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Permeation and Diffusion of Hydrogen Through Pd Membranes (U)

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Abstract

Hydrogen diffusion through Pd membranes has been measured under non-UHV conditions, i.e., the membranes are evacuated under non-UHV conditions. Despite this, the results indicate that bulk diffusion is the slow step and the diffusion constants agree with earlier workers results where UHV conditions obtained. The activation energy for H_2 permeation in the dilute phase was determined from an Arrhenius plot over a series of temperatures from 423 to 503 K. The solubilities of H_2 were determined over the same temperature range and from these data, the diffusion constants were determined. The following equation is closely satisfied for the present data: $E_{Psp} = E_d + \Delta H_H^o$ where ΔH_H^o is the enthalpy of solution of ½H_2, E_{Psp} is the activation energy for the specific permeability, and E_d is the activation energy for diffusion.

Introduction

There have been many investigations of the permeation of Pd membranes by H_2, e.g., [1-9]. The purpose of this one is to measure H_2 diffusion constants and permeabilities together with their activation energies in pure Pd activated by oxidation at higher temperatures than those commonly employed. The apparatus employed is not an ultrahigh vacuum (UHV) system but one where the vacuum is of the order of 0.1-1 Pa. 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.

Experimental

The apparatus employed has some similarity to one which might be employed for the purification of H_2 from gaseous products from the reformation of hydrocarbons because it is not an UHV system. Instead of the usual copper gasket, the membrane of interest was substituted into the Cajon fitting. The sealing of the Pd membranes proved to be quite leak free. A membrane of 138 μ was employed and after it was investigated, it was rolled to 95 μ and employed for further permeation measurements. A 120 μ membrane was also prepared and used for some longer time measurements after completion of the earlier measurements which were mainly of the initial permeation rates, i.e., up to 5 m.

Before insertion into the permeation apparatus, the Pd membranes were "activated" by oxidation for 30 m at 953 K which corresponded to ~0.5% oxidation. This is a different procedure than usually employed for fundamental studies of H_2 permeability of Pd membranes and it appears to be more successful than the usual *in situ* oxidation at, e.g., 523 K. The workers using UHV conditions, i.e., Koffler et al [2], oxidized their membranes *in situ* for 10 m at 673 K and Yamakawa et al [3] exposed their membranes to air at a "temperature between 353 and 623 K" for 3-5 m. The membranes were then reduced with H_2. It should be noted that some investigations have oxidized membranes at higher temperatures *in situ*, e.g., Rubin [7] exposed commercial type tubes of Pd to air "from 723 K to 873 K" for a half hour or more. This served to clean the tubes which may have been "mildly poisoned perhaps by organic materials left over from fabrication or by finger prints," etc. Some of the presently employed Pd membranes were oxidized under the more usual conditions, i.e., *in situ* at 523 K. The oxidized membranes were, of course, all reduced with H_2 (~523 K) after the membranes were inserted into the apparatus and prepared for the permeation studies.

The geometric areas of the membranes were 1.68 cm^2 which could be accurately measured after removal from the fitting because there was a clear delineation between the inner portion of the membrane, which had been reduced by exposure to H_2 and the outer, inactive portion because "deep surface PdO" [10] was apparent in the outer but not the inner, active portion. The permeability was measured by exposing the upstream side of the membrane to a given p_{H2}, p_{up}, and evacuating the downstream side so that p_{down}~0. The pressure fall on the upstream side of the membrane allowed the H_2 flux to be determined from the known volume of 278.5 cm^3. Measurements of the flux were taken over one minute intervals up to 5 m or longer. Generally the p_{H2} fall was negligible with time so that the permeation rates did not change appreciably with time. The times needed for the steady states to be established must be exceedingly small.

When the membranes were not being used, it was found to be helpful for maintaining the optimum H_2 permeation rates to store them with H_2 on both sides at 423 K or 473 K. The membranes were never allowed to form the hydride phase.

