THE INFLUENCE OF SELF-STRESSES ON THE DEUTERIUM DIFFUSION IN $Pd_{77}Ag_{23}$ MEMBRANE

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The permeation of deuterium through the palladium-silver $Pd_{77}Ag_{23}$ membrane was investigated. The diffusion coefficients of deuterium were determined at four temperatures between 303 and 328 K. The influence of self-stresses, created after introduction of deuterium into membrane with some initial deuterium contents, on the diffusion of deuterium was investigated at temperature 303.2 K. The solubility of deuterium in $Pd_{77}Ag_{23}$ membrane at four temperatures in the range 303–328 K was measured.

Keywords: Diffusion; Deuterium; Palladium; Silver; Alloys; Stresses; Permeation; Membranes; Solubility.

The interest in diffusion of hydrogen and deuterium in palladium-silver alloys has been large for many years because of its importance for separation and purification of gaseous hydrogen and deuterium and for hydrogen and deuterium storage in metal hydrides and deuterides. The isotherms, diffusion and solubility of hydrogen[1–14] and deuterium[15–17] in palladium-silver alloys were investigated experimentally by electrochemical and by gas methods, or in NMR studies. Kinetics of hydrogen absorption was measured[18] and different calculations and theoretical simulations of the absorption and diffusion processes were made[19–21] for palladium-silver alloys.

The chemical potential (μ_i) of interstitial component (hydrogen or deuterium) in membrane under stress conditions equals[22]

$$\mu_i = \mu_0 + RT \ln f_i c_i - V_i \sigma \,, \tag{1}$$

where μ_0 denotes a standard value of chemical potential, f_i is activity coefficient, c_i concentration, V_i partial molar volume of interstitial component, σ hydrostatic part of the stress tensor, and T temperature.

Introduction of hydrogen or deuterium into membrane with some initial content of hydrogen or deuterium creates stresses and changes the chemi-

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cal potential of interstitial component in the whole membrane due to elastic coupling in lattice. It has been evidenced in some membranes with selected initial contents of hydrogen, that under stress conditions, besides Fick's fluxes, hydrogen fluxes in the opposite direction to the concentration gradient have been created[22,23]. The total flow (J_i) of the interstitial component (i) (hydrogen or deuterium) through the membrane with concentration gradient and under stress conditions can be expressed by[22]:

$$J_i = -D_i\{[1 + (\partial \ln f_i/\partial \ln c_i)]\mathrm{grad}\, c_i - (V_i c_i/RT)\mathrm{grad}\, \sigma\} \,, \tag{2}$$

where D_i is diffusion coefficient. When in ideal solution grad σ equals zero, we have in expression (*2*) only the Fickian term and

$$J_i = -D_i\, \mathrm{grad}\, c_i \,. \tag{3}$$

Under stress conditions and when $c_\mathrm{i} \neq 0$, both Fickian and non-Fickian terms should be taken into account. The source of strain gradient and origin of uphill diffusion can be input of hydrogen or deuterium into membrane. So far, many investigations of influence of stresses on diffusion of hydrogen in palladium alloys have been carried out but only few studies were done for diffusion of deuterium at stress conditions. The uphill diffusion effects were observed during diffusion of hydrogen in Pd [24–26], in $Pd_{81}Pt_{19}$ [27–36], in $Pd_{100-x}Ag_x$: x = 9.9, 19.9, 23, 30, 39.9 at.% [24,37,38] and during diffusion of deuterium in $Pd_{81}Pt_{19}$ [39]. Theoretical problems of diffusion of hydrogen in palladium alloys under stress conditions were studied[22,23,40–46].

In this paper the influence of stresses on the diffusion of deuterium in the $Pd_{77}Ag_{23}$ membrane was investigated. For membrane without initial content of deuterium the diffusion coefficients were determined at temperatures: 303.2, 308.2, 318.2 and 328.2 K. For membrane with selected initial contents of deuterium up to $n \approx 0.2$ (atomic ratio n = D/M is the number of gram-atoms of deuterium divided by the number of gram-atoms of metal – $Pd_{77}Ag_{23}$), the permeation of deuterium through the wall of $Pd_{77}Ag_{23}$ membrane was investigated at T = 303.2 K. The solubility of deuterium in $Pd_{77}Ag_{23}$ membrane at temperatures 303.2, 308.2, 318.2 and 328.2 K was measured.

