Diffusion and Solubility of Hydrogen in Palladium and Palladium–Silver Alloys

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Diffusion coefficients and heats of solution for hydrogen in Pd and Pd–Ag alloys at low hydrogen concentration were determined from 260 to 640°. The change in activation energy for hydrogen diffusion with increasing mole fraction of silver (X_{Ag}) from Pd to $Pd_{0.5}Ag_{0.5}$ can be represented empirically by $E = 3800X_{Ag}^4 + 1500X_{Ag}^2 + 5260$ cal. The preexponential factor, D_0 showed only a slight linear decrease $D_0 = -2.65 \times 10^{-3}X_{Ag} + 2.9 \times 10^{-3}$. The molar heat of desorption, ΔH_{H_2}, increased with rising Ag concentration from 4000 cal (Pd) to a maximum between 8020 ($Pd_{0.6}Ag_{0.4}$) and 7090 cal ($Pd_{0.5}Ag_{0.5}$). The entropy of desorption, ΔS_{H_2}, remained quite constant at values between 23.3 and 24.4 cal/deg mol.

Introduction

The diffusion of hydrogen in Pd and Pd alloys is of great interest because of its fundamental importance as one of the best defined examples of interstitial diffusion in transition metals. It also has considerable technological importance. Membranes, especially of Pd alloys, are widely used for separation and purification of hydrogen gas. Despite this, there has been no systematic investigation of the hydrogen diffusion behavior in Pd–Ag alloys at elevated temperatures. The diffusion of hydrogen in Pd between 200 and 700° has, however, been studied by several authors.[1-5] Most measurements were based on results of hydrogen permeation and solubility data from Sieverts, *et al.*,[6,7] or Gillespie and Galstaun (210–313°).[8]

There are only a few limited measurements[5,9] on hydrogen diffusion and solubility in Pd–Ag alloys above 250°. Investigations of hydrogen diffusion in Pd at approximately room temperature were reported recently by many authors.[10-16] Electrochemical methods were primarily employed,[10-14] but more recently gas volumetric methods were used successfully as well.[15,16] In this temperature range, several investigators reported also on hydrogen diffusion in Pd–Ag membranes.[14,15,17-20]

Two more recent publications[14,15] discuss the electrochemical and gas volumetric hydrogen diffusion measurements in Pd and Pd–Ag alloys between 0 and 100°, with special reference to the hydrogen concentration in the metal lattice. However, some uncertainty remained about the effect on hydrogen diffusion of increasing Ag content in Pd–Ag alloys at low hydrogen concentrations.

The aim of this investigation was to clarify this point and to examine changes in hydrogen diffusion and solubility parameters with Ag content over a larger temperature range. Special care was taken to avoid inhibition at the interface which often led to erroneous results in the past.

Principle of Measurement and Diffusion Theory

Consider one-dimensional diffusion in a membrane of thickness, s, bounded by two parallel planes (this means in practice that effectively all the diffusing substance enters and leaves through the plane faces, and a negligible amount through the edges).

The initial and boundary conditions for the diffusion equation $\partial c/\partial t = D\, \partial^2 c/\partial^2 x$ are

$$c = c_0 \text{ for } 0 < x < s \text{ and } t = 0$$

$$c = 0 \text{ for } x = 0 \text{ and } c = c_1 \text{ for } x = s \text{ and } t > 0$$

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where c is the H concentration in the metal.

The more general case ($c = c_{00} \neq 0$ at $x = 0$ for $t > 0$) is reduced to the above by substituting $c' = c - c_{00}$. The resulting boundary conditions are

$$c' = c_0 - c_{00} \text{ for } 0 < x < s \text{ and } t = 0$$

$$c' = 0 \text{ for } x = 0 \text{ and } c' = c_1 - c_{00} \text{ for } x = s \text{ and } t > 0$$

This diffusion problem was dealt with by Daynes[21] and Barrer.[22]

If we solve the diffusion equation with the stated boundary conditions for the total amount of gas, Q, which emerges from the face ($x = 0$), we obtain for the time lag, L (which is represented by the intercept on the t axis of a plot Q *vs.* t[23])

$$L = \frac{s^2}{6D} - \frac{c_0 s^2}{2Dc_1} \tag{1}$$

and, for the more general case

$$L = \frac{s^2}{D(c_1 - c_{00})}\left(\frac{c_1}{6} + \frac{c_{00}}{3} - \frac{c_0}{2}\right) \tag{2}$$

In the measurements reported here, the initial membrane concentration was always 0. Thus, the diffusion coefficient is defined by

$$D = \frac{s^2}{6L} \tag{3}$$

if we can neglect the concentration c_{00} at the low pressure side of our membrane. If we take c_{00} into consideration, we obtain

$$D = \frac{s^2}{6L}\,\frac{c_1 + 2c_{00}}{c_1 - c_{00}} \tag{4}$$

When measuring the rate of permeation, J, *vs.* time, the quantity of hydrogen which has permeated the membrane at various times is obtained by integrating the rising curve.

Devanathan[24] showed that the time lag can also be obtained by determining the time at which the rate of permeation is 0.6299 times the steady-state value. He also defined the equation for the rising transient by

$$\ln\left(\frac{J_t - J_\infty}{J_\infty}\right)_{x=0} = \ln\left(1 - e^{-3t/t_0} + e^{-8t/t_0} \ldots\right) + \ln 2 - \frac{t}{t_0} \tag{5}$$

where the rise-time constant, t_0, is given by

$$t_0 = \frac{s^2}{\pi^2 D}$$

Thus, for times greater than 0, a plot of ln $[(J_t - J_\infty)/J_\infty]_{x=0}$ against t should have a gradient of $1/t_0$. Since the time lag, L, is equal to the sum of the rise-time constant and the breakthrough time, t_b, we obtain for the latter

$$t_b = \frac{s^2}{D}\left(\frac{1}{6} - \frac{1}{\pi^2}\right) = \frac{s^2}{15.3D} \tag{6}$$

Thus, the diffusion coefficient D can be determined by evaluating the transient behavior.

