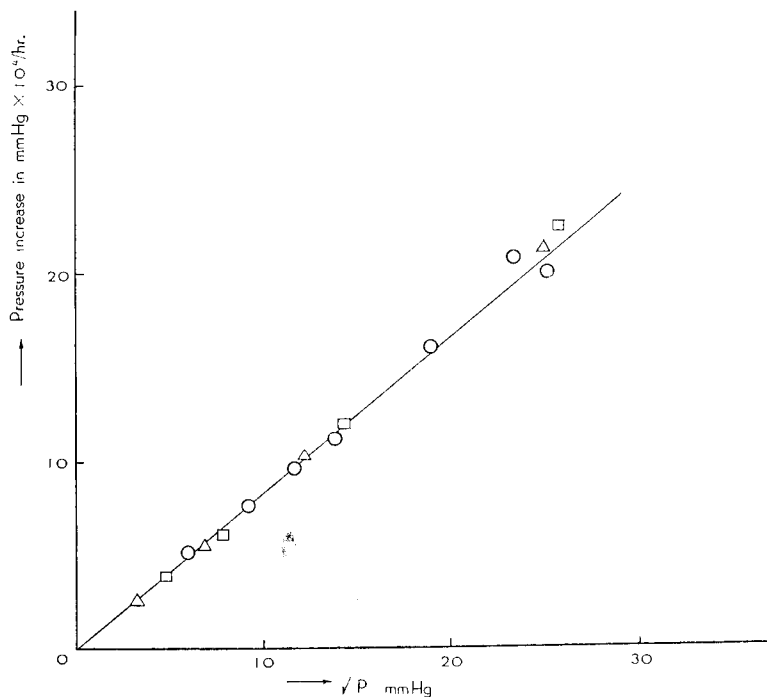


Fig. 4 Permeation rate at 260°C.

Rate of Permeation and Diffusion Coefficient of Hydrogen through Palladium

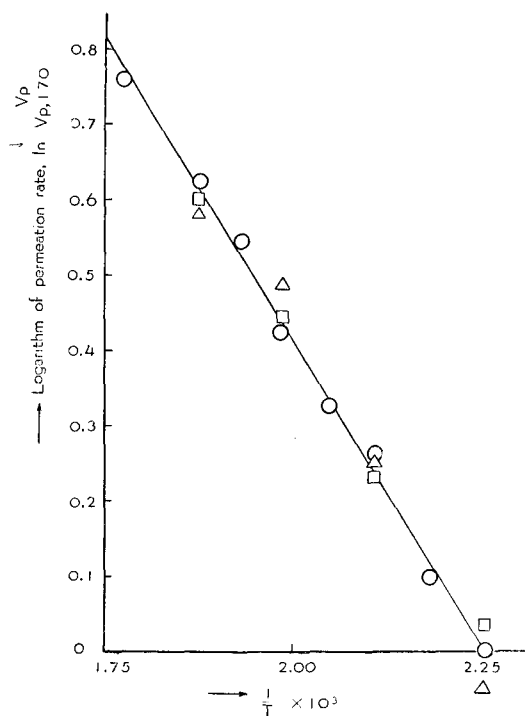


Fig. 5 Permeation rate at 55.3 cmHg.

$$V_p = 1.41 \times 10^{-2} \sqrt{P} e^{-\frac{3220}{RT}} \text{ c.c. (N.T.P.) / sec / cm}^2 \text{ / mm.} \quad (1)$$

The effect of surface contamination upon the permeation rate was observed by exposing the permeation cell preliminarily to air at 1 atm. for one day at 260°C before the permeation runs, or by using hydrogen mixed with 0.2% carbon monoxide instead of pure hydrogen. The results obtained are shown in Fig. 4 and 5 by the symbol  $\square$  for the preliminary treatment with air or by  $\triangle$  for the carbon monoxide addition respectively. No effect of surface contamination is observed within the limit of experimental error.