EXPERIMENTAL

The diffusion of deuterium through the palladium-silver $Pd_{77}Ag_{23}$ membrane was investigated. The membrane was in the form of a cylindrical tube, closed at one side. The dimensions of the tube were: length 70 mm, internal diameter 8 mm, wall thickness 0.5 mm. The $Pd_{77}Ag_{23}$ membrane was annealed for 2 h in high vacuum at 600 °C. All surfaces of the tube were covered with palladium black.

The $Pd_{77}Ag_{23}$ membrane was placed in a glass system[33] and deuterium was introduced into the membrane from gas phase. The gas pressure was measured with a capacitance manometer and tensometric gauges with accuracies ±0.15 and ±0.3%, respectively. The experiments were performed at selected constant temperatures in the range 303–328 K. The constant temperature was controlled with accuracy better than ±0.1 K.

RESULTS AND DISCUSSION

Starting from deuterium-free $Pd_{77}Ag_{23}$ membrane (at time $t = 0$ the pressure in the whole system was zero), the pressure of deuterium at the outer side of membrane (p_z) was changed from zero to about 60 hPa. The pressure of deuterium, which permeated through the membrane wall into the inner volume of the system was measured as a function of time. The measurements were carried out at four constant temperatures 303.2, 308.2, 318.2 and 328.2 K. The determined $p(t)$ lines are presented in Fig. 1.

The breakthrough times (τ) were determined as the intersections of straight lines in the stationary part of $p(t)$ lines with the time axis (see an example – line *3* in Fig. 1). The values of τ are presented in Table I. The breakthrough times decrease with increasing temperature.

The diffusion coefficients (D) were calculated from the expression[47,48]:

$$D = L^2/6\tau \,, \qquad (4)$$

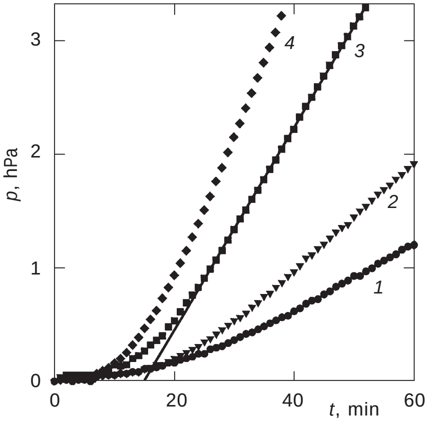

FIG. 1

The pressure (p) of deuterium, which permeated through $Pd_{77}Ag_{23}$ membrane as a function of time, measured at: *1* T = 303.2 K, $p_0 = 0$, p_z = 64.0 hPa; *2* T = 308.2 K, $p_0 = 0$, p_z = 53.8 hPa; *3* T = 318.2 K, $p_0 = 0$, p_z = 58.4 hPa; *4* T = 328.2 K, $p_0 = 0$, p_z = 58.5 hPa where L is membrane thickness. The values of D are given in Table I. In order to evaluate activation energy (E) the expression $D = D_0 \exp(-E/RT)$ was used. The logarithms of diffusion coefficients of deuterium as a function of inverse temperature are presented in Fig. 2. The determined activation energy (E) of diffusion of deuterium in $Pd_{77}Ag_{23}$ membrane and D_0 are E = 16.7 kJ/mol and $D_0 = 2.6 \times 10^{-8}$ m^2/s.

The values of diffusion coefficients determined for a $Pd_{77}Ag_{23}$ membrane without any initial content of deuterium are close to the values of diffusion coefficients determined in[15] for palladium-silver membrane with 25 mole % of Ag. The differences may be caused by accuracy of measurements, by difference in silver contents (2 mole % of Ag), or by other factors such as defects, surface effects or differences in deuterium purity.

