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Permeation of hydrogen through pre-oxidized Pd membranes in the presence and absence of CO

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Abstract

The main results of this investigation are: (a) Pd membranes activated by oxidization at 953 K have greater permeabilities than those oxidized in situ at ≈523 K; the latter is in a commonly employed temperature range for activation/oxidation of Pd membranes, (b) it is shown quantitatively that the non-ideality of H dissolved in Pd accounts for the deviations of the permeabilities at higher pressures from a direct dependence on $p_{H_2}^{1/2}$, (c) the diffusion constants of H in Pd at infinite dilution obtained here agree well with those in the literature, (d) Pd membranes prepared by oxidization at 953 K are more resistant to CO poisoning than those oxidized in situ at 523 K, (e) the permeability of a Pd membrane (oxidation at 953 K) decreases over a 60 min period in the presence but not in the absence of CO, and (f) the CO poisoning increases as the temperature decreases.
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Keywords: Permeation; Membranes; CO

1. Introduction

There have been many investigations of the permeation of Pd membranes by H_2, e.g. [1–9]. The purpose of this research is to measure H diffusion constants and permeabilities in Pd membranes after two different oxidizing procedures employed for cleaning and activation of the membranes and to determine the effect of CO in the H_2 gas stream on the H permeabilities. In addition, the effect of the non-ideality of H_2 solution on the permeability will be determined.

The apparatus employed is not an ultra-high vacuum (UHV) system but one where the vacuum is of the order of 0.1–1 Pa before the H_2 is introduced. In view of this it might be expected that the slow step for H_2 permeation would be a surface step. Surprisingly this was not the case as described below.

2. Experimental

The non-UHV system employed in this investigation has some similarity to one which might be employed for the separation of H_2 from the gaseous products resulting from the reformation of hydrocarbons because it would also not be an UHV system, i.e. the membrane is not evacuated under UHV conditions prior to measurements. Instead of the usual copper gasket, the Pd membrane of interest was substituted into the Cajon fitting. The sealing of the Pd membranes proved to be leak-free. One membrane was employed which was 138μ in thickness and, after it was investigated, it was rolled to 95μ and employed for further permeation measurements. Membranes of other thicknesses were also employed. After completion of the earlier measurements which were mainly of the initial permeation rates, i.e. up to 5 min, permeabilities were measured over a 1 h period.

The area of the membranes active for permeation was 1.68 cm^2. This could be accurately measured following removal from the fitting because the inner, active part of the membrane had been reduced by exposure to H_2 and its metallic appearance could be clearly delineated from the outer, unreduced part with its "deep surface PdO" [10]. The permeability was measured by exposing the upstream side of the membrane to a given H_2 pressure, p_{up}, and evacuating the downstream side so that $p_{down} \sim 0$ The pressure fall on the upstream side of the membrane allowed the H_2 permeation rate to be determined from the known upstream volumes of either 278.5 cm^3 or 609.1 cm^3. Although the rates were fol-

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lowed by the small decreases of p_{H_2} as monitored quite precisely by an electronic diaphragm gauge (MKS) they were nearly constant over the initial minute intervals up to 5 min without the necessity of corrections for p_{H_2} the fall. Since the rates were nearly constant over the initial 5 m, the times needed for the establishment of the steady state flux must be exceedingly small for Pd at the temperatures employed. Several studies were made over longer periods of time where p_{H_2} *did* fall appreciably and to make meaningfully comparisons of these rates, they were corrected to the average p_{H_2} during the initial 5 m by the factor of $(r_{\text{initial}}/r_{\text{at time } t})$ where $r = \text{H/Pd}$, atom ratio.

When the membranes were not being employed in order to maintain their optimum H_2 permeabilities, they were stored with H_2 on both sides at either 423 K or 473 K. The membranes were never allowed to form the hydride phase.