Results and Discussion

Equations for Permeability and Diffusion

In the ideal case, Fick's first law of diffusion applies to the steady state permeation of H through membranes, i.e., J = -(rate/ molH/s)/A = - D(dc/dx) where the units of flux, J, may be (mol H/s)/cm^2 and A is the area of the membrane (cm^2). More generally, $J=-(D_H c_H/RT)(d\mu_H/dx)$ where c_H is the concentration of H in mols/volume. Note that the exact form of Fick's law reduces to the simpler form when $\mu_H = \mu_H^o + RT\ln c_H$. It will be assumed that the simple form is applicable in the dilute phase regions employed and where it reduces to

$$J = -D\,K_s'\,p_{up}^{1/2} / d \quad / \text{ molH s/cm}^2 \qquad (1)$$

for p_{down}~0 and for the ideal dilute solubility range where $c_H = K_s' p_{H2}^{1/2}$ is applicable. When bulk diffusion is the slow step, the flux depends inversely upon the thickness, d, and directly on $p_{H2}^{1/2}$ in the ideal solubility limit.

The specific permeability, P_{sp} will be given by the following equation:

$$P_{sp} = J \times d \quad \text{(mol H/s)cm/cm}^2 \qquad (2)$$

where d is the membrane thickness in cm; P_{sp} depends on $p^{1/2}$ because J depends on it. Koffler *et al* [2] defined the specific permeability similarly but, with units of cm^3 H_2 (STP) /s.

The specific permeability can be expressed in terms of the diffusion constant as

$$P_{sp} = D_H c_H = D_H K_s' p_{up}^{1/2} \quad \text{(mol\textbackslash\ H/s)cm/cm}^2 \qquad (3)$$

where D_H = diffusion constant in cm^2/s; K_s' relates the solubility, c_H, to $p^{1/2}$ where the relationship $c_H = K_s' p^{1/2}$ assumes that the concentration is small enough so that the system is ideal, i.e., follows Sieverts' law. It is also assumed that $c_{down}=0$ which is not unreasonable since by direct evacuation p_{down}~0.

The temperature dependence of the solubility and diffusion constants can be incorporated into equation (3) giving:

$$P_{sp} = P_{sp}^o \exp[-\Delta H_H^o/RT] \exp[-E_d/RT] = P_{sp}^o \exp[-E_{Psp}/RT] \qquad (4)$$

where ΔH_H^o is the enthalpy of solution of $\frac{1}{2}H_2(g)$ at infinite dilution and E_d is the activation energy for diffusion of H in the dilute phase and P_{sp}^o is a pre-exponential factor. From equation (4), it follows that the specific permeability activation energy, E_{Psp}, is related to the other two terms by $E_{Psp} = E_d + \Delta H_H^o$ where ΔH_H^o is negative but the others are positive. (E_{Psp} is an activation energy plus an enthalpy term for the solution of H_2 and therefore it is not inappropriate for an enthalpy term to appear on the right-hand-side of the equation.)

The activation energy for diffusion, E_d, can be obtained by an Arrhenius plot of specific permeabilities or specific permeabilities for different temperatures at constant H content. Thus, under these conditions, equation (3) can be expressed as:

$$\ln P_{sp} \quad (\text{at constant } c_H) = \text{constant} + E_d/RT \quad \text{(mol H/s) cm/ cm}^2. \qquad (5)$$

From the slope of $\ln P_{sp}$ at constant c_H against 1/T, E_d can be obtained. Values of the D_H can be obtained directly from equation (3) by re-arrangement,

$$D_H = P_{sp} / c_H = P_{sp} / \; p_{up}^{1/2} K_s'. \qquad (6)$$

Solubility of Hydrogen in Pd (423-503 K)

In order to allow for the effect of the non-linearity between c_H and $p_{H2}^{1/2}$ on the permeation, H_2 solubilities over the range of interest must be available. They were measured in this research and are shown in Figure 1. In these plots non-ideality is reflected by deviations from a straight line relation, Sieverts' law of ideal solubility,

$$H/Pd = r = K_s' \, p_{H2}^{1/2}$$

where r is the H/Pd atom-ratio. (H/Pd)=r can be converted to c_H using the known density of the metal which does not differ significantly from that of the dilute hydrogen phase. It can be seen from the curvature of the plots at higher r values (Fig. 1) that non-ideality is a factor at all of the temperatures measured. The values of $|\Delta H_H|$ 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 $|\Delta H_H^o|$=9.10 kJ/mol.

The Slow Step for Hydrogen Permeation in Pd.

The Dependence of Flux on Membrane Thickness.