Solubility data can be obtained from the steady-state flux, J_∞, by

$$J_\infty = -D\frac{\partial c}{\partial x} = -D\frac{c_{00} - c_1}{s} \tag{7}$$

If the reaction ($H_{2gas} \rightleftharpoons 2\ H_{ads} \rightleftharpoons 2\ H_{Me}$) at the interface is fast compared with the diffusion rate, the hydrogen concentration in the metal lattice at the surface is in equilibrium with the gas phase and can be expressed by the hydrogen pressure. For low hydrogen concentrations in the metal, we obtain as a good approximation Sieverts' equation

$$(P/P_0)^{1/2} = K(T)n \tag{8}$$

The atomic ratio, n, and the concentration, c, are related by

$$c = n\,\frac{m_{Me}}{qs}\left(\frac{\text{g-atom}}{\text{cm}^3}\right)$$

where P_0 = 1 Torr, $K(T)$ = Sieverts' constant, n = mole ratio of H in the metal, m_{Me} = g-atom of metal in the membrane, and q = membrane area.

From eq 7 and 8, Sieverts' constant is

$$K = \frac{D\left[\left(\frac{P_1}{P_0}\right)^{1/2} - \left(\frac{P_2}{P_0}\right)^{1/2}\right]}{2J_\infty V_{Me} s} \tag{9}$$

where P_1, P_2 = high and low hydrogen pressure in Torr, V_{Me} = volume of 1 g-atom of metal, and J_∞ = steady-state flux in g-atoms of H_2/cm^2.

The system described in the following paragraphs was designed to approach the initial and boundary conditions of the time lag method as closely as possible. The measurement of the hydrogen flow emerging from the low-pressure side of the membrane is based on monitoring the pressure difference across a calibrated capillary. Generally, these pressures were between 0 and 100 μ. The extent and effect of deviations from the boundary conditions stated above will be discussed later.

Experimental Section

Apparatus. The apparatus is shown schematically in Figure 1. The vacuum side consists of a thermistor, two capillaries, and the pumping system with an oil diffusion pump (Speedivac Model 403A from Edwards High Vacuum Ltd.) and a high flow rate liquid nitrogen cold

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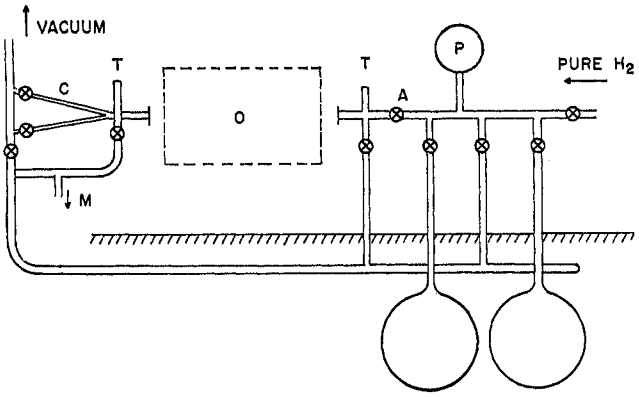

Figure 1. Hydrogen diffusion apparatus: T, thermistor; O, furnace and sample holder; P, absolute pressure gauge; M, McLeod gauge; A, wide-bore glass stopcocks, and C, capillaries.

trap. The high-vacuum part also contained an NRC ion gauge and a McLeod gauge for continuous pressure monitoring and thermistor calibration. The high-pressure side of the apparatus consisted of two 5-l. flasks and a precision absolute pressure gauge (Wallace and Tiernan, Model No. FA129).

Short, wide glass tubing and large-bore stopcocks were used throughout the system to avoid any undesired pressure gradients. The total volume of the high-pressure part of the apparatus was 14150 cm^3; the volume between the sample and the capillaries was $\sim$20 cm^3.

The sample holder (Figure 2) was machined out of stainless steel and was connected to the vacuum apparatus by two O-ring joints. A stainless steel bellows provided the necessary flexibility. The sample, a disk of 2.5 cm ϕ, was clamped between the two parts of the sample holder which were pressed together by four stainless steel bolts, leaving a well defined area of 3.14 cm^2. An aluminum ring and thick walled copper tubing provided uniform temperature distribution all around the sample. The sample holder was inserted into a 25-cm long tube furnace controlled by a Wheelco furnace control unit.

A chromel–alumel thermocouple for measuring the sample temperature was positioned to touch the side of the sample, as indicated in Figure 2. The sample temperature was measured to ±0.2°. There was no temperature drift during short runs. During runs extending over a longer time, the temperature variation stayed within ±0.2° of the preset value. At the furnace exits, the sample holder was cooled by water flowing through two windings of copper pipe.

Pressure Measurement. The measuring principle is based on the high-temperature coefficient of the thermistor resistance. A glass bead thermistor (G108, 40 kilohms at 25°, 1–2 sec time constant from Fenwal Electronics) was mounted in a glass tube with a water jacket thermostated to 25 ± 0.1° by a Haake thermostat. The thermistor was part of a Wheatstone bridge arrangement connected to a stabilized dc power supply. The bridge was balanced at high vacuum, and under our conditions the thermistor resistance was 815 kilohms. During measurements, the imbalance was followed by a variable speed compensation strip recorder (Sargent). A variable resistor was used for the fine adjustment of the zero point at high vacuum, and a similar thermistor arrangement in a very insensitive setting was used at the high-pressure side to indicate the start of the run. The thermistor bridge output was calibrated with hydrogen against a McLeod gauge. It showed an almost completely linear relationship between resistance and pressure in the range from 0 to 200 μ with a slope of 375 mV/100 μ.