TABLE I
The breakthrough times (τ) and the diffusion coefficients (D) of deuterium for $Pd_{77}Ag_{23}$ membrane without initial deuterium content ($p_0 = 0$) at different temperatures

T, K	p_z, hPa	τ, min	D, m^2/s
303.2	64.0	20	3.47e–11
308.2	53.8	18	3.86e–11
318.2	58.4	15	4.63e–11
328.2	58.5	12	5.79e–11

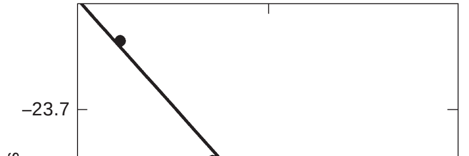

FIG. 2
The logarithm of diffusion coefficients of deuterium as a function of inverse temperature for $Pd_{77}Ag_{23}$ membrane with no initial content of deuterium

Starting at constant temperature 303.2 K from a content of deuterium in $Pd_{77}Ag_{23}$ membrane (the tube was kept at chosen deuterium pressure as long as equilibrium was attained), the pressure of deuterium at the outer side of membrane changed from p_0 to $p_z = p_0 + \Delta p_z$. The pressure of deuterium in the inner volume of the system was measured as a function of time, $p(t)$. The determined $\Delta p(t) = p(t) - p_0$ dependences at selected initial and boundary conditions are presented in Figs 3–5.

Figure 3 shows the change in deuterium pressure in the inner volume of the system at different values of p_0 and at almost the same $p_z \approx 40$ hPa. In Fig. 4 the $p(t)$ dependences for membrane with and without an initial content of deuterium are compared. When the initial condition was $p_0 = 0$, the change in the deuterium pressure p in the inner volume of the system occurred after a breakthrough time, but when the initial condition was $p_0 \neq 0$ (measurements were made for p_0 up to about 5.5 hPa), pressure p changed immediately after boundary conditions changed.

In two experiments, the results of which are presented in Fig. 5, p_0 was almost the same (about 5 hPa) and p_z was 39.7 and 60.4 hPa, respectively.

In Figs 3–5 we see on $p(t)$ dependences first a small maximum, immediately after increasing deuterium pressure at the outer side of membrane, and later a large minimum. A small maximum can be explained by mechanically induced bending of the tube and contraction of the internal volume and mainly by stresses (see the experiments with hydrogen and argon[37]).

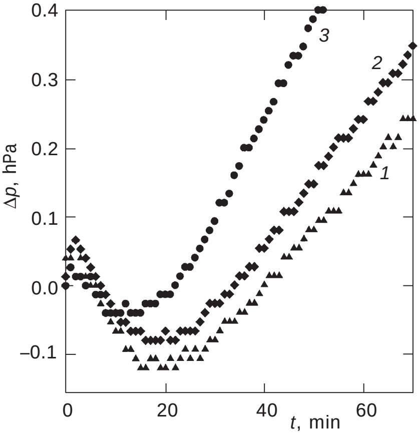

FIG. 3
The changes in pressure of deuterium in the inner volume of the system as a function of time: $\Delta p(t) = p(t) - p_0$, measured at $T = 303.2$ K and at: *1* $p_0 = 5.54$ hPa, $p_z = 39.7$ hPa; *2* $p_0 = 4.37$ hPa, $p_z = 40.8$ hPa; *3* $p_0 = 2.45$ hPa, $p_z = 40.2$ hPa

On $p(t)$ dependences in Figs 3–5, measured at $p_0 \neq 0$, large minima are observed. Stresses are responsible for these minima. Input of deuterium into membrane creates stresses and changes chemical potential of deuterium in the whole membrane – see Eq. (*1*). The flux of deuterium in the opposite direction than Fick's flux occurred. At constant temperature, in ideal solu-