In order to determine whether or not bulk diffusion is the rate-controlling step the dependence of the fluxes upon d and $p_{up}^{1/2}$ must be determined (equation 1). Two different membrane thicknesses were employed, 95 and 138 μ, where the uncertainty in d is about ±5 μ. Both were oxidized to about 0.5% (953 K). Results are shown in Table 1 for the fluxes and the specific permeabilities. In the last column specific permeabilities are given for the two different membrane thicknesses at a given temperature and p_{H2}. Since these values are quite close for the two thicknesses, this proves that the data exhibit a 1/d dependence in accord with bulk diffusion as the slow step (eqn. 1).

Table 1. H_2 Flux and Specific Permeability as a Function of d

d/μ	T/K	p_{H2}/kPa	(J/(mol H/s)/cm^2)x10^6	P_{sp}/(mol H/s) cm/cm^2 x10^8
138	453	50.1	1.86	2.57
95	453	50.1	2.67	2.54
138	423	101	2.26	3.19
95	423	101	3.30	3.14
138	423	50.5	1.46	2.01
95	423	50.5	2.08	1.98
138	473	101	3.26	4.50
95	473	101	4.68	4.45
138	473	50.5	2.17	3.00
95	473	50.5	3.09	2.94

p_{H2} Dependence

The p_{H2} dependence of J or P_{sp} in Table 1 is not quite $p_{H2}^{1/2}$. For example, at 473 K for d=95μ, P_{sp} is 4.45 x10^{-8} (mol H/s) cm/cm^2 at 101 kPa and 2.94x10^{-8} (mol H/s) cm/cm^2 at 50.5 kPa. From the latter value the expected value at 101 kPa would be ($\sqrt{2}$) x 2.94×10^{-8} (mol H/s) cm/cm^2=4.15×10^{-8} (mol H/s) cm/cm^2 instead of the experimental value of 4.45×10^{-8} (mol H)/s) cm/cm^2. This discrepancy is due to the non-linearity between c_H and $p_{H2}^{1/2}$ being greater at the higher p_{H2}. A more detailed test of the dependence on $p_{H2}^{1/2}$ is given immediately below in which the non-linearity is accounted for.

The dependence of P_{sp} on $p_{H2}^{1/2}$ was examined for the 138 μ membrane in Figure 2 (473 K) where it can be seen that there is linear behavior as $p_{H2}^{1/2} \rightarrow 0$ but positive deviations as $p_{H2}^{1/2}$ increases. The dashed line represents the experimental permeation data multiplied by the ratio (r_{exp}/r_{ideal}) = c_H(exp)/ c_H(ideal) for each $p_{H2}^{1/2}$ value according to equation (3) where these ratios are obtained from the solubility relations at 473 K (Fig. 1). It can be seen that the corrected P_{sp} data now have a linear dependence of P_{sp} on $p_{H2}^{1/2}$ in accord with a bulk diffusion-controlled slow step.

It is known that oxidation causes roughening of the surface which may help to resist CO poisoning. If, as generally believed [11], the transition $H_{chemisorbed} \rightarrow H_{subsurface}$ is very fast, then it is possible that the concentration of H in the subsurface layers is nearly the same whether or not there is some blockage of surface sites by CO. If bulk diffusion is relatively slow, then a fast $H_{chemisorbed} \rightarrow H_{subsurface}$ reaction combined with short-range diffusion parallel to the subsurface layers would lead to a concentration of subsurface H which would be the same whether or not some poisoning occurs which may explain why the permeation rates are unaffected.

Specific Permeabilities and Activation Energies

Specific Permeabilities

Values of the specific permeabilities are shown in Table 2 from this work compared to values from previous investigations. It can be seen that P_{sp} from the present work is very close to literature values; the value from reference [2] was determined under UHV conditions. Unfortunately the specific permeability values cannot be calculated from the recent data of Yamakawa *et al* [3] which was also obtained after evacuation under UHV conditions because their results are given only in terms of the p_{H2} increase on the downstream side.

