

STRAIN GRADIENT INFLUENCE ON DIFFUSION COEFFICIENTS OF DEUTERIUM IN ABSORPTION AND DESORPTION OF DEUTERIUM IN Pd₈₁Pt₁₉ MEMBRANE

Danuta DUDEK

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland; e-mail: dand@ichf.edu.pl

Received September 5, 2002
Accepted December 18, 2002

The diffusion of deuterium through a Pd₈₁Pt₁₉ membrane was investigated. At six temperatures in the range 278.2–328.2 K the diffusion coefficients were determined by breakthrough method for the membrane with no initial content of deuterium. The determined activation energy of diffusion of deuterium equals $E = 26.4$ kJ/mol. The solubility of deuterium in Pd₈₁Pt₁₉ alloy at 278.2 K was measured by volumetric method. The influence of self-stresses on diffusion of deuterium was investigated by determination of diffusion coefficients for the Pd₈₁Pt₁₉ membrane with different initial contents of deuterium at 278.2 K.

Keywords: Diffusion; Hydrogen; Deuterium; Alloys; Stresses; Palladium; Platinum; Membranes.

It has been evidenced in many theoretical^{1–6} and experimental^{7–15} studies that diffusion of hydrogen in palladium-platinum alloys with some initial contents of hydrogen can be changed by strain gradients created in solution processes. The introduction of hydrogen or deuterium into membrane causes expansion of metal lattice and creation of stresses and, due to elastic coupling between lattice sites, propagation of stresses in the whole membrane at sound velocity. The gradient of chemical potential of hydrogen caused by stresses is responsible for the hydrogen flux in the opposite direction than the Fick flux^{5,6}. The magnitude of non-local flux in palladium-platinum alloy depends on initial content of hydrogen in membrane and on change in hydrogen concentration caused by introduction or removal of hydrogen into or from membrane^{5–15}.

In many studies transport of hydrogen under stress conditions was investigated and diffusion coefficients of hydrogen were determined for Pd₈₁Pt₁₉ membranes by different methods and for different initial and boundary conditions^{5–22}. The influence of stresses on diffusion of hydrogen resulted

in a decrease in diffusion coefficient with increasing initial hydrogen content in membrane^{8,14,15}.

So far, the diffusion coefficients for deuterium in Pd₈₁Pt₁₉ membrane have not been determined and the influence of stresses on diffusion of deuterium was not investigated. Uphill effects, forced by stresses, were observed in Pd, Pd-Pt and Pd-Ag^{7-15,23-25} alloys, but only in diffusion of hydrogen, not deuterium.

In this paper the diffusion coefficients of deuterium in Pd₈₁Pt₁₉ membrane at six temperatures ranging from 278.2 to 328.2 K were determined and the activation energy of diffusion of deuterium in Pd₈₁Pt₁₉ was calculated. At 278.2 K the measurements of deuterium solubility in Pd₈₁Pt₁₉ alloy were performed up to a pressure of ca 900 hPa. At temperature 278.2 K, the diffusion coefficients of deuterium were determined for the Pd₈₁Pt₁₉ membrane with different initial deuterium contents and the influence of stresses on diffusion of deuterium was investigated.

EXPERIMENTAL

The experiments were performed with a Pd₈₁Pt₁₉ membrane, which was in the form of a cylindrical tube closed on one side. The length of tube was 70 mm, internal diameter 8 mm and the wall thickness 0.5 mm. Before measurements, the membrane was annealed at 650 °C in high vacuum for 2 h.

The tube was placed in a glass system¹⁴. The inner and outer surfaces of the membrane were covered with palladium black. Deuterium gas was introduced into the tube. The measurements of pressure of deuterium, that permeated through the tube wall were performed as a function of time at constant temperature, under related initial and boundary conditions.

The pressure of deuterium in the range 0–130 hPa was measured by Baratron capacitance manometer with accuracy ±0.15%, higher pressures (up to about 900 hPa) were measured by tensometric pressure gauge with accuracy ±0.3%. The measurements were carried out in the temperature range 278.2–328.2 K. The temperature in the system was controlled with accuracy better than ±0.1 K.