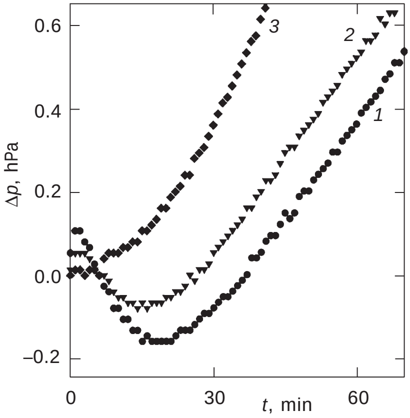

FIG. 4
The changes in pressure of deuterium in inside volume of the system as a function of time: $\Delta p(t) = p(t) - p_0$, measured at T = 303.2 K and at: *1* p_0 = 5.21 hPa, p_z = 60.4 hPa; *2* p_0 = 3.21 hPa, p_z = 57.4 hPa; *3* p_0 = 0, p_z = 64.0 hPa

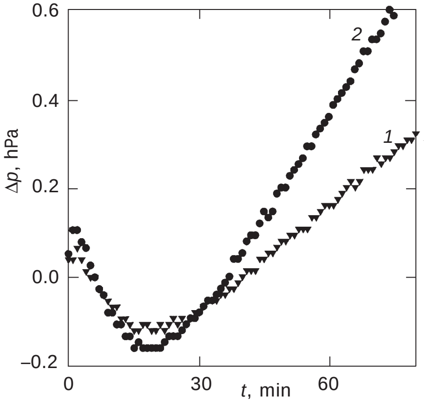

FIG. 5
The changes in pressure of deuterium in the inner volume of the system as a function of time: $\Delta p(t) = p(t) - p_0$, measured at T = 303.2 K and at: *1* p_0 = 5.54 hPa, p_z = 39.7 hPa; *2* p_0 = 5.21 hPa, p_z = 60.4 hPa

tion, the total flux of deuterium through the membrane depends on deuterium concentration, on concentration gradient and on gradient of stresses. In Figs 3–5 we see that magnitude of uphill diffusion depends on initial concentration and on boundary conditions. Figures 3 and 4 illustrate that the minima on $p(t)$ dependences increase with increasing p_0 in the investigated pressure region.

The breakthrough time for diffusion of deuterium in $Pd_{77}Ag_{23}$ membrane with an initial content of deuterium was determined by intersection of the straight line fitted to the stationary part of $p(t)$ line with the line $p(t) = p_0$. The diffusion coefficients were calculated from Eq. (*4*). The results are presented in Table II and in Fig. 6.

TABLE II
The breakthrough times (τ) and the diffusion coefficients (D) of deuterium for $Pd_{77}Ag_{23}$ membrane, at T = 303.2 K, under different initial and boundary conditions

p_0, hPa	p_z, hPa	τ, min	D, m^2/s
2.45	40.2	23	3.02e–11
3.21	57.4	27	2.57e–11
4.37	40.8	34	2.04e–11
5.21	60.4	37	1.88e–11
5.54	39.7	40	1.74e–11

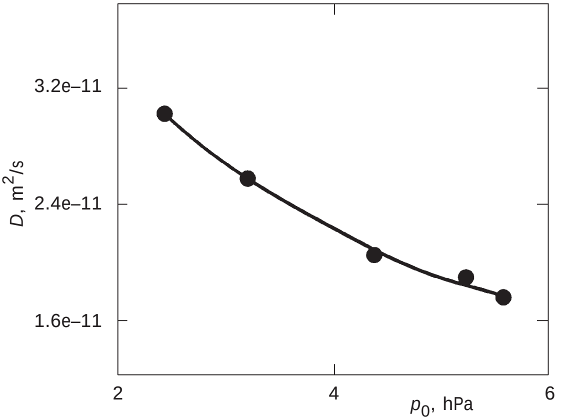

FIG. 6
The dependence of diffusion coefficient (D) of deuterium for the $Pd_{77}Ag_{23}$ membrane on the initial pressure p_0, at T = 303.2 K (the solid line is an eye guide)

Equation (*4*) precisely determines values of D at constant initial and boundary conditions[47,48]. Unfortunately, in our measurements the values of p_z and corresponding boundary concentrations changed with time during each measurement because of high solubility of deuterium in membrane. The values of p_z given in Tables I and II are the starting values in each measurement. The error in diffusion coefficients, caused by changing p_z with time, was 20%.