3. Results and discussion

3.1. Equations for permeability and diffusion

Fick's first law of diffusion applies to the steady state flow of H through membranes, i.e., $|J| = \text{rate}/A = D_H(\mathrm{d}c_H/\mathrm{d}x)$ where $|J|$ is the flux whose units employed here will be (mol H/s)/cm^2 where A is the area of the membrane and c_H is the concentration of H in (mol/vol). More generally, $|J| = (D^*_H c_H/RT)(\mathrm{d}\mu_H/\mathrm{d}x)$ which reduces to the simpler form if $\mu_H = \mu^0_H + RT\ln c_H$. In order to obtain diffusion constants at infinite dilution, D^*_H, the observed values of D_H at a given c_H should be divided by the thermodynamic factor, $f = c_H(\partial\ln(p^{1/2})/\partial c_H)_T$, which can be obtained from the isotherms [6] at each c_H. For $p_{\text{down}} \sim 0$ the flux reduces to:

$$|J|\,(\text{mol H}/(\text{s cm}^2)) = D^*_H\left(\frac{\Delta c_H}{\Delta x}\right) = \frac{D^*_H K'_s p^{1/2}_{\text{up}}}{d} \quad (1)$$

in the ideal dilute solubility range where $c_H = K'_s p^{1/2}_{H_2}$; f is unity and d is the thickness of the membrane. The flux is seen to depend inversely upon the thickness, d, and directly on $p^{1/2}_{H_2}$ in the ideal solubility limit.

The specific permeability, P'_{sp} which depends on $p^{1/2}_{H_2}$ but is independent of d, is given by the following equation:

$$P_{sp}\,(\text{mol H/s})\text{cm/cm}^2 = |J|d = D^*_H K'_s p^{1/2}_{\text{up}}. \quad (2)$$

P_{sp} depends on $p^{1/2}_{H_2}$ because, in the ideal solubility range, J depends directly on it. In the non-ideal range P_{sp} no longer depends directly on $p^{1/2}_{H_2}$ but on c_H. Koffler et al. [2] defined the specific permeability similarly but employed units of (cm^3 H_2 (STP)/s)cm/cm^2.

3.2. Solubility of hydrogen in Pd (423–503 K)

In order to allow for the effect of the non-linearity between $p^{1/2}$ and c_H, the H_2 solubilities over the temperature range of interest must be available. While there is extensive solubility data for H_2 in Pd, there is, nonetheless, a lack of sufficiently detailed data in the temperature range needed here. Solubilities were measured in this research from 423 to 503 K up to about $r = \text{H/Pd} = 0.03$ (Fig. 1). In these plots non-ideality is reflected by the deviations from straight-line relations between r and $p^{1/2}_{H_2}$, i.e. deviations from Sieverts' law of ideal solubility,

$$\frac{\text{H}}{\text{Pd}} = r = K'_s p^{1/2}_{H_2}$$

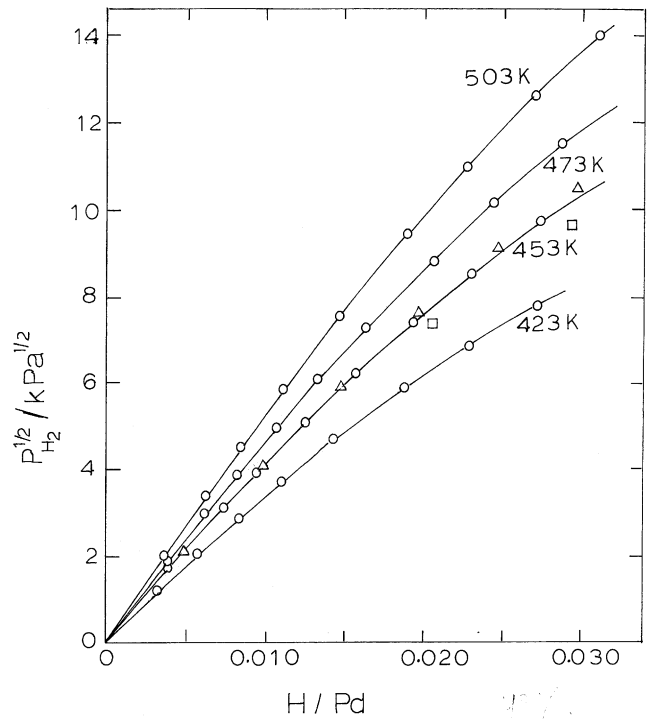

Fig. 1. H_2 solubility in the dilute phase of annealed Pd. (○) Present data, (△) data from reference [12], (□) data from equation in reference [11].

The present data at 453 K are compared with results from an equation given by Manchester et al. [11] on the basis of their evaluation of data in the literature which they considered as most reliable and the present data are also compared with several experimental solubilities for this temperature given by Lässer et al. [12]. The agreement of the present data with predictions of the equation given by Manchester [11] are quite good (Fig. 1) except at high H contents where the present results show greater deviations from ideality; the present solubilities are somewhat smaller than those measured by Lässer et al. [12] (Fig. 1).

