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Hydrogen Permeation Measurements of Partially Internally Oxidized *Pd*-Al Alloys in the Presence and Absence of CO (U)

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Abstract

Specific permeabilities and diffusion constants for H have been measured in a series of *Pd*-Al alloy membranes using a new method for activation of the membranes. The membranes have been partially internally oxidized at an elevated temperature before inserting into the apparatus for measuring H_2 permeabilities. If the percent internal oxidation is small relative to the membrane thickness, the diffusion takes place essentially through the unoxidized alloys. The activation energy for diffusion of H increases with atom fraction Al from 23.2 kJ/mol $1/2H_2$ (X_{Al}=0) to 25.1 J/mol $1/2H_2$ (X_{Al}=0.08). It is shown that the partially oxidized alloys are more resistant to CO poisoning than unoxidized alloys. The resistance of the partially internally oxidized alloys towards poisoning by $CO_{(g)}$ increases and the diffusion constants decrease with X_{Al}.

Introduction

It has been observed that the kinetics of H_2 absorption are faster for internally oxidized *Pd*-Al alloys than for pure Pd foil [1] and, in addition, the partially internally oxidized alloys offer a greater resistance to poisoning by CO(g) [2]. For these reasons it was believed to be useful to examine the H_2 permeation of partially internally oxidized *Pd*-Al membranes. They will be partially, rather than completely, internally oxidized because the latter may lead to structural problems, e.g., cracking. The present investigation concerns partially internally oxidized *Pd*-Al alloys with X_{Al}=0.02, 0.045, 0.06 and 0.08. Besides measuring the specific permeabilities, the solubilities were measured over the same temperature range, 423-503K, allowing diffusion constants to be determined from the specific permeabilities. From the slopes of Arrhenius' plots of the permeabilities at constant H contents, the activation energy for diffusion, E_D, can be obtained. Sakamoto *et al* [3] measured the solubilities in *Pd*-Al alloys at 273-423K and found that $|\Delta H_H^o|$ increased slightly with X_{Al} while $|\Delta H_{plat}|$ decreased.

The specific permeabilities and diffusion constants of partially internally oxidized *Pd*-Al alloys will basically correspond to those for the unoxidized alloys because there is only a small (~9% ± 3%) contribution from the oxidized portions. The diffusion constants for *Pd*-M alloys generally decrease with increase of M but not in a linear way, e.g., for *Pd*-Ag alloys the values do not decrease very much until $X_{Ag}>0.20$ [4]. There have been few measurements of diffusion constants of *Pd*-M alloys where M decreases the solubility markedly such as Al.

Experimental

Materials and Apparatus

The alloy membranes were prepared by arc-melting the pure components and then annealing the buttons at 1133K for 72 h which were then rolled into foils about 1.5x1.5 cm and from 100 to 200μ in thickness. They were partially internally oxidized in the atmosphere at 953K which also caused some oxidation of Pd which can be described as a “deep surface oxide" [5]. The weights after internal oxidation reflect not only internal oxidation but also the oxidation of Pd and therefore the weights were also measured after completion of the permeation experiments because the PdO, at least in that part of the membrane which was active for permeation took place, is reduced by exposure to H_2. For instance, the % internal oxidation based on the weights before and after the permeation experiments were 9.9% and 8.7%, respectively, for the $Pd_{0.94}Al_{0.06}$ alloy. The active portion of the membranes is about 75% of the total area and therefore some error is introduced into the 8.7% by the remaining unreduced 25% fraction. This error is minor, however, in view of the small difference between the total membrane weights before and after their employment as membranes. The degree of internal oxidation was from 6% ($X_{Al}=0.08$) to 12% ($X_{Al}=0.02$). The H_2 solubilities (423 to 503K) were measured using foils of unoxidized alloys.

The apparatus for the H_2 permeation measurements is relatively straightforward. The membranes (1.63 cm^2) were mounted in a Cajon fitting which took the place of the normal gasket. The active area was easy to measure because it had a bright metallic sheen whereas the inactive area was dull blackish in appearance because it had not been reduced. The fitting was placed within a furnace controlled to the desired temperature.

Procedure

The *Pd*-Al alloy membranes were internally oxidized at 953K in the atmosphere for 30 m. After this they were heated to 523K for about 1-2 h at $p_{H2}\approx0.8$ bar and then the temperature and p_{H2} were reduced to 423K and 0.5 bar, respectively, where they were left overnight. They were then evacuated and the permeation measurements started. The permeation was followed by the p_{H2} fall on the upstream side of the membrane using an MKS pressure gauge while the downstream side was maintained *in vacuo*. The volume of the upstream side was 0.279 dm^3. Values of p_{H2} were recorded over 5 m or longer periods at 1 m intervals. Generally the p_{H2} fall during these determinations over 5 m was small. If the fall was significant, the permeation was taken for the first minute; in fact, the permeation rate was almost the same over the whole monitoring time if the p_{H2} decrease was allowed for. The system was evacuated before and between measurements and continuously during the runs on the downstream side using mechanical pumps and therefore it is not a “clean" system and some irreducibility due to poisoning by gaseous impurities might be expected but surprisingly this appeared to be minimal.

Experiments carried out in the presence of CO(g)+ $H_{2(g)}$ were generally carried out by their simultaneous addition on the upstream side.

Equations Employed for Evaluating Specific Permeability and Diffusion Constants.

The steady state diffusion of H through a membrane of thickness d, and area A, where the downstream concentration, $c_{down}=0$, is given by

$$J = (\text{rate/mol H/s})/A = -(D_H c_{up}/d)/(\text{mol H/s})/\text{cm}^2. \qquad (1)$$

The specific permeability (also referred to as the permeability constant [6]) has been given various definitions but the important point is that it reflects the total H passing through the membrane at a given p_{H2}. The definition of specific permeability will be that used by Kofler *et al* [7], although, different units will be employed here, i.e.,

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

The specific permeability in the dilute phase can also be expressed in terms of the diffusion constant, D_H, as

$$P_{sp} = D_H c_H = (A/d)p_{up}^{1/2}K_s \exp(-\Delta H_H^o/RT)\exp(-E_D/RT) \qquad (3)$$

where c_H is the H concentration in mol H/cm^3, K_s is a solubility constant in the appropriate units, ΔH^o is the enthalpy of solution of $1/2H_2$ at infinite dilution and E_D is the activation energy for diffusion of H in the dilute phase and $p_{down}\approx 0$. The diffusion constant obtained from P_{sp} after correction for non-ideality is D_H which at very small H contents becomes D_H^*, i.e., the value at infinite dilution. The two are related by equation (4)

$$D_H = D_H^* f \qquad (4)$$

where $f=(c_H/RT)(\partial\mu/\partial c_H)_T = (r/p^{1/2}\}dp^{1/2}/dr$ and is called the thermodynamic factor, f, [4] where r, the H/metal atom ratio, is proportional to c_H; f reduces to unity in the ideal range of solubilities. It follows from equation (3) that at infinite dilution $E_{Psp}=\Delta H_H^o + E_D$ where E_{Psp} is the observed activation energy for the specific permeability. E_D can be obtained by measurements of the specific permeability at constant H contents at different temperatures as can be seen from equation (3) because in the case of a constant H content the temperature dependence of P_{sp} will be determined by the $\exp\{-E_D/RT\}$ term.