From Tables I and II we see that, in the investigated pressure region, the breakthrough times for membranes with some deuterium contents are always larger (even by 100%) than those for membrane with no initial content of deuterium. The diffusion coefficients in Fig. 6 decrease with increasing p_0. The differences between D values in Table I and those in Table II are caused by stresses and by dependence of diffusion coefficient on deuterium concentration.

The solubility of deuterium in $Pd_{77}Ag_{23}$ membrane was measured by volumetric method at temperatures 303.2, 308.2, 318.2 and 328.2 K. The results are presented in Fig. 7. The solubility of deuterium decreases with increasing temperature.

The measurements of $p(t)$ presented in Figs 3–5 were carried out for initial pressures of deuterium up to about 5.5 hPa, which corresponds to $n \approx 0.2$.

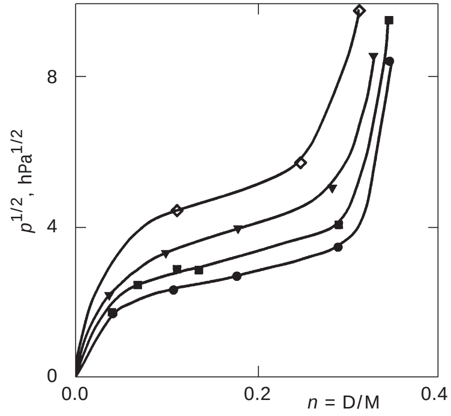

FIG. 7
The deuterium content n = D/M (see the text) in $Pd_{77}Ag_{23}$ membrane as a function of $p^{1/2}$ at different temperatures T (in K): ● 303.2, ■ 308.2, ▼ 318.2, ◇ 328.2 (the solid lines are eye guides)

CONCLUSIONS

The diffusion of deuterium through the $Pd_{77}Ag_{23}$ membrane was investigated at temperatures 303.2, 308.2, 318.2 and 328.2 K. The influence of stresses was studied at temperature 303.2 K. The uphill diffusion effects were evidenced under different initial and boundary conditions. The breakthrough times and diffusion coefficients were determined for the $Pd_{77}Ag_{23}$ membrane without or with initial contents of deuterium up to about to $n \approx 0.2$. The solubility of deuterium at the above temperatures was measured by a volumetric method.