Table 2. Specific Permeabilities and Activation Energies for Permeation of H in Palladium

T/ K	p_{up}/ kPa	*Psp*/ (mol H/s)cm/cm^2	E_{Psp}/ kJ/mol H	ref.
473	10.13	1.18×10^{-8}	12.98(13.52)	present
473	10.13	1.13×10^{-8}	13.47	[1]
473	10.13	0.82×10^{-8}	15.67	[2]
-	-	-	13.90	[3]

Activation Energy for Permeability

The specific permeabilities were determined at 10.13 kPa and at 16.0 kPa over the temperature range from 423 to 503 K (Fig. 3). The activation energies for the specific permeabilities, E_{Psp}, are shown in Table 2 where the value of 12.98 kJ/ mol H from this work is for p_{H2}=10.13 kPa. For 16.0 kPa, E_{Psp}=13.05 kJ/ mol H. The experimental values can be corrected for non-ideality using results from Figure 1 and multiplying the observed specific permeabilities by the ratio: (r_{ideal}/r_{exp}) as noted above and shown by the dashed lines in Figure 3. Only the values at 423 K and 453 K are affected at 10.13 kPa and the corrected E_{Psp} is 13.52 kJ/ mol H (shown in parenthesis in Table 2) is closer to the values determined at lower p_{H2} [2,3]. When the data at 16.0 kPa are treated in the same way, the corrections are significant at every temperature and E_{Psp}= 13.47 kJ/ mol H which agrees quite well with the corrected value obtained at the lower pressure.

Diffusion Constants and the Activation Energy for Diffusion

The D_H values were calculated from the specific permeabilities and solubilities using equation (6) and the solubilities from Figure 1. They are seen to be in reasonably good agreement with literature values (Table 3).

Table 3. Hydrogen Diffusion Constants in Pd

T/K	D_H/ cm^2/s(x10^6)	D_o (x10^3)	exp[E_d/RT]	ref.
423	7.7	5.6±0.1	exp[-23160/RT]	present work
423	6.2	5.18	exp[-23,640/RT]	[1]
423	5.3	4.94	exp[-24037/RT]	[2]
423	5.4	4.30	exp[-23,510/RT]	[4]
423	8.1	5 ± 2	exp[-23,430/RT]	[6]
423	6.6	5.95	exp[-23,932/RT]	[8]
423	5.5	4.30	exp[-23,430/RT]	[9]
423	5.3	2.90	exp[-22,190/RT]	[12]

The activation energy, E_d, was determined experimentally by plotting ln P_{sp} at constant H content versus 1/T (equation 5). The P_{sp} values were changed to D_H values for the purposes of Figure 4 where the H contents (constant) were relatively small. The values of E_d fall slightly with decrease of r from 23.24 kJ/mol H (r=0.012) to 23.08 kJ/mol H (r=0.008) which is attributed to some experimental uncertainty because there should be no effect of deviations from Sieverts' law on these values because the experimental values of c_H have been employed to determine D_H; the value shown in Table 3 is an average.

Using $E_{Psp} = E_d + \Delta H_H^o$ where the latter quantity is negative and the others are positive, we obtain using the values extrapolated to r=0,

$$13.50 = (23.16 - 9.10 = 14.06 \text{ kJ/mol H}) \qquad (8)$$

It can be seen that the agreement is reasonable indicating self-consistency of the data.

The equation for D_H from the present work from Figure 4 is given in Table 3 compared with equations from the literature. The diffusion equation given in reference [12] is from a compilation of data from 25 references over a wide temperature range (230 to ~800 K) and quoting Vőlkl and Alefeld "the consistency of the data is remarkably good". The old value 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 from stopcocks. The Pd black's role may be similar to the role of the oxidation/reduction in the present experiments.

Permeation Rates of a Pd Membrane Oxidized over Longer Times

The fluxes and specific permeabilities shown in Table 1 are based on the first five minutes of permeation. It was of interest to determine the fluxes over longer time periods to learn if there is any decrease in rate with time. For this purpose a 120 μ thick membrane was employed which had been oxidized at 923K for 20 m and the 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 flux compared to those given above, i.e., ~10%. In any case, this membrane was quite reproducible and the fluxes were followed up to 60 m. Results are shown in Table 4 at 423K and 473K for 50.5 kPa. These are in quite close agreement indicating that there is negligible fall in the permeation rate.