The values of r can be converted to c_H using the known density of Pd, which does not differ significantly from that of the dilute H phase of Pd, i.e. $c_H = r\rho_{Pd}/M_{Pd}$ where M_{Pd} and ρ_{Pd} are the molar mass and density of Pd which is approximately the same as that for the dilute solution. It can be seen from the curvature of the plots at higher r values (Fig. 1) that non-ideality is a factor at all the temperatures. $|\Delta H_H|$

values derived from these solubility isotherms increase with r from 9.51 kJ/mol H ($r = 0.010$) to 10.18 kJ/mol H ($r = 0.025$) and an extrapolation of the $|\Delta H_H|$ values to $r = 0$ gives $|\Delta H^\circ_H| = 9.10$ kJ/mol in reasonable agreement with the value given by Kuji et al. [13] for this temperature range. It should be noted that $|\Delta H^\circ_H|$ decreases with increase of temperature and that is why this value is smaller than that reported for 298 K [14].

4. Evidence that the slow step for H permeation of the Pd membranes employed is bulk diffusion

4.1. Dependence of flux on membrane thickness

In order to verify that bulk diffusion is the rate-controlling step, the dependence of the fluxes on d and $p_{up}^{1/2}$ must be established (Eq. (1)). Two membranes were activated by oxidization ex situ to about 0.5% at 953 K and two oxidized to a much lower percentage at 573 K. The fluxes and the specific permeabilities are shown in Table 1 and it should be recalled that the flux depends on $1/d$ whereas the specific permeability does not. The specific permeabilities (column 6) are given for the different membrane thicknesses at a given temperature and p_{up} and the closeness of the P_{sp} values for the various thicknesses proves the dependence on $1/d$ in accord with bulk diffusion as the slow step (Eq. (1)). The data in the last two rows of the table are for membranes activated by oxidation at 573 K and although their permeation rates are slower than for the higher temperature oxidation, these two sets of data also closely confirm the $1/d$ dependence.

4.2. Hydrogen pressure dependence

The p_{H_2} dependence of $|J|$ or P_{sp} in Table 1 is not quite the expected $p_{H_2}^{1/2}$. For example, at 473 K, $P_{sp} = 4.45 \times 10^{-8}$ and 2.94×10^{-8} (mol H/s)cm/cm^2 for $p_{H_2} = 0.101$ and 0.051 MPa, respectively, for $d = 95\mu$. The value at 0.101 MPa would, however, be expected to be $\sqrt{2} \times 2.94 \times 10^{-8}$ (value at 0.051 MPa) $= 4.15 \times 10^{-8}$ (mol H/s)cm/cm^2 according to Eq. (1) whereas the experimental value is 4.45×10^{-8} (mol H/s)cm/cm^2. This discrepancy is due to the non-linearity between c_H and $p_{H_2}^{1/2}$ which becomes a factor at higher c_H. A more detailed test of the dependence on $p_{H_2}^{1/2}$ is given below in which this non-linearity is allowed for.

Table 1
H_2 flux and specific permeability as a function of d for Pd membranes

d/μ	Oxidation T (K)	T (K)	p_{H_2} (MPa)	(J/(mol H/s)/cm^2) ($\times 10^6$)	P_{sp} (mol H/s) cm/cm^2 ($\times 10^8$)
138	953	453	0.051	1.86	2.57
95	953	453	0.051	2.67	2.54
110	573	423	0.101	2.25	2.48
200	573	423	0.101	1.16	2.33
138	953	423	0.101	2.26	3.19
95	953	423	0.101	3.30	3.14
138	953	423	0.051	1.46	2.01
95	953	423	0.051	2.08	1.98
138	953	473	0.101	3.26	4.50
95	953	473	0.101	4.68	4.45
138	953	473	0.051	2.17	3.00
95	953	473	0.051	3.09	2.94