Results and Discussion

Hydrogen Isotherms

Isotherms for the unoxidized *Pd*-Al alloys were measured up to about 0.1-0.2 MPa at 423, 453, 473 and 503K except for the $Pd_{0.955}Al_{0.045}$ alloy which was measured at 393K but not at 473K. To illustrate the type of data obtained, H_2 isotherms are shown for the $Pd_{0.92}Al_{0.08}$ alloy in Figure 1.

Two phases do not form at these temperatures and p_{H2} as indicated by the absence of a constant pressure region. Solubilities for all of the alloys at 423K are shown in Figure 2 where there is seen to be a steady decrease of solubility with X_{Al}. The $\Delta\mu_H=RT\ln(p^{1/2}_{H2}\}$ values evaluated at r=0.020 increase steadily with X_{Al} (Table 1) whereas ΔH_H^o and ΔS_H^o do not show any clear trend with X_{Al} (Table 1); this is probably due to experimental error since the total change in $\Delta\mu_H$ is only about 1.4 kJ/ mol H and there may be changes in both $|\Delta H_H^o|$ and $|\Delta S_H^o|$ with X_{Al}. Sakamoto *et al* [3] report small changes in both $|\Delta H_H^o|$ and $|\Delta S_H^o|$ with X_{Al} from p-c-T data from 273 to 433K. Since the *Pd*-Al alloys have contracted unit cells compared to Pd, it would be expected that the $|\Delta H_H^o|$ values would decrease [8]. Sakamoto *et al* did find that |ΔHplat| decreases with X_{Al} which differs from the behavior of most other contracted alloy systems where both enthalpies decrease with X_M [8].

Specific Permeabilities and Diffusion Constants in the Absence of CO.

The reproducibility of the partially internally oxidized *Pd*-Al alloys is very good and therefore their use as permeation membranes may offer a means of measuring the specific permeabilities and diffusion constants of unoxidized alloys such as *Pd*-M where M=Al, Zr, Ti, etc., i.e., solutes which can be internally oxidized. Aside from a small error introduced by the outer internally oxidized region, the diffusion parameters will correspond to those of the unoxidized alloy membranes. The reproducibility and resistance to poisons is better for the internally oxidized *Pd*-—Al alloys than for their unoxidized counterparts and presumably this will be the true for other *Pd*-M alloys.

For a typical alloy, e.g., the X_{Al}=0.08, permeation rates were measured at 0.101 MPa and at 0.0505 MPa at temperatures from 423 to 503K. Typical reproducibilities were excellent. Data are shown in Fig. 3 for the specific permeabilities measured at these two p_{H2} where the two slopes give E_p=15.1 kJ/mol and E_P=15.2 kJ/mol H, respectively. For the X_{Al}=0.08 alloy the solubility is nearly ideal from 453K to 503K and ideal also at 423K at 0.0505 MPa (Fig. 1). Specific permeabilities were also measured at constant H content, H/Pd=r, which gives E_D from the slopes. Figure 4 shows these data for all of the alloys after the specific permeabilities have been converted to D_H values or D_H^* in the very dilute range. D_H^* is independent of p_{H2} to a first approximation but P_{sp} depends on it. D_H^* is obtained by dividing P_{sp} by c_H in units of mol H/cm^3 of alloy (equation 3). Since the

Table 1. Thermodynamic Parameters for Hydrogen Solution in *Pd*-Al Alloys at Infinite Dilution (423-503K)[*]

X_{Al}	$\Delta\mu_H$ (r=0.020 (423K))	ΔH_H^o	ΔS_H^o
0	-1.74	-9.2	-52.3
0.02	-1.36	-9.7	-53.0
0.045	-1.10	-9.4	-54.7
0.06	-0.68	-9.5	-54.0
0.08	-0.32	-9.5	-55.5

(*) the units of $\Delta\mu_H$ and ΔH_H^o are kJ/mol H and ΔS_H^o is J/K mol H.

Table 2. Parameters for Diffusion and Permeability of Partially Internally Oxidized *Pd*-Al Alloys determined from 423 to 503K.[*]

X_{Al}	D_H(473K)/cm^2/s	D_o/cm^2/s	E_D	E_P	ΔH_H^o **
0	$1.59\text{x}10^{-5}$	$5.6\text{x}10^{-3}$	23.2	13.0	-9.2(-9.9)
0.02	$1.48\text{x}10^{-5}$	$5.8\text{x}10^{-3}$	23.5	13.4	-9.7(-10.1)
0.045	$1.14\text{x}10^{-5}$	$5.0\text{x}10^{-3}$	23.9	13.0	-9.4(-10.9)
0.06	$9.7\text{x}10^{-6}$	$4.9\text{x}10^{-3}$	24.5	14.1	-9.5(-10.4)
0.06***	$9.3\text{x}10^{-6}$	-	-	14.1	-9.5(-10.4)
0.08	$9.1\text{x}10^{-6}$	$5.5\text{x}10^{-3}$	25.1	15.4	-9.5(-9.7)

* E_D, E_P and ΔH_H^o are in units of kJ/mol H.

** The values of ΔH_H^o in parenthesis are those determined from $\Delta H_H^o = E_p - E_D$ and the others were determined directly from the experimental solubilities (e.g., Fig. 1).

*** *not* partially internally oxidized.

actual solubility relations (Figs. 1, 2) are employed to obtain c_H, there will be no effect of non-ideality due to deviations from Sieverts' law such as observed for the permeabilities as a function of p_{H2}. This is demonstrated by the observation that Arrhenius plots of D_H for a given alloy determined at different concentrations of H were almost superimposable indicating that to good approximation $D_H=D_H^*$.

From the relationship $E_P=\Delta H_H^o+ E_D$, we have, for example, for the $Pd_{0.92}Al_{0.08}$ alloy at infinite dilution, $E_p=15.2 + 9.5= 24.7$ kJ/mol H compared to the measured value of 25.1 kJ/mol H, i.e., the agreement is good for it and for the other alloys (Table 2).

Figure 5 shows values of D_H^* and P_{sp} as a function of X_{Al}. The former is not linear but shows a small initial region where the change is small followed by a sharp decline and then a further leveling off. The activation energy for diffusion increases with X_{Al} which accounts for the change of D_H^* with X_{Al} because D_o does not change very much (Table 2). The specific permeability dependence on X_{Al} is similar to the D_H^* dependence (Fig. 5).