RESULTS AND DISCUSSION

The Permeation of Deuterium Through Pd₈₁Pt₁₉ Membrane with no Initial Deuterium Content

The diffusion coefficients of deuterium in the Pd₈₁Pt₁₉ membrane were determined by the breakthrough method. After removing deuterium from the membrane and from the whole system, the deuterium pressure on the outer side of the membrane was increased from zero to ca 50 hPa. The pressure of deuterium, that permeated through the membrane wall p , was measured as

a function of time. The measurements of $p(t)$ for the $\text{Pd}_{81}\text{Pt}_{19}$ membrane with no initial content of deuterium were performed at temperatures 278.2, 288.4, 298.2, 308.2, 318.2, and 328.2 K. In Fig. 1 an example of the measured dependence $p(t)$ at 318.2 K is presented.

The intersection of the straight line with the time axis determines the breakthrough time (τ). The diffusion coefficients (D) of deuterium at different temperatures were calculated from the expression $D = L^2/6\tau$, where L is the thickness of the membrane²⁶. The calculated values of D are given in Table I.

TABLE I

The diffusion coefficients of deuterium for the $\text{Pd}_{81}\text{Pt}_{19}$ membrane with no initial deuterium content, at different temperatures

T , K	$D \times 10^{12}$, m^2/s
278.2	7.04
288.4	11.7
298.2	16.8
308.2	24.2
318.2	30.3
328.2	43.3

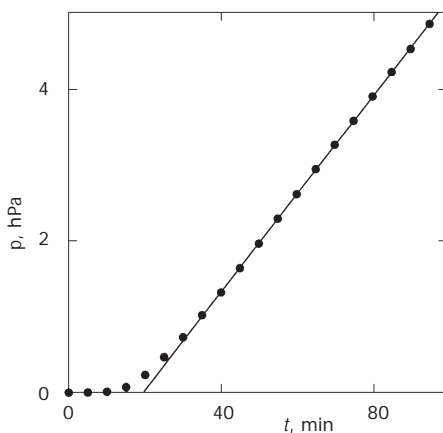


FIG. 1

The pressure of deuterium, which permeated through $\text{Pd}_{81}\text{Pt}_{19}$ membrane, as a function of time at $T = 318.2$ K

Diffusion coefficients increase with temperature. Comparing the diffusion coefficients of deuterium (D) determined here with those of hydrogen (D_{H}) determined earlier¹⁴ in the same membrane, we see that at each temperature the values of D are about 20% larger than the values of D_{H} . This means that under the same conditions deuterium permeated through the membrane wall *ca* 20% faster than hydrogen (inverse isotope effect).

In Fig. 2 the dependence of $\ln D$ on $(1/T)$ is presented. A straight line was fitted to the experimental points in Fig. 2 and the activation energy (E) of diffusion of deuterium and the D_0 value were determined from the relation $D = D_0 \exp(-E/RT)$: $E = 26.4$ kJ/mol, $D_0 = 6.8 \times 10^{-7}$ m²/s. The value of E is lower than the activation energy of diffusion of hydrogen ($E_{\text{H}} = 27.2$ kJ/mol, $D_{0\text{H}} = 7.61 \times 10^{-7}$ m²/s¹⁴) for the same membrane.

The inverse isotope effect was observed earlier in diffusion of hydrogen and deuterium in palladium²⁷⁻²⁹. The inverse isotope effect is due to the fact that in the case of octahedral-octahedral jumps, the potential wells for vibrating interstitial atoms in the ground state are broader and flatter than in the transition state. The energy difference between the ground state and the activated state decreases with increasing isotope mass^{28,29}.

Permeation of Deuterium Through Pd₈₁Pt₁₉ Membrane with an Initial Deuterium Content

Both sides of the membrane were kept at pressure p_0 , unless equilibrium was attained and then the pressure of deuterium on the outer side of the

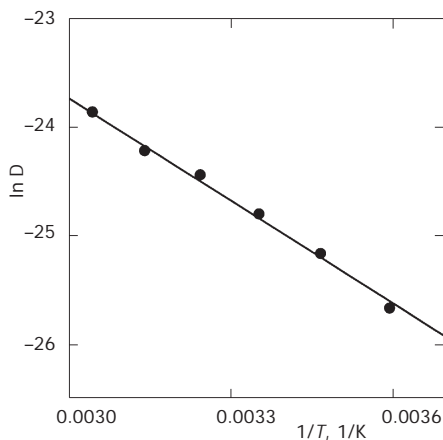


FIG. 2

The logarithm of diffusion coefficient of deuterium, $\ln D$ (D in m²/s), as a function of inverse temperature for Pd₈₁Pt₁₉ membrane with no initial content of deuterium

membrane was changed from p_0 to p_1 . The pressure of deuterium after permeation through the membrane was measured as a function of time. The measurements were carried out at 278.2 K under different initial and boundary conditions during absorption and desorption of deuterium, but always the difference $|p_1 - p_0|$ was *ca* 300 hPa. The breakthrough times were determined by intersection of the straight line fitted to the stationary part of the $p(t)$ dependence and the line given by $p(t) = p_0$. The diffusion coefficients were calculated from the relationship $D = L^2/6\tau$ ^{15,30}. The conditions under which measurements were performed and the values of the calculated diffusion coefficients are given in Table II. In Fig. 3 the diffusion coefficients of deuterium are given as a function of initial pressure of deuterium in the membrane during absorption.