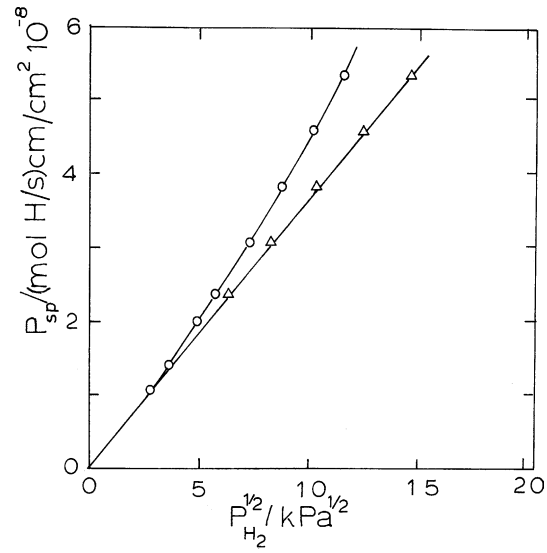

Fig. 2. Specific permeability (138μ membrane) plotted as a function of $p_{H_2}^{1/2}$ at 473 K. (○) Experimental data and (△) experimental data corrected for non-ideality.

The detailed dependence of P_{sp} on $p_{H_2}^{1/2}$ was examined for the 138μ membrane as shown in Fig. 2 (473 K) where it can be seen that there is linear behavior as $p_{H_2}^{1/2} \to 0$ but positive deviations appear as $p_{H_2}^{1/2}$ increases. The triangles represent the experimental permeation data multiplied by the ratio $(r_{exp}/r_{ideal}) = c_H(\text{exp})/c_H(\text{ideal})$ for each value of $p_{H_2}^{1/2}$ where these ratios are obtained from the solubility isotherms at 473 K (Fig. 1). It can be seen that the corrected P_{sp} are linearly dependent on $p_{H_2}^{1/2}$ in accord with a bulk diffusion-controlled slow step.

4.3. Comparison of permeabilities of Pd membranes oxidized in situ at 523 K and ex situ at 953 K

Before insertion into the permeation apparatus the Pd membranes were either oxidized for 30 min at 953 K or else they were oxidized at 523 K after insertion into the apparatus. Most studies of H_2 permeability through Pd membranes have employed in situ oxidation at a temperature well below 953 K. For example, Koffler et al. [2], oxidized their membranes in situ for 6 min at 673 K and Yamakawa et al. [3] exposed their membranes to air at a "temperature between 353 and 623 K" for 3–5 min. Some investigators have employed Pd membranes oxidized at higher temperatures in situ, e.g. Rubin [7] exposed commercial type tubes of Pd to air "from 723 to 873 K" for half an hour or more. This served to clean the tubes which may have been "mildly poi-

soned perhaps by organic materials left over from fabrication or by finger prints." The oxidized membranes were, of course, all reduced with H_2 (~523 K) after insertion into the permeation apparatus.

Most membranes oxidized at 953 K corresponded ~0.5% oxidation and were found to have greater permeabilities ≈30–40% than those oxidized in situ at 573 K. Despite this, the activation energies for diffusion and permeation for membranes oxidized at either temperature were similar and those oxidized at 523 K also gave the correct d and p_{H_2} dependences for diffusion-controlled permeation. The smaller specific permeabilities of the membranes oxidized at 573 K may be due to a smaller active surface compared with membranes oxidized at higher temperatures; this active surface must be in rapid equilibrium with the bulk leading to diffusion control. It has been shown from SEM that the surfaces of oxidized (953 K) Pd foils are much rougher than the surface of unoxidized Pd [15]. As shown below, the susceptibility of the membranes to CO poisoning is lower for the membrane oxidized at 953 K rather than 573 K.

4.4. Specific permeabilities and their activation energies

Values of the specific permeabilities from this work for membranes oxidized at 953 K are compared to those from previous investigations (Table 2). It can be seen that the $P_{sp}(r \to 0)$ obtained is very close to the literature values; the value from reference [2] was determined with an UHV system. Unfortunately the specific permeability values are not available from the recent data of Yamakawa et al. [3] employing evacuation under UHV conditions because their results are given in terms only of the p_{H_2} increase on the downstream side.

Specific permeabilities were determined at $p_{up} = 10.1$ and at 16.0 kPa over the temperature range from 423 to 503 K (Fig. 3). These data can be corrected for non-ideality using the solubilities (Fig. 1) and multiplying the observed specific permeabilities by the ratio: (r_{ideal}/r_{exp}) at each p_{H_2} as shown by the dashed lines passing through the filled symbols (Fig. 3). The corrected E_{sp} of 13.52 kJ/mol H (Table 2) is from data at 10.1 kPa and the corresponding value at 16.0 kPa is $E_{sp} = 13.47$ kJ/mol H. These values agree with those from references [1] and [3] but not with the result of Koffler et al. [2] which appears to be erroneous.