Data were obtained for a representative alloy, $X_{Al}=0.06$, which had *not* been partially internally oxidized. It was exposed to air at 523K for 10 m while in the permeation apparatus and then reduced in H_2. The diffusion constant is shown in Table 2 and it can be seen that it is within 5% of the value for the partially internally oxidized alloy indicating that the small amount of internal oxidation does not significantly affect the permeation parameters and the data for the partially internally oxidized alloys represent *Pd*-Al alloys.

Pressure Dependence of Permeability

Permeability data are shown in Figure 6 (473K) for the various alloys as a function of $p_{H2}^{1/2}$ showing that the slope at small $p_{H2}^{1/2}$ is linear indicating that bulk diffusion is the rate-controlling step. At higher $p_{H2}^{1/2}$ there are deviations from the straight line relation the extent of which decreases as X_{Al} increases. This is in agreement with the solubility relationships which behave more ideally with increase of X_{Al}. The corrected data for the $X_{Al}=0.02$ alloy are also shown by the dashed line which is nearly linear, i.e., the permeability data are corrected by multiplying the values at a given p_{H2} by the ratio of the (r_{exp}/r_{ideal}) where the experimental value is taken from the solubilities and the ideal is from the linear relationship as r→0. At higher X_{Al} values the P_{sp} - $p^{1/2}_{H2}$ plots do not appear to intersect the origin.

The Effect of $CO_{(g)}$ on the Permeation Rates of Partially Internally Oxidized *Pd*-Al Membranes

Generally for each *Pd*-Al membrane H_2 rates of permeation were measured over the initial 5 m at 423K at P_{CO}=0.66, 2.00 and 6.67 kPa. Results are shown in Table 3 where the % decrease refers to the decrease of P_{sp} compared to the value for the same internally oxidized alloy in the absence of CO. For example, for the X_{Al}=0.02 alloy the specific permeability at 0.0505 MPa (473K) is 2.54 x 10^{-8} (mol H/s)cm/cm^2 in the absence of CO and 2.31 x 10^{-8} (mol H/s)cm/cm^2 in the presence of p_{CO}=0.66 kPa corresponding to a 9% decrease.

Some of these results are presented in Figures 7 and 8 where the % decrease in specific permeabilities are plotted against X_{Al}. All of these data show that the resistance to poisoning by CO increases with X_{Al}. It also shows that the poisoning compared at a constant p_{H2} increases with increase of p_{CO} as might be expected (Fig. 7). The permeabilities increase with increase of p_{H2} at constant p_{CO}. The poisoning also decreases with increase of temperature for a given p_{CO} and p_{H2} (Fig. 8).

After exposure to CO + H_2 mixtures, the permeation rates of the internally oxidized alloys can be recovered by several consecutive treatments with H_2 at 423K times followed by evacuation after each. Pd which had been oxidized at 953K for 30 m did not recover after such a H_2 treatment but generally recovered after several exposures to H_2 and evacuation at 473K.

Data are also shown for the X_{Al}=0.06 alloy membrane which had *not* been partially internally oxidized in Table 3. It can be seen that the effect of CO is much more significant for the unoxidized membrane especially at 423K. This clearly shows the advantages of partial internal oxidation.

Table 3. Change of the Specific Permeabilities of Pd-Al Partially Internally Oxidized Alloys due to CO.

X_{Al}	p_{H2} / MPa	p_{CO} / kPa	% change	
	{423K}			
0	0.0505	0.66	-28.3	
0.02	0.0505	0.66	-16.0	
0.045	0.0505	0.66	-11.1	
0.060	0.0505	0.66	-7.5	
0.080	0.0505	0.66	-5.4	
0	0.101	0.66	-	
0.02	0.101	0.66	-12.7	
0.045	0.101	0.66	-7.7	
0.060	0.101	0.66	-4.7	
0.060*	0.101	0.66	-22.2	*, *not* oxidized
0.080	0.101	0.66	-3.7	
0	0.101	2.00	-	
0.02	0.101	2.00	-20.5	
0.045	0.101	2.00	-11.2	
0.06	0.101	2.00	-7.3	
0.08	0.101	2.00	-6.0	
0.0	0.101	6.67	-68.8	
0.02	0.101	6.67	-39.4	
0.045	0.101	6.67	-19.9	
0.060	0.101	6.67	-11.5	
0.080	0.101	6.67	-8.2	
	(473K}			
0	0.0505	0.66	-15.0	
0.02	0.0505	0.66	-9.0	
0.045	0.0505	0.66	-6.4	
0.060	0.0505	0.66	-3.7	
0.060*	0.0505	0.66	-3.7	
0.080	0.0505	0.66	-2.8	
0.060	0.101	0.66	-2.8	
0.060*	0.101	0.66	-11.8	
0.080	0.101	0.66	-2.4	
0.060	0.101	2.00	-4.9	
0.080	0.101	2.00	-4.4	
0.060	0.101	6.67	-6.8	
0.060*	0.101	6.67	-25.5	
0.080	0.101	6.67	-7.3	

The Effect of $CO_{(g)}$ on the Hydrogen Flux through Pd and Partially Internally Oxidized $Pd_{0.955}Al_{0.045}$ Membranes over a long Time Period.

The data given above, e.g., Table 3, are based on five measurements of flux over the initial 5 m interval. In this section results are described in which the permeabilities were continuously measured over a longer period of time for a representative partially internally oxidized *Pd*-Al alloy. A $Pd_{0.955}Al_{0.045}$ alloy (128 ±6μ) was chosen for this purpose which had been internally oxidized to 11%. The flux was measured in the absence and presence of $CO_{(g)}$ (Fig. 9) and compared to similar results for Pd (120μ). The fluxes have been corrected for the different thicknesses of Pd and the alloy membranes. In the absence of $CO_{(g)}$ the fluxes of both are constant over the 60 m period. For Pd membranes the flux in the presence of CO is initially much smaller than that in its absence and it then decreases slowly with time. The flux in the presence of CO for the partially internally oxidized $Pd_{0.955}Al_{0.045}$ alloy initially decreases less dramatically from its CO-free value, but then also falls slowly. While the flux is greater for Pd than for the $Pd_{0.955}Al_{0.045}$ alloy in the absence of CO, mainly because of the greater H_2 solubility in the former, in the presence of the CO the rates are comparable after about 10 m (Fig. 9) and then the alloy flux overtakes the Pd flux.