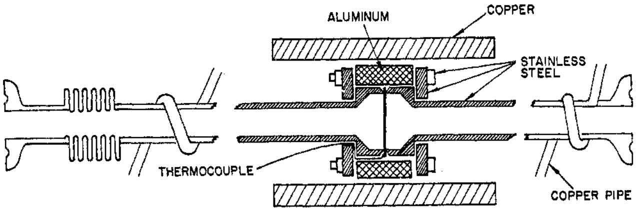

Figure 2. Sample holder.

Flux Measurement. For the calibration of flux through the capillaries, a flask of known volume was connected to the low-pressure part of the system. Since the pressure change with time was recorded during evacuation through a capillary, a calibration curve for each capillary was thus determined. The flow rate at low pressures was 4×10^{-3} and 6×10^{-3} cm^2 of H_2 (STP)/min μ. For the actual determination of H_2 flow, the calibration curve was used because of deviations from linearity at higher pressures.

Materials. Tank hydrogen was purified by passing it through an Engelhard hydrogen purifier (this apparatus is based on the principle of hydrogen diffusion through a Pd–Ag alloy at elevated temperatures). The Pd samples (99.9+) were obtained from Engelhard Industries. The Pd–Ag alloys were prepared at Tyco Laboratories from a Pd sponge (99.95%+, Engelhard Ind.) and silver (99.999%) under a positive argon pressure and then rolled into sheets. Four different membranes of Pd and two to four different membranes of each Pd–Ag alloy were employed. The thickness ranged from 0.0800 to 0.2025 cm.

Preparation of the Samples and Experimental Procedure. A disk 2.5 cm in diameter was punched out, washed with acetone, mechanically cleaned with fine emery paper, etched for a short time in concentrated nitric acid, and electrolytically palladized in an acidic palladium nitrate solution. After careful washing with triply distilled water, the sample was mounted in the sample holder, connected to the vacuum system, and evacuated. Before starting the furnace, the arrangement was checked for leaks. After the sample reached a constant temperature, it was treated with hydrogen

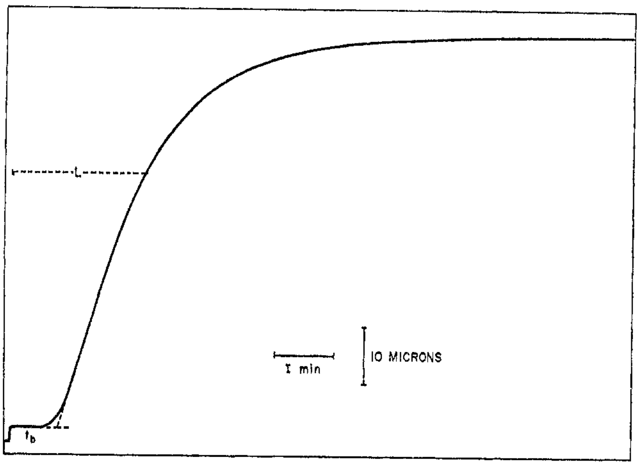

Figure 3. Typical recording of pressure rise with time. The first step marks the start of the run; hydrogen permeation through 0.11-cm $Pd_{0.9}Ag_{0.1}$ at 263°.

and evacuated. The stopcocks to the vacuum line were then closed, the capillaries opened, and the recorder started. By opening stopcock A (Figure 1), a constant H_2 pressure was applied to the high-pressure side of the sample. This starting point was indicated by a small thermistor signal on the recorder. After an induction time, the pressure on the opposite side of the membrane started to rise and finally reached a constant value, indicating a steady-state flux. A typical recording is shown in Figure 3. Before the next run at different pressure, the sample was again completely evacuated.

Results

The results reported here are based on permeation measurements in the temperature range of 250 to 640° and hydrogen pressures between 30 and 500 Torr. A typical recording of hydrogen flux against time is shown in Figure 3.

Values for the time lag, L, were evaluated from plots of Q *vs.* t and from the time elapsed until the flux was equal to 0.63 of the steady-state value (Q was obtained by graphical integration of the flux *vs.* time curve). Both methods led to the same result for L. Diffusion coefficients calculated from L, t_b, and t_0, according to eq 4, 5, and 6, agree within experimental error. However, values for D obtained from t_b were generally slightly higher ($\sim$5%) than those from L and t_0, and showed a larger scatter. The breakthrough time, t_b, reflects the time elapsed until the first hydrogen appears at the low-pressure side of the foil. Since $t_b \sim s^2$, it is very sensitive to differences in sample thickness and will have a value corresponding to the thinnest parts of the membrane. If the membrane thickness is not completely uniform, values of t_b will tend to be too short compared with the average sample thickness, thus leading to values of D which are too large. Due to the rolling of relatively small sheets, some samples are indeed not completely uniform in thickness over the whole 3.14 cm². The fact that a commercially obtained Pd sheet with more uniform thickness yielded the same values for D from L and t_b seems to confirm this explanation. The results are therefore generally based on the evaluation of L. Values obtained for L were between 10 and 2000 sec, depending on sample composition, thickness, and temperature.