Table 4. H Fluxes through a Pd Membrane as a Function of Time with the Initial p_{H2} = 50.5 kPa

T /K	t_{av}/m	p_{av}/kPa	J/(mol H/s)	corrected J/(mol H/s)
423	2.5	48.65	$1.45x10^{-6}$	--
423	57.5	20.55	$9.0x10^{-7}$	$1.38 (1.41)x10^{-7}$
473	2.5	47.82	$2.09x10^{-6}$	--
473	57.5	11.92	$9.33x10^{-7}$	$1.86(2.00)x10^{-6}$

The corrections in Table 4 are made by multiplying the flux at t=57.5 m by $\{p_{av}(2.5\ m)/p_{av}(57.5\ m)\}$ or more accurately by $\{r_{av}(2.5\ m)/r_{av}(57.5\ m)\}$ where these concentrations are obtained from the appropriate p_{H2} in Figure 1. The latter corrections are in parenthesis and it can be seen in column 5 (Table 4) that the latter correction works quite well at both temperatures and shows that there is no decrease in rate up to 60 m.

Comparison of Permeabilities of Pd Membranes Oxidized *in situ* at 523 K and *ex situ* at 953K

The permeabilities were consistently smaller for Pd membranes oxidized *in situ* at 523 K than for Pd membranes activated by the higher temperature oxidation, i.e., about 20%, and there was no trend in this difference with temperature. Despite this, the activation energies for diffusion and permeation were similar for each and the membranes oxidized at 523 K also gave the correct d and $p_{H2}^{1/2}$ dependences for diffusion controlled permeation. The smaller D_o value for the membranes oxidized at 523 K may be due to a smaller surface area compared with Pd oxidized at higher temperatures. It has been shown from SEM that the surfaces of oxidized (953 K) Pd foils are much rougher than unoxidized Pd [13].

Effect of CO on H_2 Permeation of Pd Membranes Oxidized either at 953 K or 523 K

CO is known to poison Pd to some extent for H_2 absorption and permeation through Pd membranes [14]. In the present experiments CO was mixed with H_2 and the subsequent permeation rates were measured. It was found that Pd oxidized 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% when p_{CO}=0.66 kPa was added to p_{H2}=0.101 MPa (423 K) whereas it was reduced by ~28% for the Pd oxidized at 523 K under similar conditions except with p_{H2}=0.050 MPa which would tend to cause a greater inhibition than the 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.

Table 5 shows the results of the CO poisoning over a relatively long time period, 60 m. The p_{CO} is initially 1.3% of the total and after 60 m, it is 2.4% and it has been ignored in the calculation of the corrections shown in column 5. The important point is that while the corrections shown in Table 4 gave fluxes which agreed very well with the initial ones (2.5 m), this is not the case in the presence of CO. It is clear that the flux falls off with the time of exposure to the CO.

Table 5. H Fluxes through a Pd Membrane in the Presence of 0.67 kPa CO as a Function of Time with the Initial p_{H2}=50.5 kPa.

T /K	t_{av}/m	p_{av}/kPa	J/(mol H/s)	corrected J/(mol H/s)
423	2.5	49.75	1.08×10^{-6}	--
423	57.5	37.20	4.22×10^{-7}	$4.88(5.62) \times 10^{-7}$
473	2.5	48.81	2.09×10^{-6}	--
473	57.5	28.00	9.33×10^{-7}	$1.23(1.30) \times 10^{-7}$

Conclusions

Hydrogen diffusion constants and specific permeabilities have been measured in a non-UHV system for Pd membranes oxidized at 953 K and at 523 K. The results are quite reproducible and somewhat faster permeabilities were found after oxidation of the Pd at an elevated temperature as compared to the lower temperature *in situ* oxidation. The dependence of the permeation rates upon $p_{H2}^{1/2}$ and their inverse dependence upon membrane thickness show that H bulk diffusion is the slow step rather than surface steps. It is shown that the dependence on $p_{H2}^{1/2}$ obtains over a wide range of p_{H2} if the data are corrected for non-ideality, i.e., deviations from Sieverts' law are allowed for. In view of the possibility for surface poisoning in the non-UHV system, it is surprising that bulk diffusion is the slow step. The magnitude of D_H agrees very well with previous investigations and the data are consistent with the relation $E_{Psp} = E_d + \Delta H_H^o$.