Conclusions

It is shown that partial internal oxidation of *Pd*-Al alloys is helpful for their reproducibility for H_2 permeation. The H_2 permeations through these membranes reflect the unoxidized alloys because the fraction of the internal oxidation is small. The sensitivity of the partially internally oxidized alloys to inhibition of the permeation by CO is less significant than for Pd and their sensitivity towards CO decreases with X_{Al}. Over a relatively long period of time the flux is nearly constant for Pd and for a representative internally oxidized alloy, $Pd_{0.955}Al_{0.045}$. In the presence of CO the permeabilities both decrease with time, however, the decrease of the internally oxidized alloy is significantly smaller. After ~10 m, the internally oxidized alloy permeability exceeds that of the Pd despite its smaller H solubility and D_H.

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Figure Captions

Fig. 1. H_2 solubilities of the X_{Al}=0.08 unoxidized alloy at elevated temperatures.

Fig. 2. H_2 solubility plots for Pd and *Pd*-Al alloys at 423K.

Fig. 3. The temperature dependence of the specific H_2 permeabilities through a partially internally oxidized $Pd_{0.92}Al_{0.08}$ alloy at two different p_{H2}.

Fig. 4. Diffusion constants for the internally oxidized *Pd*-Al alloys and pure Pd. ●, Pd (oxidized 953K); □, X_{Al}=0.02; ▼, X_{Al}=0.045; Δ, X_{Al}=0.06; ○, X_{Al}=0.08.

Fig. 5. Diffusion constants and specific permeabilities (0.101 MPa) for the internally oxidized *Pd*-Al alloys as a function of X_{Al} at 473K.

Fig. 6. Plots of permeation rates at different p_{H2} for the various alloys at 473K. The dashed line is the data corrected for non-ideality for the X_{Al} =0.02 alloy.

Fig. 7. Plot of decrease of permeation rates at various P_{CO} (423K) as a function of X_{Al}.

Fig. 8. Plot of decrease of permeation rates at different temperatures at P_{CO}=0.66 kPa and p_{H2}=0.0505 MPa as a function of X_{Al}.

Fig. 9. Plot of the fluxes for an initial p_{H2} of 0.0505 MPa at 423K for a Pd membrane and a partially internally oxidized $Pd_{0.955}Al_{0.045}$ alloy in the absence of CO and in the presence of p_{CO}=0.66 kPa. Δ, Pd in the absence of CO and ○, Pd in the presence of CO. The filled symbols refer to the partially internally oxidized $Pd_{0.955}Al_{0.045}$ alloy.

Figure 1.

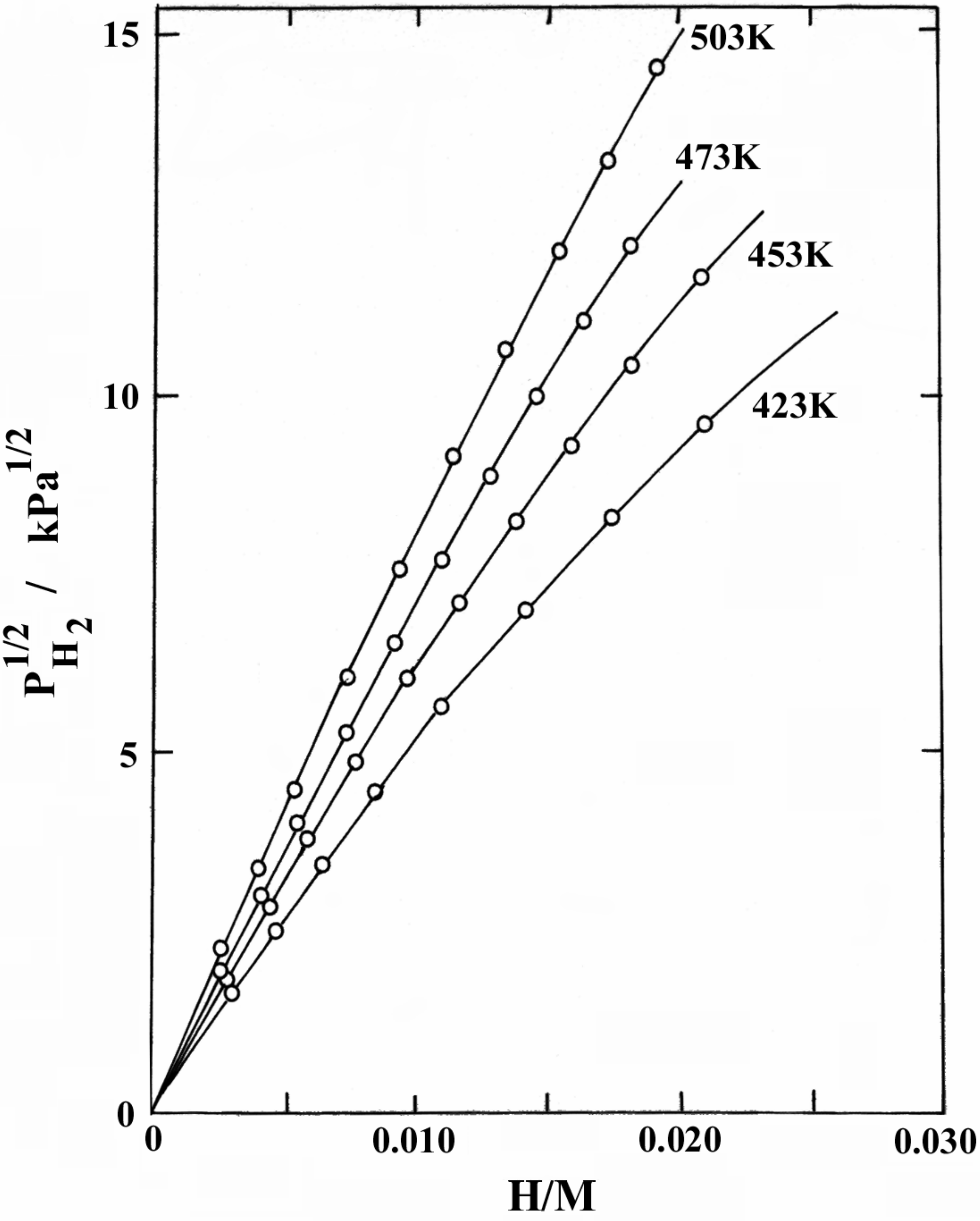
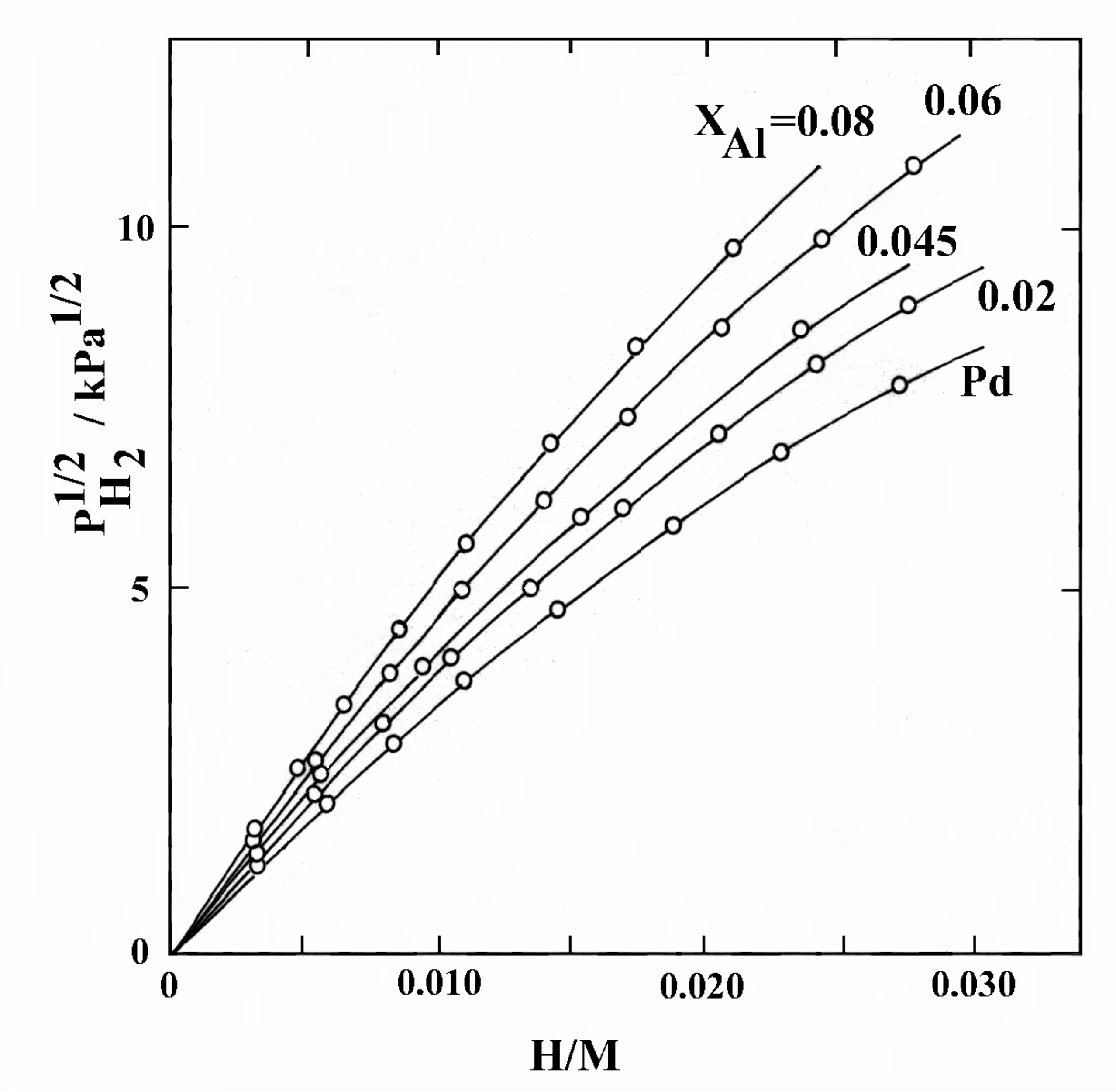