In absorption and desorption of deuterium, the diffusion coefficients decrease with increasing initial content of deuterium in the membrane. When the initial pressure of deuterium in the system was 600 hPa, the deuterium permeation through the membrane wall was *ca* 10 min shorter than in the case when $p_0 = 100$ hPa, which corresponds to a decrease in diffusion coefficient from 8.76×10^{-12} m²/s (for $p_0 = 102.8$ hPa) to 7.69×10^{-12} m²/s (for $p_0 = 600.1$ hPa).

Starting from the same initial deuterium content in membrane and for the same $|p_1 - p_0|$ differences, the diffusion of deuterium during desorption was a little faster than during absorption (see Table II). In diffusion of hydrogen in the Pd₈₁Pt₁₉ membrane, investigated earlier¹⁵, the same phenom-

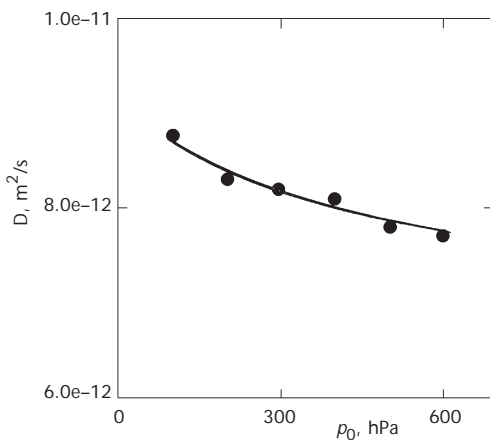


FIG. 3

The diffusion coefficient of deuterium for the Pd₈₁Pt₁₉ membrane, as a function of initial pressure of deuterium during absorption of deuterium at $T = 278.2$ K

enon was observed, *i.e.* diffusion coefficients of hydrogen in desorption were larger than in absorption.

All these measurements were performed for deuterium pressures up to *ca* 900 hPa, which corresponds to the maximum deuterium content in membrane about $n = 0.009$ (atomic ratio deuterium/metal) (Fig. 4).

The dependence $p(n)$ for deuterium in the Pd₈₁Pt₁₉ alloy was determined at 278.2 K by a volumetric method. The dependence $p^{1/2}(n)$ in Fig. 4 is a straight line. At $T = 278.2$ K the deuterium content is lower than the hydrogen content in Pd₈₁Pt₁₉ alloy at the same pressure (for comparison, see Fig. 4 and refs^{18,31,32}). Assuming an ideal solution state, the Sievert constant (K), as determined by fitting the expression $p^{1/2} = K(n/(1 - n))$ ²⁸ to experimental points, equals $K = (33.7 \pm 0.5) \times 10^2$ hPa^{1/2}.

In general, diffusion coefficients of hydrogen or deuterium in metals can be influenced by various factors: defects (grain boundaries, dislocations, vacancies), stresses, concentration dependence (blocking of random walk

TABLE II

The diffusion coefficients of deuterium for the Pd₈₁Pt₁₉ membrane at $T = 278.2$ K, under different initial pressures of deuterium (p_0) and pressures of deuterium on the outer side of membrane (p_1)

p_0 , hPa	p_1 , hPa	$ p_1 - p_0 $, hPa	$D \times 10^{12}$, m ² /s
Absorption			
102.8	401.7	298.9	8.76
202.2	497.7	295.5	8.30
296.7	605.6	308.9	8.19
400.3	700.0	299.7	8.09
502.4	800.5	298.1	7.79
600.1	898.5	298.4	7.69
Desorption			
398.4	96.8	301.6	8.30
498.1	201.7	296.4	8.19
596.7	302.6	294.1	8.09
702.2	409.3	292.9	7.98
796.5	505.0	291.5	7.79
898.0	601.6	296.4	7.60

diffusion)^{7,14,28,33-36}. So far, the dependence of diffusion coefficient of deuterium on its concentration in the Pd₈₁Pt₁₉ membrane has not been published. Since all our measurements were performed in a narrow range of small deuterium contents (see Fig. 4) we assume that the change in diffusion coefficient influenced by the blocking effect is small and can be neglected.