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Figure Captions

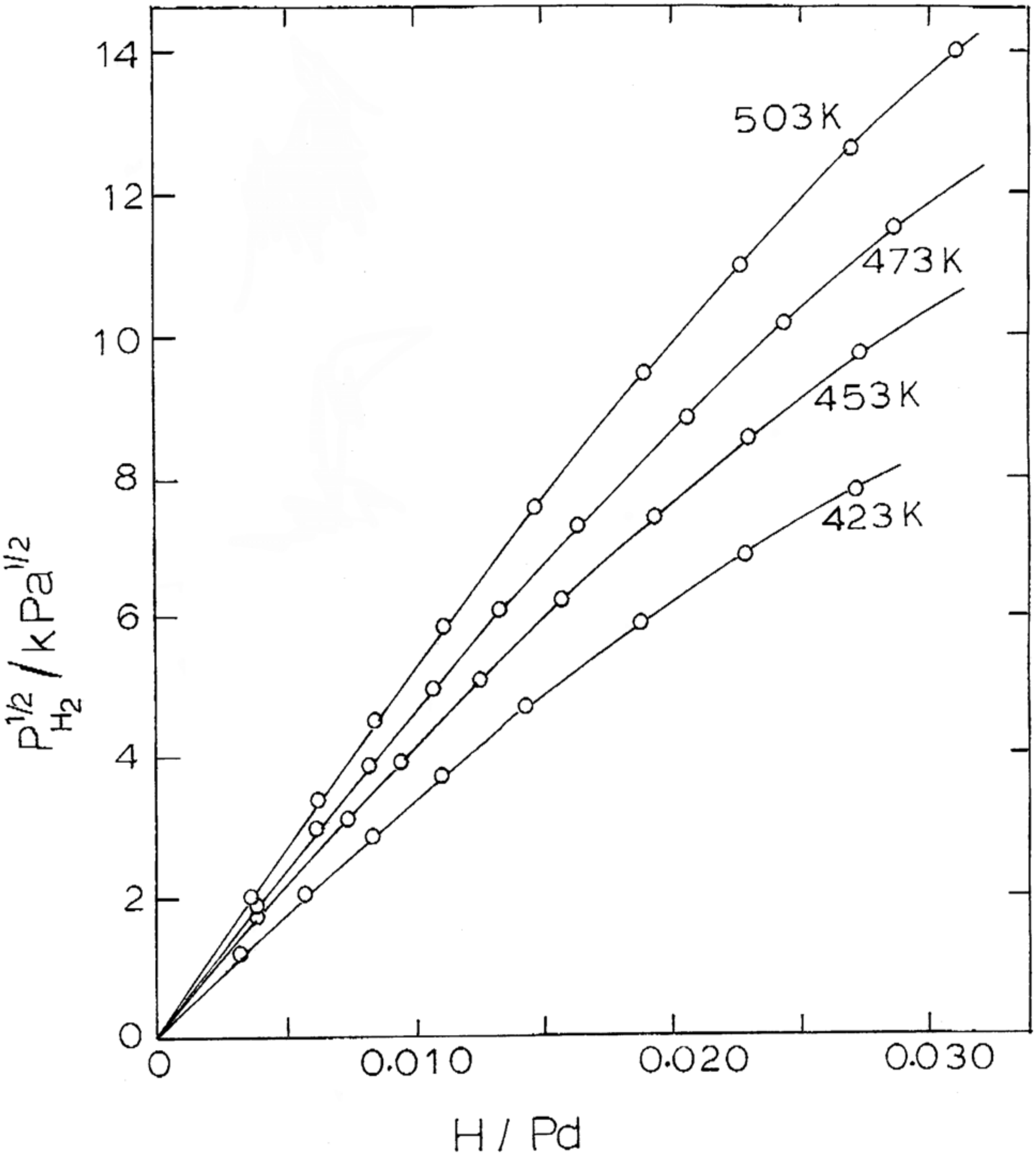
Fig. 1. H_2 solubility in the dilute phase of annealed Pd.

Fig. 2. Specific permeability (138μ membrane) plotted as a function of $p_{H2}^{1/2}$at 473 K. Circles, experimental data; triangles, experimental data corrected for non-ideality.

Fig. 3. Arrhenius plots of specific permeability (138μ membrane) against 1/T at the p_{H2} indicated. Circles, at p_{H2}=16.0 kPa; triangles, at p_{H2}=10.0 kPa. The open symbols are the experimental data and the filled ones are the experimental data corrected for non-ideality.