Table 2
Specific permeabilities of H in Pd ($d = 140\mu$, oxidation at 953 K) at 473 K and $p_{up} = 0.101$ MPa and the activation energies

P_{sp} ((mol H/s)cm/cm^2)	E_{sp} ((kJ/mol H)	Reference
1.18×10^{-8}	13.47 (13.52)	Present research
1.13×10^{-8}	13.47	[1]
0.82×10^{-8}	15.67	[2]
–	13.90	[3]

Where the value in Table 2 with parenthesis is for $p_{H_2} = p_{up} = 16.0$ kPa and the permeabilities have been corrected for non-ideality where appropriate.

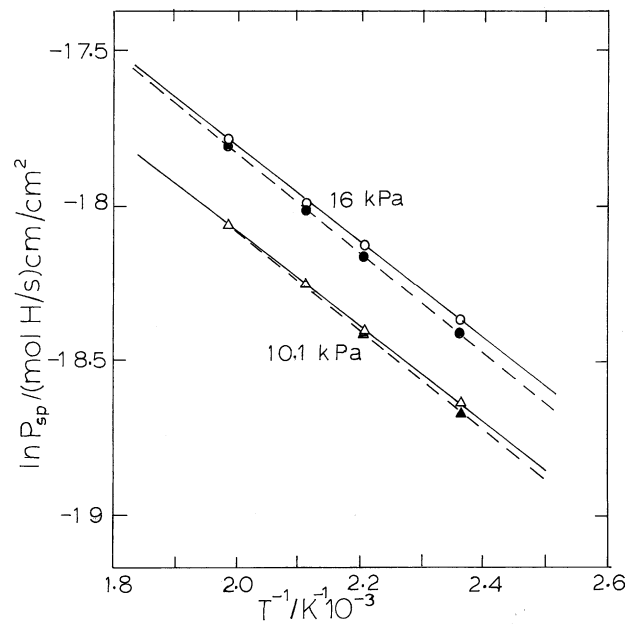

Fig. 3. Arrhenius plots of specific permeability (138μ membrane) against $1/T$ at the p_{H_2} indicated. (○) Permeabilities at $p_{H_2} = 16.0$ kPa and (△) permeabilities at $p_{H_2} = 10.0$ kPa. The open symbols are the experimental data and the filled ones are the experimental data corrected for non-ideality.

4.5. Diffusion constants, activation energy and pre-exponential factor

D^*_H values can be calculated from the specific permeabilities and solubilities (Fig. 1) using Eq. (3) and then corrected where necessary by the thermodynamic factor, f,

$$P_{sp}\,(\text{mol H/s})\text{cm/cm}^2 = D^*_H c_{H,up} \quad (3)$$

When the concentrations are small enough, $c_{H,up}$ can be replaced by $K'_s p_{up}^{1/2}$, i.e., when the system follows Sieverts' law. The activation energy for diffusion, E_d, can then be determined from a plot of ln D^*_H against $1/T$ (Fig. 4). The temperature dependence of D^*_H is given by the equation $D^*_H = D_0 \exp(-E_d/RT)$ and the pre-exponential factor, D_0, can be determined from the intercepts of the plots in Fig. 4. The diffusion constants at a typical temperature, 423 K, determined here are seen to be in reasonably good agreement with those values from the literature which seem most reliable (Table 3).

The E_d values decrease slightly with r from 23.24 kJ/mol H ($r = 0.012$) to 23.08 kJ/mol H ($r = 0.008$) and this is attributed to experimental uncertainty rather than to non-ideality in the D^*_H values since c_H values for Eq. (3) have been derived from p_{up} (Fig. 1) thereby allowing for the non-ideality. The D_0 and E_d values from the present work given in Table 3 are average values. The expression for D^*_H from the present work is compared with some given in the literature (Table 3). The equation from reference [16] is based on a compilation of data from 25 different studies over a wide temperature range (230 to ~800 K) and, quoting the authors, "the consistency of the data are remarkably