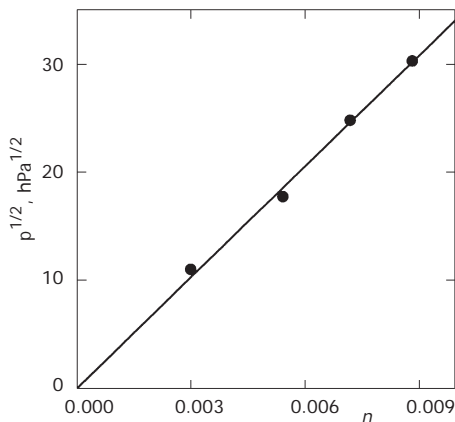


FIG. 4

The deuterium content (atomic ratio deuterium/metal) in Pd₈₁Pt₁₉, as a function of deuterium pressure

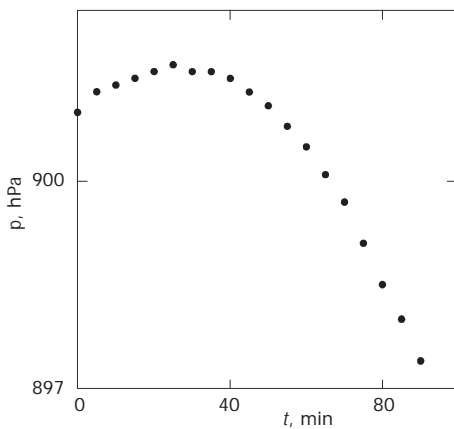


FIG. 5

The pressure of deuterium, which permeated through the Pd₈₁Pt₁₉ membrane, as a function of time at $p_0 = 901.4$ hPa, $p_1 = 0$, $T = 278.2$ K

At $T = 278.2$ K the diffusion coefficient of deuterium in the $\text{Pd}_{81}\text{Pt}_{19}$ membrane with no initial content of deuterium is lower than the diffusion coefficients of deuterium in the same membrane with various initial contents of deuterium (see Tables I and II) due to a trapping effect. The fraction of lattice containing defects acts as a trapping region where the mean residence time of interstitial atoms is longer than in the defect-free regions^{23,35,36}. In the cases when the trapping regions were occupied by deuterium atoms, *i.e.* when the membrane had some initial content of deuterium, the trapping effect could not change the diffusion coefficient.

Taking into account all the above arguments on the influence of different factors on the diffusion coefficient, a decrease in diffusion coefficient of deuterium with its increasing initial content can be explained reasonably only by the existence of stresses, created during introduction or removal of deuterium in absorption or desorption processes.

The changes on $p(t)$ lines for small times (up to the breakthrough time), caused by stresses, could be observed as maxima during desorption or minima during absorption. On the $p(t)$ line presented in Fig. 5, a maximum is observed. The non-local deuterium fluxes are proportional to the concentration of the interstitial component^{5,6} flowing in the opposite direction than Fick flux, and changing the breakthrough times only in membranes with some initial deuterium content. The solubility of deuterium is lower than that of hydrogen in the $\text{Pd}_{81}\text{Pt}_{19}$ alloy at the same temperature (see Fig. 4 and refs^{18,31,32}) and lower uphill effects on $p(t)$ lines were observed for deuterium than for hydrogen diffusion.

CONCLUSIONS

The diffusion coefficients were determined for a $\text{Pd}_{81}\text{Pt}_{19}$ membrane: (i) with no initial deuterium content at six temperatures ranging from 278.2 to 328.2 K; (ii) with different initial contents of deuterium, when $|p_1 - p_0|$ was ca 300 hPa, at $T = 278.2$ K. The activation energy of deuterium diffusion $E = 26.4$ kJ/mol was found. The inverse isotope effect in the $\text{Pd}_{81}\text{Pt}_{19}$ membrane was described. The deuterium solubility in $\text{Pd}_{81}\text{Pt}_{19}$ was measured at $T = 278.2$ K. A decrease in diffusion coefficients of deuterium with its increasing initial content was observed and explained by the influence of stresses on permeation of deuterium.