Fig. 4. Arrhenius plots of the hydrogen diffusion constant (138μ membrane) against 1/T. Circles, at r=0.012; triangles, at r=0.008.

Figure 1.



503 K
473 K
453 K
423 K
0
2
4
6
8
10
12
14
$P_{H_2}^{1/2}$ / kPa$^{1/2}$
0
0.010
0.020
0.030
H / Pd

Figure 2.

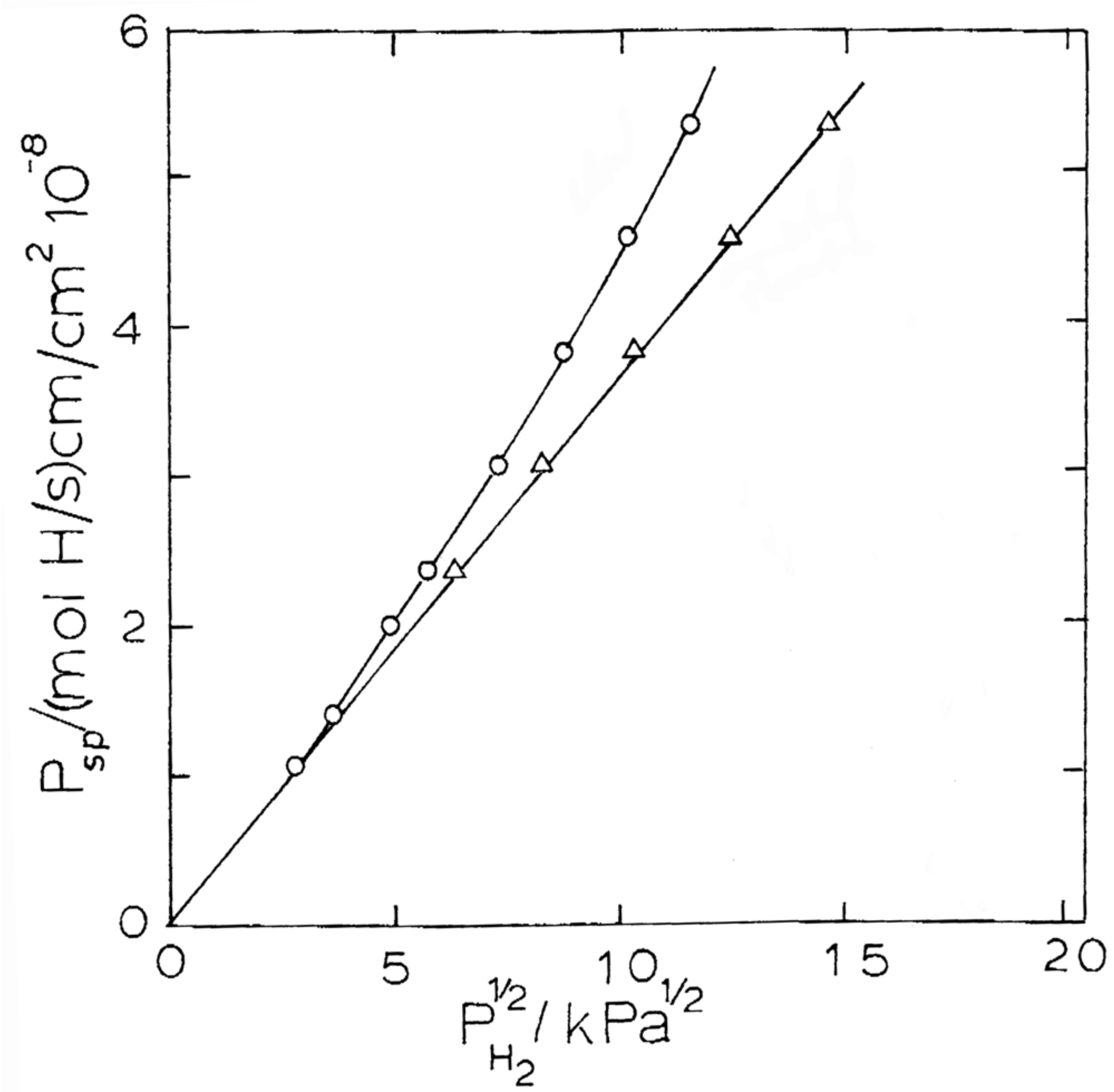


Figure 3.