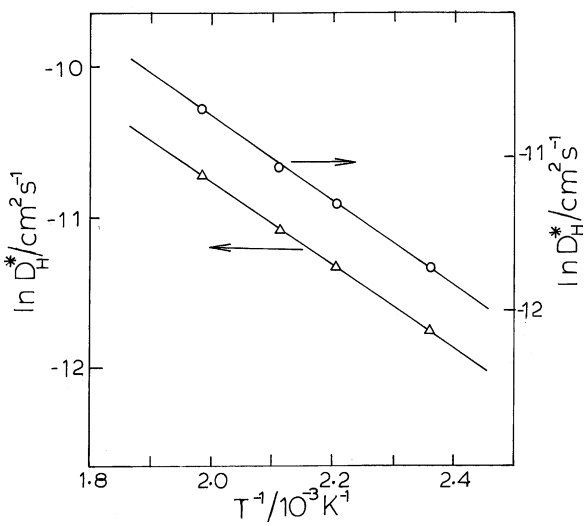

Fig. 4. Arrhenius plots of the hydrogen diffusion constant where $D_H \sim D_H^*$ (138μ membrane) against 1/T. (○) Data obtained at $r = 0.012$ and (△) data obtained at r=0.008.

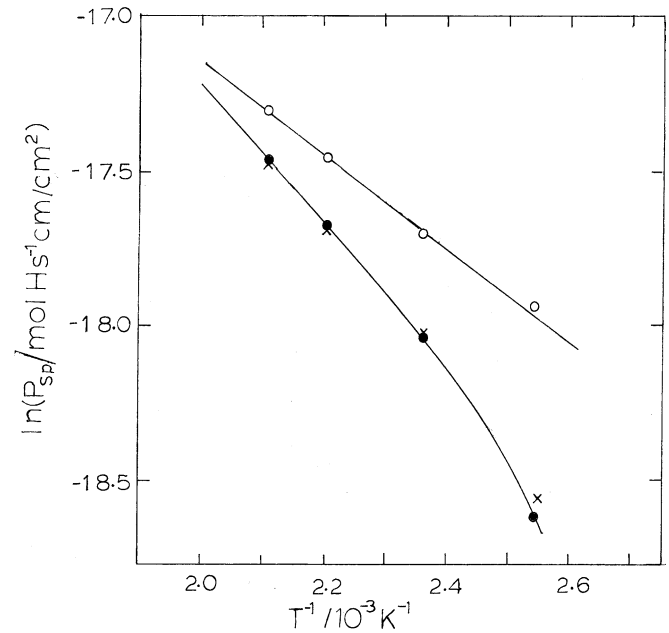

Fig. 5. Specific H_2 permeabilities for $p_{H_2} = 0.051$ MPa and $p_{CO} = 0.66$ kPa. Symbols (○) and (●) present data in the absence and presence of CO; (×) data calculated as described in the text.

good". The expression given in the ~70-year-old work of Jost and Widmann [8] agrees relatively well with the newer values. It is based on the rate of H_2 absorption by a Pd sphere which was coated with Pd black; measurements were made in a glass apparatus containing potential poisons such as grease and mercury. The role of the Pd black may be similar to the role of oxidation/reduction in the present experiments, i.e. both act to maintain the surface activity despite some contaminants.

By taking the derivative of $\ln P_{sp}$ in Eq. (3) with respect to T^{-1}, it follows that $E_{sp} = E_d + \Delta H_H{}^\circ$ where the last quantity is negative and the others are positive. We obtain for these values (23.16 − 9.10 = 14.06 kJ/mol H) at $r \to 0$ which is in reasonable agreement with the experimental value of $E_{sp} = 13.50$ kJ/mol H and attests to the self-consistency of the data.

4.6. Effect of CO on H_2 permeation of Pd membranes

CO is known to partially poison the permeation of H_2 through Pd membranes, i.e., in reference [18] it states that "Huber found in a study with carbon monoxide that it blocks the hydrogen passage through the gas/metal interface by strong chemisorption". More recently, Amano et al. [17] found that high concentrations of CO below about 523 K caused slowing of the permeation. Some results are shown in Table 4 where the CO was either mixed with the H_2 before entering into the chamber containing the membrane or else it was added before the H_2 as indicated in the table.

The effect of temperature on the degree of CO poisoning was investigated with another membrane (oxidized at 953 K) at p_{CO} and p_{H_2} held constant at 0.66 kPa and 0.051 MPa H_2, respectively (Fig. 5). It is clear that the effect of CO is much greater at lower temperatures as Amano et al. [17] and others [19] found.