The response time of the thermistor arrangement was determined to establish its influence on small values of L. When measuring the steady-state reflux through a membrane, a pressure change follows the opening or closing of the second capillary. From this transient, one obtains a value for the time constant of the measuring system. It can be shown that the evaluated time constants of 1.4 to 1.8 sec change the smallest values of L less than 1%. Table I shows an example of measured values for the 0.110-cm $Pd_{0.9}Ag_{0.1}$ membrane. Diffusion coefficients, D', are calculated from eq 3. Values for D are obtained from eq 4 by substituting the ratio of the hydrogen concentrations in the metal by the ratio of the square roots of the hydrogen pressures.

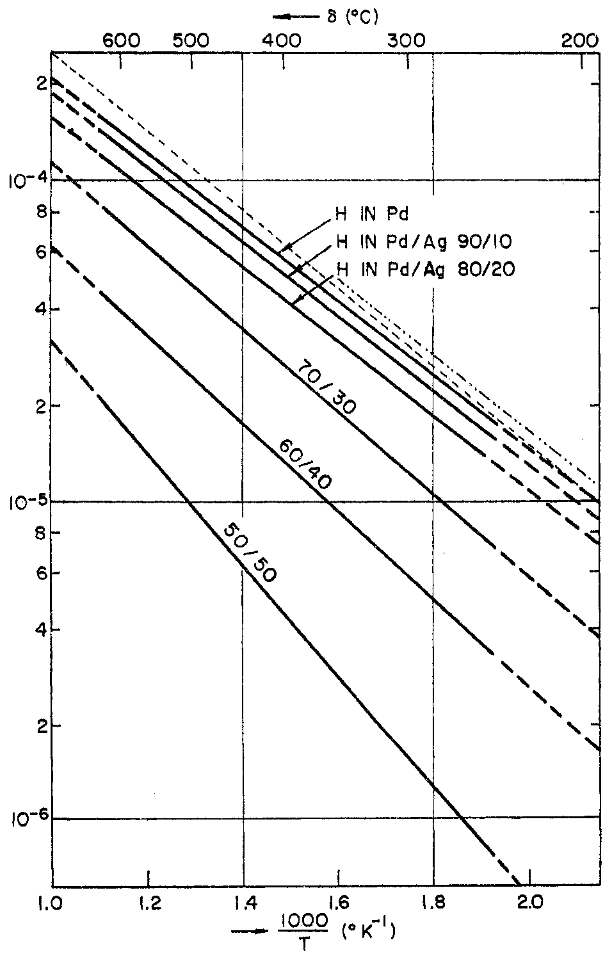

Figure 4. Diffusion coefficients of hydrogen in Pd and Pd–Ag alloys at low hydrogen concentrations. Arrhenius diagram: —, this investigation, – – –, H in Pd ref 2, –·–·– H in Pd ref 4.

Table I: Evaluation Example, Hydrogen Diffusion through 0.11-cm $Pd_{0.9}Ag_{0.1}$

δ^a	P_1, Torr	P_2, Torr $\times 10^{-3}$	J, cm³/cm² sec $\times 10^{-3}$	L, sec	D', cm²/sec $\times 10^{-5}$	D, cm²/sec $\times 10^{-5}$
245.0	45.0	45.3	1.4278	163.0	1.24	1.36
263.0	85.5	68.0	2.1762	135.0	1.49	1.62
265.0	202.0	68.3	3.4607	124.0	1.63	1.72
265.0	399.0	149.2	5.0849	119.0	1.69	1.79
416.0	42.6	95.2	3.1263	44.3	4.55	5.23
416.0	201.0	131.3	7.1125	41.9	4.81	5.19
416.0	400.0	178.5	10.0159	40.4	4.99	5.31
416.0	112.5	97.2	5.0425	43.4	4.65	5.07
416.0	33.5	82.5	2.6805	45.6	4.42	5.12
614.0	36.0	84.5	4.3418	17.5	11.52	13.28
614.0	52.5	101.2	5.2601	16.5	12.22	13.91
614.0	91.0	132.6	7.1921	16.5	12.22	13.68
614.0	150.0	167.0	9.3047	15.4	13.10	14.45
614.0	200.0	182.3	10.5679	15.1	13.36	14.60

[a] δ = temperature in °C.

Table II: Diffusion and Solubility Parameters of Hydrogen in Pd and Pd–Ag Alloys between 260 and 640° at Low Hydrogen Content in the Metal

	No. of measurements	D_0, cm²/sec $\times 10^{-3}$	E, cal/g-atom	ΔH_{H_2}, cal/g-atom	ΔS_{H_2}, cal/deg g-atom
Pd	57	2.94 ± 0.2	5260 ± 50	4000	23.3
$Pd_{0.9}Ag_{0.1}$	43	2.69 ± 0.2	5300 ± 60	5535	23.6
$Pd_{0.8}Ag_{0.2}$	30	2.33 ± 0.2	5335 ± 100	6740	24.0
$Pd_{0.7}Ag_{0.3}$	31	2.21 ± 0.2	5900 ± 100	7330	23.5
$Pd_{0.6}Ag_{0.4}$	19	1.50 ± 0.2	6300 ± 150	8020	24.4
$Pd_{0.5}Ag_{0.5}$	19	1.82 ± 0.2	8000 ± 150	7090	24.1

The example clearly illustrates the difference in the calculated diffusion coefficients. Values of D' are somewhat smaller than values of D and show a noticeable pressure dependence leading to increasing values of D' with rising hydrogen pressure. Since D' approaches D at higher pressures, and the latter shows no systematic pressure dependence, this indicates that the pressure dependence of the diffusion coefficient is a reflection of the deviations from the boundary condition $c = 0$ at $x = 0$ for $t > 0$ and does not represent a true concentration dependence of the hydrogen diffusion coefficient in the membrane. The latter would also be unlikely in view of the low hydrogen concentration in the metal lattice during all measurements.[14,15] The average concentration extremes were $n \approx 5 \times 10^{-5}$ for Pd at 640° and $n \approx 4 \times 10^{-2}$ for $Pd_{0.6}Ag_{0.4}$ at 250°.