Fig. 6 shows one of the result of "time lag" measurement. Constant permeation rate is attained three hours after the beginning of the permeation. The "time lag" is determined from the results at  $1 \frac{7}{8}$  hours, from which the diffusion coefficient is calculated at

$$D = 3.3 \times 10^{-5} \text{ cm}^2 \text{ / sec, } 260^\circ \text{C.} \quad (2)$$

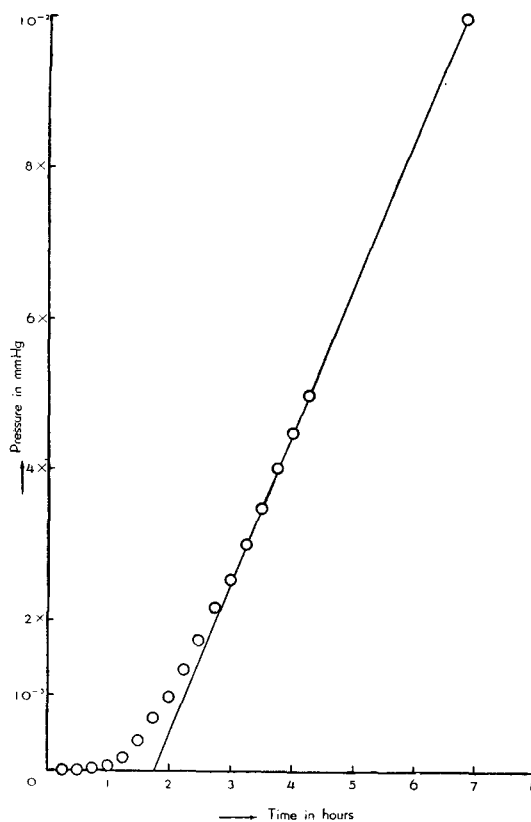


Fig. 6 Permeation time lag 260°C.

### Discussion

It has been found that the permeation rate is proportional to  $\sqrt{P}$  throughout and not perceptibly affected by surface contamination. These results strongly speak for the diffusion controlling the permeation. For the further evidence for the diffusion control, the diffusion coefficient is quantitatively derived from the present  $V_p$ -observation and compared with data from other source.

We have at the steady state of the permeation,

$$V_p = -\frac{dc}{dl} D = \frac{c_i - c_o}{l} D$$

where  $l$  is length of palladium wire,  $c_i$  and  $c_o$  the surface concentration of hydrogen in metal at the ends in hydrogen and in vacuum respec-

tively, and  $D$  the diffusion coefficient. Assuming the diffusion control or the preliminary equilibrium of hydrogen dissolution, we have ignoring  $c_0$

$$V_p = \frac{c_i}{l} D. \quad (3)$$

The dissolution equilibrium of hydrogen in palladium was studied by SIEVERTS and DANZ<sup>5)</sup> at temperatures from 180° to 350°C and at pressures from 8.9 to 74.0 cm Hg. Their results are reproduced, with the special reference to the temperature range from 180° to 290°C of our observations, as

$$c_i = 2.72 \times 10^{-1} \times \sqrt{P} e^{\frac{2130}{RT}} \text{ c.c. H}_2/\text{c.c. Pd} \quad (4)$$

We have from (1), (3) and (4)

$$D = 5.18 \times 10^{-3} e^{-\frac{5650}{RT}} \text{ cm}^2/\text{sec}. \quad (5)$$

Eq. (5) gives  $D$  at 260°C as  $2.6 \times 10^{-5}$  cm<sup>2</sup>/sec which agrees satisfactorily with the value of (2) determined by "time lag" method.

The diffusion coefficient given by (5) is further in good agreement with the value previously measured by JOST and WIDMANN<sup>6)</sup> by the method of sorption rate of hydrogen by palladium ball of 15 mm diameter, i.e.  $5.95 \times 10^{-3} e^{-\frac{5720}{RT}}$  cm<sup>2</sup>/sec. at the temperatures between 192° and 302.5°C.

These results closely verify the above conclusion that the permeation of hydrogen through palladium is governed by diffusion.

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