Figure 2.



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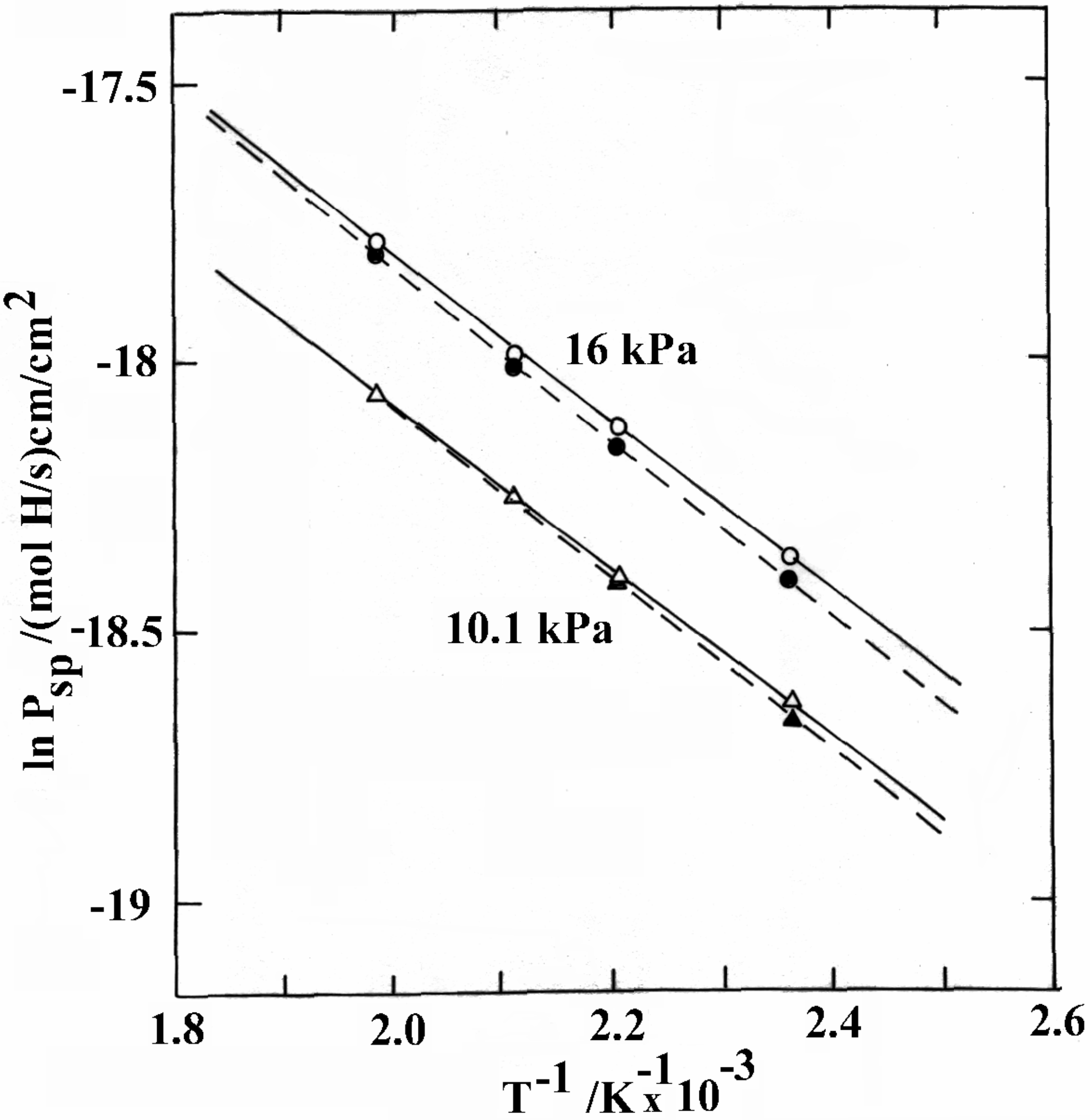
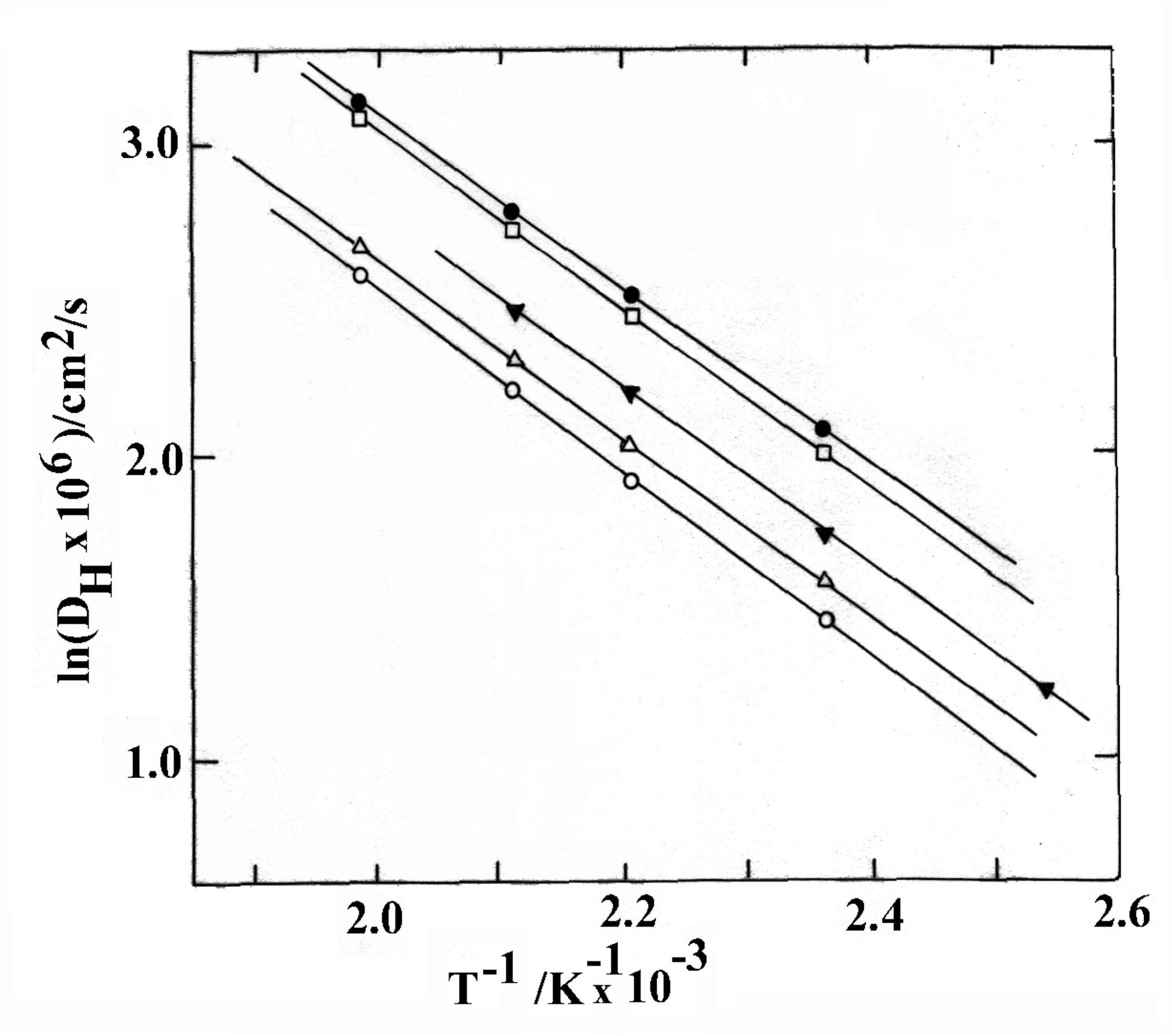

-17.5
-18
-18.5
-19
1.8
2.0
2.2
2.4
2.6
16 kPa
10.1 kPa
$\ln P_{sp}$ /(mol H/s)cm/cm^2