All diffusion coefficients reported here were obtained by eq 4, and are independent of membrane thickness. The temperature dependence of the diffusion coefficients can be expressed by

$$D = D_0 \exp(-E/RT) \qquad (10)$$

where D_0 = frequency factor and E = activation energy.

An Arrhenius plot of log D against $1/T$ is shown in Figure 4. It can be seen that there is little change in the absolute values and in the activation energy of the hydrogen diffusion coefficients from pure Pd up to $Pd_{0.8}Ag_{0.2}$. With an increase of Ag content, the hydrogen diffusion coefficients decrease progressively and the activation energy increases. Values of D_0 and E for Pd and the Pd–Ag alloys were obtained by a least-squares fit of log D against $1/T$, and are given in Table II with the number of measurements upon which they are based. Figure 5 shows a typical example of the statistical distribution of experimental values for D around the calculated least-squares line. The change in activation energy with the mole fraction of Ag (X_{Ag}) up to $Pd_{0.5}Ag_{0.5}$ can be approximately described by

$$E = 3800X_{Ag}^4 + 1500X_{Ag}^2 + 5260 \text{ (cal)} \qquad (11)$$

The frequency factor, D_0, decreases slightly with increasing Ag content. Its change between Pd and $Pd_{0.5}Ag_{0.5}$ can be described by a linear relationship between D_0 and X_{Ag}

$$D_0 = -2.65 \times 10^{-3}X_{Ag} + 2.9 \times 10^{-3} \qquad (12)$$

Figure 6 shows a typical plot of the steady-state hydrogen flux at constant temperature *vs.* the difference of the square roots of the hydrogen pressures. The

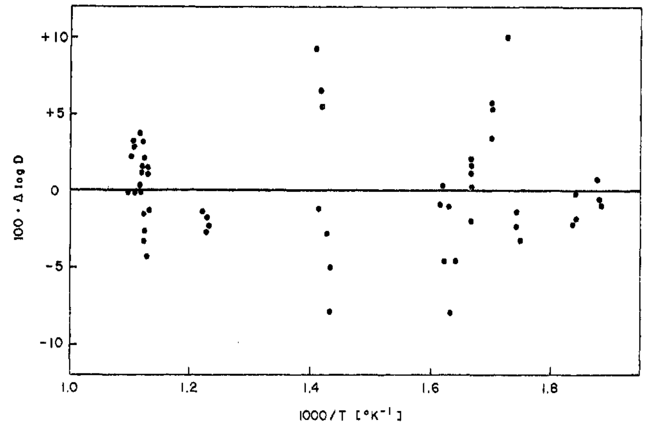

Figure 5. Typical distribution of experimental values of the hydrogen diffusion coefficient around the straight line calculated by a least-squares fit. Values obtained at four Pd membranes of different thickness.

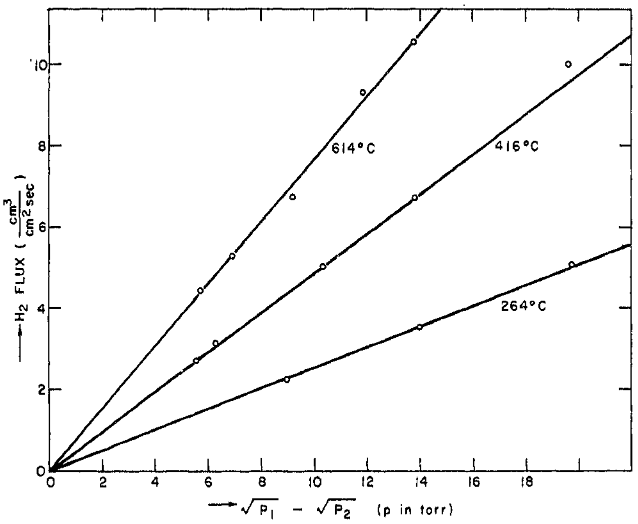

Figure 6. Hydrogen flux at different temperatures against the square root of the pressure; $Pd_{0.9}Ag_{0.1}$ membrane of 0.11 cm thickness.

measured points fall on straight lines which intersect the origin. There were no systematic deviations. The slopes, which depend on the membrane and the temperature, were used to calculate values of Sieverts' constant K (eq 9). The diffusion flux was found to be directly proportional to $1/s$ in accordance with eq 7.

This has two important implications; (1) it suggests that there is no significant inhibition at the interface, and (2) that the whole sample area is active for diffusion. The lack of dependence of D and $J_{\infty}s$ on membrane thickness and the reproducibility indicates that the diffusion equations (with the stated boundary conditions) can be applied to the experiments reported here.

Figure 7 shows the temperature dependence of Sieverts' constant K in an Arrhenius plot. The hydrogen solubility at very low hydrogen content in the lattice increases considerably from Pd to $Pd_{0.8}Ag_{0.2}$; this is followed by a slower increase with a maximum between $Pd_{0.6}Ag_{0.4}$ and $Pd_{0.5}Ag_{0.5}$. The standard values for the heat of desorption, ΔH_{H_2}, and the entropy of desorption, ΔS_{H_2} (based on H_2) obtained by

$$\ln K' = -\frac{\Delta H_{H_2}}{2RT} + \frac{\Delta S_{H_2}}{2R} \qquad (13)$$

are also given in Table II (K' = Sieverts' constant, pressure unit atmospheres).