A simple model using a Langmuir isotherm for the CO coverage, i.e., $P_{sp} = (1-\theta)^2 P_{sp}(p_{CO} = 0) = [1/(1 + ce^{+|\Delta H_{ads}|/RT})]^2 P_{sp}(p_{CO} = 0)$ with the assumption that the H_2 needs two sites for dissociative chemisorption, was employed in an attempt to duplicate the experimental results. θ is an effective surface coverage, i.e. the fraction of the surface active for permeation. The fit was carried out by trial and error and is quite good for $|\Delta H_{ads}| = 30.7$ kJ/mol and $c = 3.1 \times 10^{-5}$ (Fig. 5). This value for the heat of chemisorption is small in comparison to the measured heat of chemisorption of about 125 kJ/mol for the (1 1 1) face to $\theta = 0.5$ which then falls more or less continuously [20]. It is possible that the fraction of the surface where the heat of chemisorption = 125 kJ/mol is permanently covered with CO and inactive for H_2 dissociation → permeation. Because the perme-

Table 3
Hydrogen diffusion constants in Pd (oxidation at 953 K) at 423 K and $D_0 e^{[-E/RT]}$ expressions

D_H^* (cm^2/s ($\times 10^6$))	D_0 (cm^2/s) ($\times 10^3$)	Exp[$-E_d/RT$]	Reference
7.7	5.6 ± 0.1	Exp[−23,160/RT]	Present work
6.2	5.18	Exp[−23,640/RT]	[1]
5.3	4.94	Exp[−23,037/RT]	[2]
5.4	4.30	Exp[−23,510/RT]	[4]
8.1	5 ± 2	Exp[−23,510/RT]	[6]
6.6	5.95	Exp[−23,510/RT]	[8]
5.5	4.30	Exp[−23,430/RT]	[9]
5.3	2.90	Exp[−22,190/RT]	[16]
5.4	3.06	Exp[−2,230/RT]	[17]

Table 4
Hydrogen permeation at 423 K and 0.101 MPa H_2 of a Pd membrane (200μ oxidized in situ at 573 K) for the addition of CO before H_2 and simultaneously with H_2

p_{sp} ((mol H_2 H/s)cm/cm^2)	p_{CO}/kPa	Decrease (%)	P^*_{sp}/(mol H/s)cm/cm^2	p^*_{CO}/kPa	Decrease[a] (%)
2.20×10^{-8}	0	0	2.20×10^{-8}	0	0
1.10×10^{-8}	0.15	−50	1.03×10^{-8}	0.15	−53
1.00×10^{-8}	0.27	−55	8.71×10^{-9}	0.27	−63
9.30×10^{-9}	0.67	−58	8.34×10^{-9}	0.53	−64
8.83×10^{-9}	1.17	−60	–	–	–
8.58×10^{-9}	2.00	−61	–	–	–
7.11×10^{-9}	6.7	−67	–	–	–

[a] The last three columns indicate CO added before the H_2.

ation rates in the presence of CO (0.66 kPa) and in its absence are within 15% of each other at 473 K (Fig. 5), this suggests that the CO sites where $|\Delta H_{ads}|$ is much smaller than 125 kJ/mol CO are the same ones active for H_2 dissociation → permeation.

Table 4 also shows the permeation rates obtained when CO is added to the upstream side of the membrane *before* the H_2 (at 423 K) and it can be seen that the inhibition is slightly greater than when they are added simultaneously. When the H_2 and CO are added simultaneously, the former appears to partially block the surface coverage by CO.

4.7. Effect of CO on H_2 permeation of Pd membranes oxidized in situ at 523 K and ex situ at 953 K

Pd activated by oxidation at 953 K was more resistant to CO poisoning than that oxidized at 523 K. For example, for Pd oxidized at 523 K the permeation rates were reduced by ∼58% for $p_{CO} = 0.66$ kPa mixed with $p_{H_2} = 0.101$ MPa (423 K). With $p_{H_2} = 0.051$ MPa, but otherwise similar conditions, the rate for Pd oxidized at 953 K was reduced by ∼28%; note for the latter that the lower p_{H_2} employed would cause a greater inhibition than for $p_{H_2} = 0.101$ MPa. It is of interest that the specific permeabilities of the Pd membranes oxidized at different temperatures do not differ as much as do their susceptibilities to CO poisoning at least at 423 K.