REFERENCES

1. Kuesner A.: *Z. Phys. Chem. (Frankfurt am Main)* **1963**, *36*, 383.
2. Brodowsky H., Poeschel E.: *Z. Phys. Chem. (Frankfurt am Main)* **1965**, *44*, 143.
3. Kuesner A.: *Z. Naturforsch., A* **1966**, *21*, 515.
4. Bohmholdt G., Wicke E.: *Z. Phys. Chem. (Frankfurt am Main)* **1967**, *56*, 133.
5. Carson A. W., Lewis F. A.: *Trans. Faraday Soc.* **1967**, *63*, 1453.
6. Holleck G. L.: *J. Phys. Chem.* **1970**, *74*, 503.
7. Zuechner H.: *Z. Naturforsch., A* **1970**, *25*, 1490.
8. Buchold H., Sicking G., Wicke E.: *Ber. Bunsen-Ges. Phys. Chem.* **1976**, *80*, 446.
9. Sakamoto Y., Hirata S., Nishikawa H.: *J. Less-Common Met.* **1982**, *88*, 387.
10. Bucur R. V., Ersson N. O., Tong X. Q.: *J. Less-Common Met.* **1991**, *172–174*, 748.
11. Zuechner H., Rauf T.: *J. Less-Common Met.* **1991**, *172–174*, 816.
12. Lindsay W. T., Jr.: *Int. J. Thermophys.* **1997**, *18*, 1051.
13. Serra E., Kemali M., Perujo A., Ross D. K.: *Metall. Mater. Trans. A* **1998**, *29*, 1023.
14. Zuechner H., Barlag H., Majer G.: *J. Alloys Compd.* **2002**, *330–332*, 448.
15. Holleck G., Wicke E.: *Z. Phys. Chem. (Frankfurt am Main)* **1967**, *56*, 155.
16. Hickman R. G.: *J. Less-Common Met.* **1969**, *19*, 369.
17. Laesser R., Powell G. L.: *J. Less-Common Met.* **1987**, *130*, 387.
18. Auer W., Grabke H. J.: *Ber. Bunsen-Ges. Phys. Chem.* **1974**, *78*, 58.
19. Opara L., Klein B., Zuechner H.: *J. Alloys Compd.* **1997**, *253–254*, 378.
20. Lovvik O. M., Olsen R. A.: *J. Alloys Compd.* **2002**, *330–332*, 332.
21. Ke X., Kramer G. J.: *Phys. Rev. B* **2002**, *66*, 184304.
22. Baranowski B. in: *Advances in Thermodynamics, Flow Diffusion and Rate Processes* (S. Sieniutycz and P. Salomon, Eds), p.168. Taylor and Francis, New York 1992.
23. Baranowski B.: *J. Less-Common Met.* **1989**, *154*, 329.
24. Lewis F. A., Sakamoto Y., Kandasamy K., Tong X. Q.: *Defect Diffusion Forum* **1994**, *115–116*, 39.
25. Tong X. Q., Sakamoto Y., Lewis F. A., Bucur R. V., Kandasamy K.: *Int. J. Hydrogen Energy* **1997**, *22*, 141.
26. Sakamoto Y., Tanaka H., Lewis F. A., Tong X. Q.: *Int. J. Hydrogen Energy* **1992**, *17*, 965.
27. Lewis F. A., Magennis J. P., Mc Kee S. G., Seebuwufu P. J. M.: *Nature* **1983**, *306*, 613.
28. Lewis F. A., Baranowski B., Kandasamy K.: *J. Less-Common Met.* **1987**, *134*, L27.
29. Baranowski B., Lewis F. A.: *Ber. Bunsen-Ges. Phys. Chem.* **1989**, *93*, 1225.

30. Kandasamy K., Lewis F. A., Magennis J. P., Mc Kee S. G., Tong X. Q.: *Z. Phys. Chem.* **1991**, *171*, 213.
31. Kandasamy K., Tong X. Q., Lewis F. A.: *J. Phys.: Condens. Matter.* **1992**, *4*, L439.
32. Lewis F. A., Tong X. Q., Kandasamy K., Bucur R. V., Sakamoto Y.: *Thermochim. Acta* **1993**, *218*, 57.
33. Dudek D., Baranowski B.: *Pol. J. Chem.* **1995**, *69*, 1196.
34. Dudek D., Baranowski B.: *Z. Phys. Chem.* **1998**, *206*, 21.
35. Dudek D.: *J. Alloys Compd.* **2001**, *329*, 1.
36. Dudek D.: *Defect Diffusion Forum* **2002**, *203–205*, 225.
37. Tong X. Q., Lewis F. A.: *J. Less-Common Met.* **1991**, *169*, 157.
38. Sakamoto Y., Tanaka H., Sakamoto F., Lewis F. A.: *Int. J. Hydrogen Energy* **1995**, *20*, 35.
39. Dudek D.: *Collect. Czech. Chem. Commun.* **2003**, *68*, 1046.
40. Larche F. C., Cahn J. W.: *Acta Metall.* **1973**, *21*, 1051.
41. Li J. C. M.: *Metall. Trans. A* **1978**, *9*, 1953.
42. Larche F. C., Cahn J. W.: *Acta Metall.* **1982**, *30*, 1835.
43. Larche F. C., Cahn J. W.: *Acta Metall.* **1985**, *33*, 331.
44. Kandasamy K.: *Int. J. Hydrogen Energy* **1995**, *20*, 455.
45. Zoltowski P.: *J. Electroanal. Chem.* **2001**, *501*, 89.
46. Legawiec B., Zoltowski P.: *J. Phys. Chem. B* **2002**, *106*, 4933.
47. Crank J.: *The Mathematics of Diffusion*, p. 48. Oxford University Press, Oxford 1956.
48. Barrer R. M.: *Diffusion in and through Solids*, p. 19. Cambridge University Press, Cambridge 1951.