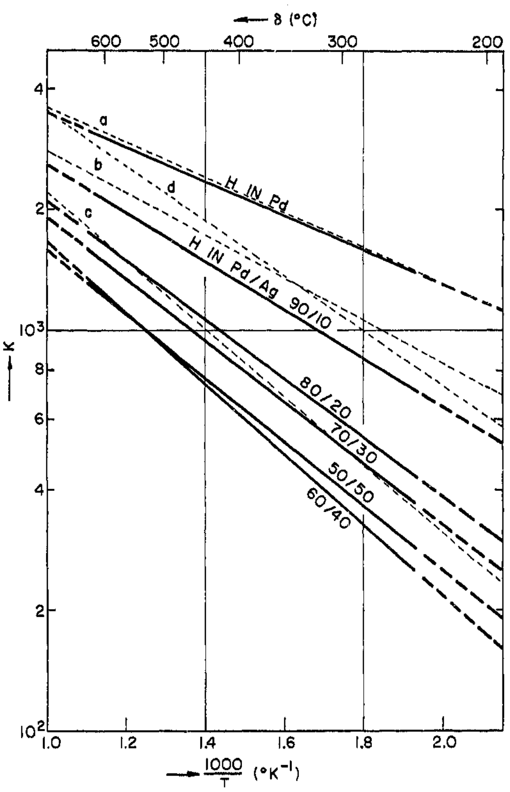

Figure 7. Temperature dependence of Sieverts' constant K for Pd and Pd–Ag alloys: —, this investigation; ----, Sieverts, *et al.*; a, Pd; b, $Pd_{0.9}Ag_{0.1}$; c, $Pd_{0.6}Ag_{0.4}$; d, $Pd_{0.5}Ag_{0.5}$.

The heat of desorption increases with rising Ag content and has a maximum between $X_{Ag} = 0.4$ and $X_{Ag} = 0.5$, whereas the entropy of desorption changes little. Figure 8 shows the change in total hydrogen flux as a function of membrane composition and temperature. As a consequence of the changes in D and K reported above, there is a maximum hydrogen permeability for a membrane of an approximate composition $Pd_{0.76}Ag_{0.24}$. This is in keeping with prior findings.[25]

Discussion

It should be recalled that Ag forms random substitutional alloys with Pd, in which hydrogen atoms are located in the octahedral interstices of the fcc lattice.[26,27]

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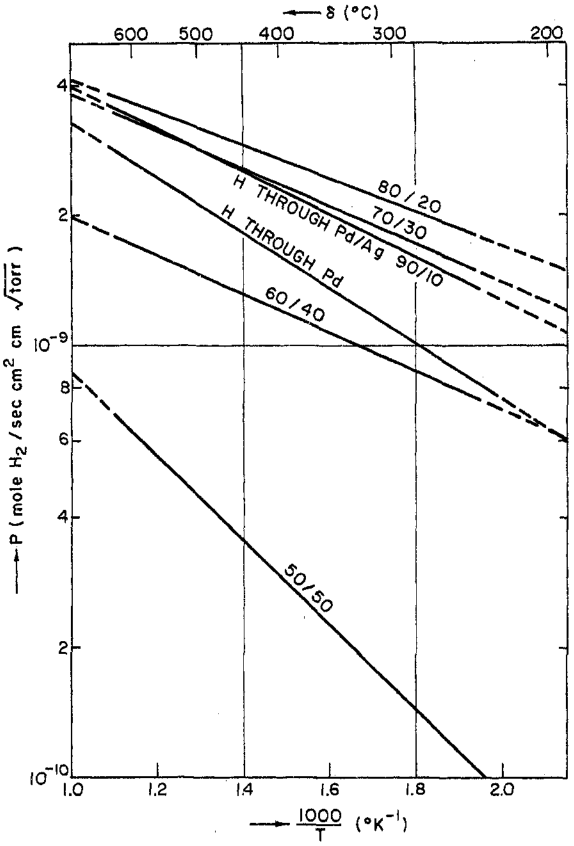

Figure 8. Temperature dependence of hydrogen permeation through membranes of Pd and Pd–Ag alloys.

Hydrogen Diffusion. The theory of hydrogen diffusion has been discussed several times,[14,15,23,28] and will not be repeated in detail here. As a result, one obtains for the frequency factor in eq 10

$$D_0 = a_0^2 \nu_0 \kappa_0 Z_p \frac{2\,kt}{h\nu_0} \sinh\left(\frac{h\nu_0}{2kT}\right) \exp\left(\frac{\Delta S^\circ}{R}\right) \quad (14)$$

where a_0 = lattice constant, ν_0 = vibrational frequency of H in the octahedral interstice, κ = transmission factor of the order of 1, and Z_p = number of exits for an H atom from its octahedral interstice ($Z_p = 12$ if the H atom jumps through in edge of the octahedron; $Z_p = 8$ if it leaves through a face of the octahedron—the latter is probably more favorable from an energetic point of view), k = Boltzmann constant, h = Planck constant, and ΔS° = entropy of activation.