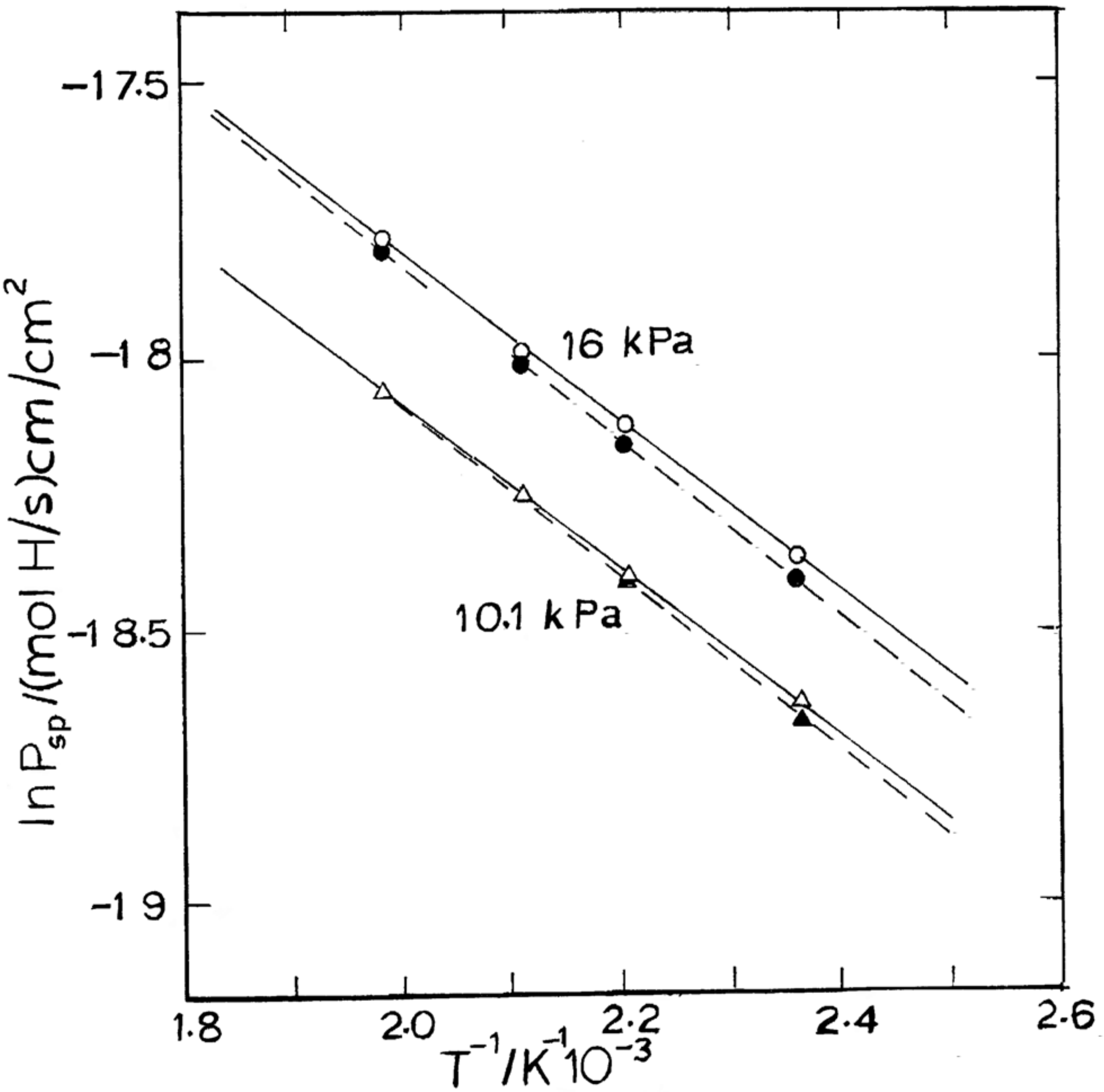

-17.5
-1 8.
-1 8.5
-1 9
1.8
2.0
2.2
2.4
2.6
$\ln P_{sp}$ /(mol H/s)cm/cm^2
$T^{-1}/K^{-1}10^{-3}$
16 kPa
10.1 kPa

Figure 4.