T^{-1} /K^{-1} x 10^{-3}

Figure 4.



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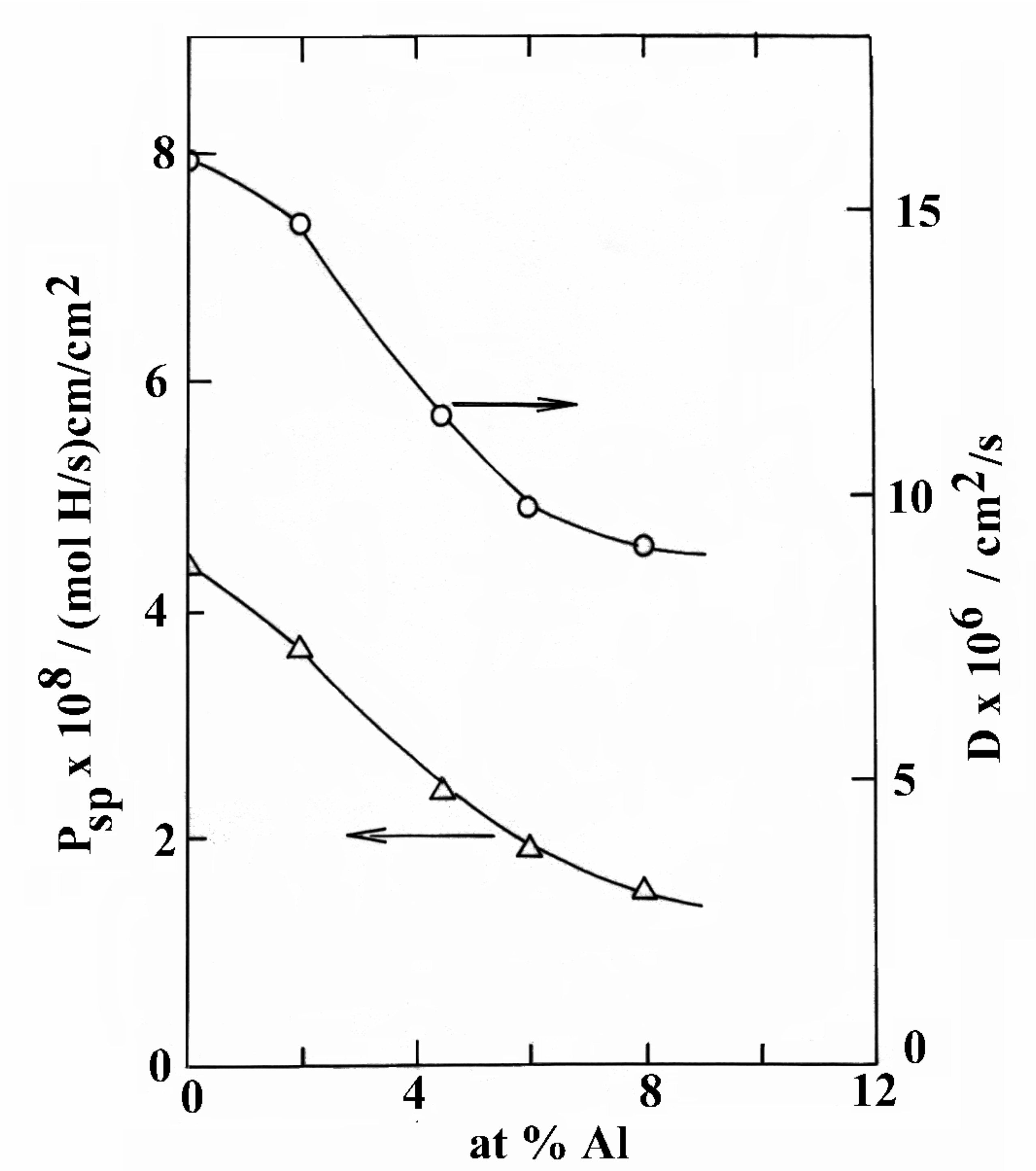
$P_{sp} \times 10^8$ / (mol H/s)cm/cm^2
0
2
4
6
8
$D \times 10^6$ / cm^2/s
0
5
10
15
0
4
8
12
at % Al