For a_0 = 3.89 Å, a linear expansion coefficient of 11.76×10^{-6}, $\nu_0 = 12.3 \times 10^{12}$ (estimated from equilibrium measurements[29]), $\kappa = 1$, and $Z = 8$, one obtains for ΔS° a value of −2.9 cal/deg g-atom at 400° (400° was chosen as a median value of the temperature range covered by the experiments). This result differs from the assumption of Zener that positive entropies of activation should be expected for interstitial diffusion. A similar negative value for ΔS° was also observed for H diffusion in Pd at low temperatures.[15]

As can be seen from Table II, D_0 decreases slightly with increasing Ag content, in spite of an increase in the lattice constant, a_0. There is probably not much change in the vibrational frequency, ν_0, in view of the nearly constant entropy of desorption. Thus, the remaining parameters Z_p and ΔS° would have to account for the decrease in D_0 in spite of an increase in a_0. Most likely, this is accomplished by an increasingly negative entropy of activation, possibly as a result of high vibrational frequencies perpendicular to the jump direction at the saddle point.

The activation energies for hydrogen diffusion show little change from Pd to $Pd_{0.8}Ag_{0.2}$, and a progressive increase at higher Ag concentrations. Hydrogen diffusion measurements[30] in pure Ag from 388 to 600° ($D = 2.82 \times 10^{-3} \exp(-7500/RT)$,) suggest the presence of a maximum in E between $Pd_{0.5}Ag_{0.5}$ and pure Ag.

Earlier diffusion measurements of hydrogen in Pd in the temperature range of this investigation are summarized in Table III. Results obtained by permeation measurements in the intermediate temperature range[3,4] of 175 to 375° were recalculated[15] using newer equilibrium data obtained by interpolating the results of Nernst,[29] and those of Gillespie and Galstaun.[8] The permeation rates observed by Davis[12] are close to those reported here, as are his diffusion coefficients obtained by using Sieverts' solubility data. However, the activation energy is somewhat larger.

Table III: Diffusion of Hydrogen in Palladium at Low Concentrations above 200°

D_0, cm²/sec × 10^{-3}	E, kcal/g-atom		
5.4–8.4	5.72	190–400°	Jost and Widmann[1]
4.3	5.62	200–700°	Davis[2]
8.5	5.45	175–375°	Toda[3]
4.1	5.45	200–375°	Katz and Gulbransen[4]

Extrapolation of hydrogen diffusion coefficients for Pd from measurements between 0 and 100° to high temperatures results in values close to those reported here. For example, Bohmholdt and Wicke[15] found for Pd

$$D = (3.65 \pm 0.8) \times 10^{-3} \exp\left(-\frac{5600 \pm 100}{RT}\right)$$

It seems reasonable to assume that the activation energy for hydrogen diffusion changes with tempera-

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ture, as indicated by the experimental results. An approximate estimate of the magnitude of this effect can be made by following Jost[23] in representing the dependence of the activation energy on the lattice distance by

$$E_1 \approx E_2\left(\frac{a_2}{a_1}\right)^u \qquad (15)$$

where E_1 and a_1 are the activation energy and the lattice constant, respectively, at temperature 1; E_2 and a_2 are the corresponding quantities at temperature 2; and u is of the order of magnitude of 10. Using an average temperature of 400° for the results reported here and $\alpha = 11.76 \times 10^{-6}$ for the linear expansion coefficient of Pd, a value of $u \approx 14$ would be required to account for a decrease in activation energy from 5600 at 25° to 5260 at 400°. This seems to be reasonably in agreement with general experience.

There are no reports on hydrogen diffusion in Pd–Ag alloys which could be directly compared with the results presented here. Around room temperature (0 to 90°), however, a few contradictory data on hydrogen diffusion in Pd–Ag alloys at low hydrogen concentrations do exist.[14,15,17] Küssner,[17] for example, found a large decrease in values of D_0 at a constant activation energy of 5700 cal when the Ag content was increased from 25 to 50%. In comparison, Holleck and Wicke[14] reported at low hydrogen concentration only a small change in hydrogen diffusion coefficents for Pd and Pd-rich alloys, as suggested by the present investigation. It should be noted, however, that there seem to be significant differences in the hydrogen diffusion behavior at high hydrogen concentrations.[14,15]

In a recent publication, Bersier and Küssner[31] reported on the concentration dependence of hydrogen diffusion coefficients in $Pd_{0.77}Ag_{0.23}$ from 30 to 280°. Their results at very low hydrogen concentration were represented by $D = 5.1 \times 10^{-4} \exp(-4440/RT)$. This activation energy seems to be quite low compared with 5500 cal interpolated from results reported here. Furthermore, they found a very strong concentration dependence in D at very low hydrogen concentrations. In the present work, no indication of such behavior could be detected.

Hydrogen Solubility. Hydrogen solubility in Pd and Pd alloys has been the subject of many investigations,[32] and a model has been developed allowing a quantitatively satisfactory interpretation for the isotherms.[31,33-35] Here we will discuss only the hydrogen solubility at very small concentrations as reflected in Sieverts' constant K (see eq 13). Such values are given in Table IV. They were obtained by a least-squares fit of log K against $1/T$. In the case of Pd, they were calculated with and without the two measurements above 600°. The numbers of data points are, in all cases, quite small, however. If one disregards the measurements above 600°, there is a reasonably good agreement between Sieverts' values and the results given here. With the Pd–Ag alloys, the discrepancy is somewhat larger, showing, however, the same general trend.