4.8. Permeation rates of a Pd membrane monitored over longer times

The fluxes and specific permeabilities shown in Table 1 are based on the first 5 min of permeation. It was of interest to measure the fluxes over longer time periods to learn if there are any decreases over time. For this purpose a 120μ thick membrane was employed which had been oxidized at 923 K for 20 min and whose weight gain was 0.09% which is smaller than the others where the weight gain was ∼0.5%. This may account for its slightly lower permeability, ∼10%, compared to those discussed above. In any case, this membrane was quite reproducible and the fluxes were followed up to 60 min. Average fluxes over the initial (2.5 min) and final (57.5 min) 5 min periods are shown in Table 5 for $p_{H_2} = 0.051$ MPa at 423 and 473 K. Corrections are needed during the 60 min period because of the H_2 which has diffused through membrane causing p_{up} to fall which, of course, causes the flux to decrease (Eq. (1)).

Table 5
H fluxes through a Pd membrane as a function of time with the p_{H_2} (initial) = 0.051 MPa and $p_{CO} = 0$

T (K)	t_{av} (min)	p_{av} (MPa)	$\|J\|$ (mol H/(s cm^2))	Corrected $\|J\|$ (mol H/(s cm^2))
423	2.5	0.0487	1.47×10^{-6}	–
423	57.5	0.0206	9.07×10^{-7}	1.40 (1.52) $\times 10^{-6}$
473	2.5	0.0478	2.21×10^{-6}	–
473	57.5	0.0192	9.08×10^{-7}	1.82 (1.97) $\times 10^{-6}$

The corrections in Table 5 were made by multiplying the experimental flux (column 4) at $t = 57.5$ m by $\{p_{av}(2.5\,\text{min})/p_{av}(57.5\,\text{min})\}^{1/2}$ or more accurately by $\{r_{av}(2.5\,\text{m})/r_{av}(57.5\,\text{m})\}$ where these concentrations are obtained from the appropriate H_2 pressures (Fig. 1). The uncorrected and corrected fluxes are shown in columns 4 and 5, respectively, and in the latter column, those with and without parenthesis are corrected by the concentration and the $p_{av}^{1/2}$ ratios, respectively. The corrected fluxes for 57.5 min are very similar to those after 2.5 min indicating that there is negligible fall in the permeation rate.

Table 6 shows the corresponding results in the presence of CO. Initially p_{CO} is initially 1.3% of the total p and after 60 min, it is 2.4%; this change has been ignored in the calculation of the corrections shown in column 5. The important point is that while the corrected fluxes shown in

Table 6
H fluxes through a Pd membrane in the presence of 0.67 kPa CO as a function of time with the initial $p_{H_2} = 0.051$ MPa

T (K)	t_{av} (min)	p_{av} (MPa)	$\|J\|$ (mol H/(s cm^2))	Corrected $\|J\|$ (mol H/(s cm^2))
423	2.5	0.0498	1.10×10^{-6}	–
423	57.5	0.0372	4.91×10^{-7}	5.65 (5.88) $\times 10^{-7}$
473	2.5	0.0488	1.78×10^{-6}	–
473	57.5	0.0280	4.91×10^{-7}	6.50 (6.83) $\times 10^{-7}$

Table 5 after exposure for 57.5 min agree quite well with the initial ones (2.5 min) this is definitely not the case in the presence of CO (Table 6).

5. Conclusions

Hydrogen diffusion constants and specific permeabilities have been measured for Pd membranes oxidized either at 953 K or 523 K using a non-UHV system. The results are quite reproducible for each of the two types of activation and the permeabilities were greater after oxidation at 953 K. The dependences of the permeation rates upon $p_{H_2}^{1/2}$ and their inverse dependence upon membrane thickness show that bulk diffusion is the slow step in both cases. A linear dependence of permeabilities on $p_{H_2}^{1/2}$ obtains over a wide range provided that the permeabiities are corrected for non-ideal H_2 solubility. The values of D_H^* agree very well with previous investigations which again indicates that bulk diffusion is the slow step. The experimental data at infinite dilution of H are consistent with the relation: $E_{Psp} = E_d + \Delta H_H{}^\circ$.

The presence of CO causes the fluxes to fall significantly and the fall is greater at lower temperatures. During 60 min periods in the absence of CO at 423 and 473 K there is no significant decrease of permeation after correction for the p_{H_2} fall whereas in the presence of CO there is a significant decrease with time. Preadsorption of CO causes a somewhat greater inhibition than the simultaneous introduction of H_2 and CO.

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