Figure 6.

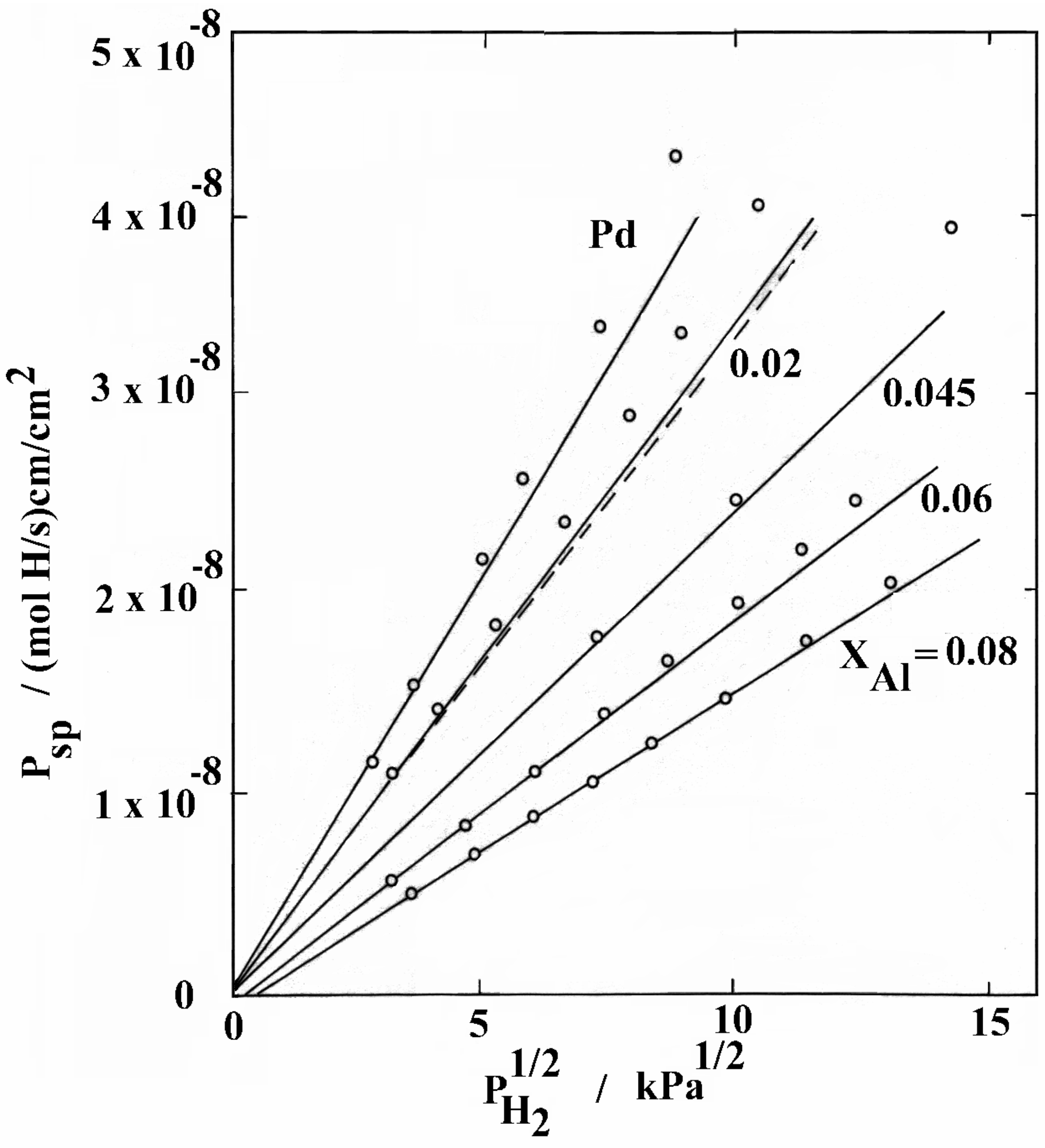
5×10^{-8}
4×10^{-8}
3×10^{-8}
2×10^{-8}
1×10^{-8}
0
P_{sp} / (mol H/s)cm/cm^2
0
5
10
15
$P_{H_2}^{1/2}$ / kPa$^{1/2}$
Pd
0.02
0.045
0.06
$X_{Al} = 0.08$

Figure 7.