Table IV: Heats and Entropies of Desorption for Hydrogen in Pd and Pd–Ag Alloys Calculated from Solubility Data

	ΔH_{H_2}, cal/g-atom	ΔS_{H_2}, cal/deg g-atom	T, °C	
Pd	3522	21.2	200–800	Sieverts[6]
	3912	23.1	200–600	
Pd	3328	22.4	300–800	Sieverts and Zapf[7]
	3790	23.1	300–600	
$Pd_{0.9}Ag_{0.1}$	5000	23.5	317–822	Sieverts[9]
$Pd_{0.6}Ag_{0.4}$	7700	25.1	221–621	
$Pd_{0.5}Ag_{0.5}$	6400	25.8	221–822	

Brodowsky and Poeschel[35] have reported on hydrogen in Pd–Ag alloys at temperatures of 0 to 175°. They find similarly increasing values for the heat of desorption from 4500 cal/mol of H_2 for Pd[29] to 11660 cal/mol of H_2 for $Pd_{0.6}Ag_{0.4}$ at $n \rightarrow 0$. Besides the fact that the values are generally higher, there seems to be a larger increase with rising Ag content. The ΔS_{H_2} values were found to rise from 25.1 for Pd[29] to 31.4 cal/deg mol of H_2 for $Pd_{0.6}Ag_{0.4}$, compared to only a slight change in the present investigation.

It is, however, reasonable to assume that the heat of hydrogen desorption from Pd will change with temperature. An estimate of the magnitude and direction of this effect can be obtained in the following way. The heat of desorption at temperature, T_2, is given by

$$\Delta H_{H_2}(T_2) = \Delta H_{H_2}(T_1) + \int_{T_1}^{T_2} \Delta c_p \mathrm{d}T \qquad (16)$$

For Δc_p we will consider only hydrogen, since the heat capacity of Pd for pure Pd and for PdH ($n_H \rightarrow 0$) will not differ significantly. Therefore

$$\Delta c_p = c_{pH_2} - 2c_{pH\,abs} \qquad (17)$$

The heat capacity of hydrogen gas can be expressed by

$$c_{pH_2} = 6.947 - 0.2 \times 10^{-2}T + 4.8 \times 10^{-7}T^2 \qquad (18)$$

To arrive at a value for $c_{pH\,abs}$ we regard hydrogen in Pd as an Einstein oscillator with $\nu_H = 16.9 \times 10^{12}\ sec^{-1}$ (determined for the α phase by neutron scattering experiments). At relatively high temperatures, the heat capacity for a solid is

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$$c_{\mathrm{pH\,abs}} = 3R\left[1 - \frac{1}{12}\left(\frac{\theta}{T}\right)^2\right] \tag{19}$$

From eq 17 through 19, and for $\theta = h\nu_H/k = 812$, $T_1 = 298°K$, and $T_2 = 673°C$, one obtains for the integral in eq 16 a value of -636 cal/mol of H_2. This compares favorably with a difference of -500 cal/mol of H_2 from heats of hydrogen desorption experimentally determined for an average temperature of 400° (4000 cal/mol H_2) and 25° (4500 cal/mol H_2).

It is interesting to note that the values for K calculated from hydrogen equilibrium measurements in Pd by Gillespie and Galstaun[8] (at 200 to 313°) fit exactly between the extrapolations from high and low temperatures. This suggests that there is a continuous decrease in the heat of desorption with increasing temperature, similar to the activation energy for hydrogen diffusion.

Inhibitions at the Membrane–Gas Interface. In a recent publication,[36] Wicke and Meyer discussed extensively the reactions occurring at the Pd–gas interface during hydrogen permeation. They showed that inhibition is present even at an interface activated by a cover of Pd black. The effect of such inhibition on the diffusion and solubility results reported above may be determined as follows. At the presence of an inhibition at the interface, the hydrogen pressure at the entering side, P_1, will be larger than the equilibrium pressure, P_{1e}: $P_1 = P_{1e} + \Delta P_1$. The hydrogen pressure at the exit side, P_2, will be smaller than the equilibrium pressure, P_{2e}: $P_2 = P_{2e} - \Delta P_2$. From eq 7 and 8, we obtain for the hydrogen flux through the membrane

$$J = \frac{D}{V_{\mathrm{MeS}}K}[(P_{1e})^{1/2} - (P_{2e})^{1/2}] \quad \text{(mol of H/cm}^2\text{ sec)}$$

which can be written

$$\left(\frac{P_1}{J}\right)^{1/2}\left(1 - \frac{\Delta P_1}{P_1}\right)^{1/2} = \frac{KV_{\mathrm{MeS}}}{D}J^{1/2} + \left(\frac{P_2 + \Delta P_2}{J}\right)^{1/2} \tag{20}$$

Plots of $(P_1/J)^{1/2}$ *vs.* $J^{1/2}$ at a given temperature showed a linear relationship, with an intercept $A = [(P_2 + \Delta P_2)/J]^{1/2}$. From values of A, the pressure difference due to the interface inhibition at the low-pressure side of the membrane, ΔP_2, can be easily obtained

$$\Delta P_2 = A^2 J - P_2$$

The actual values of A were dependent on the individual activation and ranged between 0.5×10^3 to 2×10^3, with a majority of samples yielding values of 0.6×10^3 to 1×10^3. At the same membrane, values of A decreased slightly with increasing temperature, often showing a minimum at approximately 400°. The slight increase at 600° could be due to sintering of the activating Pd black layer. Thus, values of ΔP_2 ranged approximately from 0 to 2 Torr, depending on sample activity and hydrogen flux. Assuming the same values for ΔP_1, it can easily be seen that the factor $\Delta P_1/P_1$ in eq 20 becomes small compared with 1 at larger values of P_1, and can then be neglected. If we take into account the inhibition at the interface, we find values of D which are approximately up to 5% higher than those reported above. However, this is still within the limits of experimental error. There is practically no change in the energy of activation for hydrogen diffusion, since the slight decrease in values of A is compensated by an increase in J. Also, there will be practically no change in values of K (eq 9), since the increase in values of D is nearly compensated by a decrease in the values of the term $[(P_{1e})^{1/2} - (P_{2e})^{1/2}]$.

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