REFERENCES

1. Larche F. C., Cahn J. W.: *Acta Metall.* **1973**, 21, 1051.
2. Li J. C. M.: *Met. Trans.* **1978**, 9A, 1953.

3. Larche F. C., Cahn J. W.: *Acta Metall.* **1982**, 30, 1835.
4. Larche F. C., Cahn J. W.: *Acta Metall.* **1985**, 33, 331.
5. Baranowski B.: *J. Less-Common Met.* **1989**, 154, 329.
6. Baranowski B. in: *Advances in Thermodynamics, Flow Diffusion and Rate Processes* (S. Sieniutycz and P. Salomon), p. 168. Taylor and Francis, New York 1992.
7. Lewis F. A., Magennis J. P., Mc Kee S. G., Seebuufu P. J. M.: *Nature* **1983**, 306, 613.
8. Lewis F. A., Baranowski B., Kandasamy K.: *J. Less-Common Met.* **1987**, 134, L27.
9. Baranowski B., Lewis F. A.: *Ber. Bunsen-Ges., Phys. Chem.* **1989**, 93, 1225.
10. Kandasamy K., Lewis F. A., Magennis J. P., Mc Kee S. G., Tong X. Q.: *Z. Phys. Chem.* **1991**, 171, 213.
11. Kandasamy K., Tong X. Q., Lewis F. A.: *J. Phys. Condens. Matter.* **1992**, 4, L439.
12. Lewis F. A., Tong X. Q., Kandasamy K., Bucur R. V., Sakamoto Y.: *Thermochim. Acta* **1993**, 218, 57.
13. Lewis F. A., Sakamoto Y., Kandasamy K., Tong X. Q.: *Defect Diffusion Forum* **1994**, 115–116, 39.
14. Dudek D., Baranowski B.: *Pol. J. Chem.* **1995**, 69, 1196.
15. Dudek D., Baranowski B.: *Z. Phys. Chem.* **1998**, 206, 21.
16. Čermak J., Kufudakis A., Gardavska G., Lewis F.: *Proceedings JIMIS-2, Hydrogen in Metals, Japan*, p. 125. Minakami, Gunma Pref. 1979.
17. Zoltowski P., Makowska E.: *Phys. Chem. Chem. Phys.* **2001**, 3, 2935.
18. Dudek D.: *J. Alloys Compd.* **2001**, 329, 1.
19. Dudek D.: *Defect Diffusion Forum* **2002**, 203–205, 225.
20. Zoltowski P.: *J. Electroanal. Chem.* **2001**, 501, 89.
21. Zoltowski P.: *J. Electroanal. Chem.* **2001**, 512, 64.
22. Legawiec B., Zoltowski P.: *J. Phys. Chem. B* **2002**, 106, 4933.
23. Tong X. Q., Sakamoto Y., Lewis F. A., Bucur R. V., Kandasamy K.: *Int. J. Hydrogen Energy* **1997**, 22, 141.
24. Tong X. Q., Lewis F. A.: *J. Less-Common Met.* **1991**, 169, 157.
25. Lewis F. A., Tong X. Q.: *J. Alloys Compd.* **1992**, 179, L13.
26. Crank J.: *The Mathematics of Diffusion*, p. 48. Oxford University Press, Oxford 1956.
27. Bohmholdt G., Wicke E.: *Z. Phys. Chem., N.F.* **1967**, 56, 133.
28. Wicke E., Brodowski H., Zuechner H. in: *Hydrogen in Metals II* (G. Alefeld and J. Völkl, Eds), p. 73. Springer Verlag, Berlin 1978.
29. Kehr K. W. in: *Topics in Applied Physics, 28, Hydrogen in Metals I* (G. Alefeld and J. Völkl, Eds), p. 197. Springer Verlag, Berlin 1978.
30. Barrer R. M.: *Diffusion in and Through Solids*, p. 19. Cambridge University Press, Cambridge 1951.
31. Noh H., Clewley J. D., Flanagan T. B.: *Scr. Mater.* **1996**, 34, 665.
32. Noh H., Flanagan T. B., Sonada T., Sakamoto Y.: *J. Alloys Compd.* **1995**, 228, 164.
33. Völkl J., Alefeld G.: *Top. Appl. Phys.* **1978**, 28, 321.
34. Majorowski S., Baranowski B.: *J. Phys. Chem. Solids* **1982**, 43, 1119.
35. Bucur R. V., Ersson N. O., Tong X. Q.: *J. Less-Common Met.* **1991**, 172–174, 748.
36. Bucur R. V., Lewis F. A.: *Z. Phys. Chem.* **1993**, 181, 209.