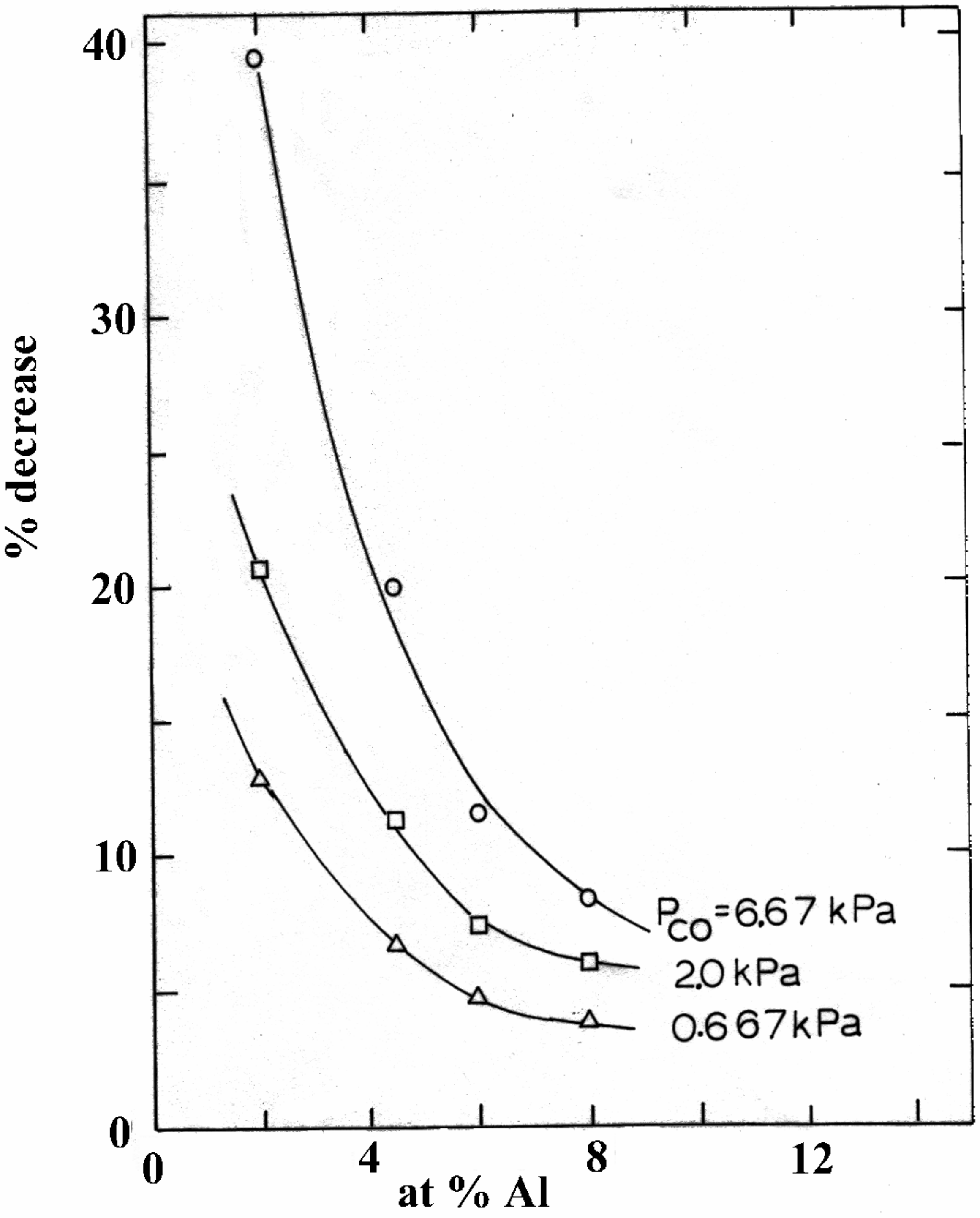

Figure 8.

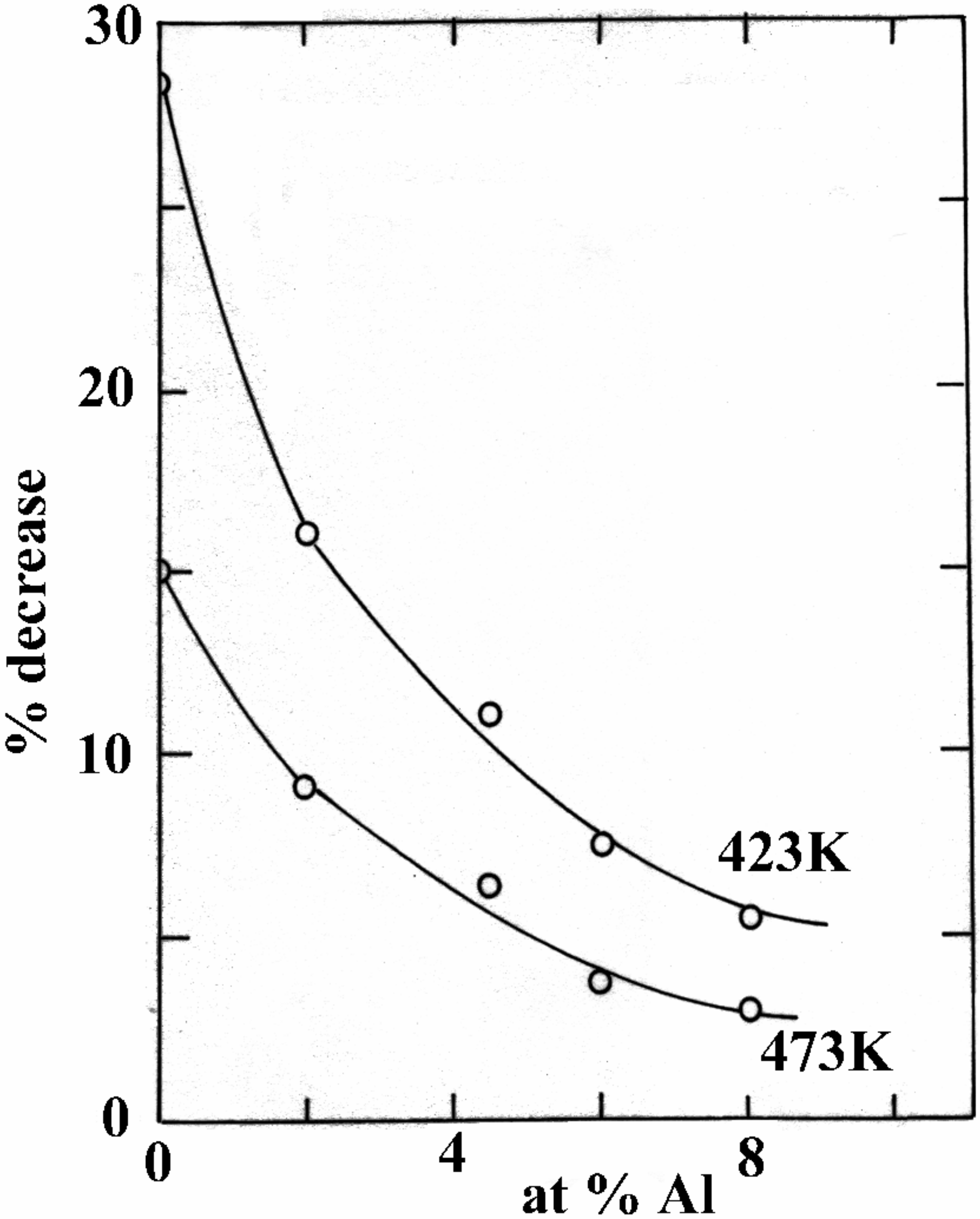

Figure 9.