## LITERATURE CITED

1. Khr. Boyadzhiev, Inzh.-Fiz. Zh., 59, No. 1, 92-98 (1990).
2. Khr. Boyadzhiev and E. Toshev, Inzh.-Fiz. Zh., 59, No. 2, 277-286 (1990).
3. Yu. V. Fumer, Yu. V. Aksel'rod, V. V. Dal'man, and A. A. Lashkov, Teor. Osn. Khim. Tekhnol., 5, No. 1, 134-136 (1971).
4. V. I. Kosorotov, R. V. Dzhagatspanyan, B. Ya. Stul', and B. P. Luzyanin, Teor. Osn. Khim. Tekhnol., 5, 239-243 (1971).
5. V. I. Kosorotov, R. V. Dzhagatspanyan, B. Ya. Stul', and V. I. Zetkin, Teor. Osn. Khim. Tekhnol., 5, 474-476 (1971).
6. Khr. Boyadzhiev and V. Beshkov, Mass Transfer in Moving Liquid Films [in Russian], Moscow (1988).
7. T. K. Sherwood, R. L. Pigford, and C. R. Wilke, Mass Transfer, McGraw-Hill, New York, (1975).
8. D. A. Frank-Kamenetskii, Diffusion and Heat Transfer in Chemical Kinetics [in Russian], Moscow (1987).

---

# EFFECT OF THE CONCENTRATION DEPENDENCE OF THE DIFFUSION COEFFICIENT ON THE DISTRIBUTION AND FLOW OF HYDROGEN IN PALLADIUM MEMBRANES

L. I. Smirnov

UDC 539.219.3:669.234.788

Results are presented from the calculation of steady-state profiles of the distribution and flow of hydrogen in palladium membranes. The distributions are obtained with allowance for features of the dependence of the diffusion coefficient on hydrogen concentration.

The study [1] examined the effect of a nonlinear hydrogen distribution through the thickness of metallic membranes, due to the concentration dependence of the diffusion coefficient, on the permeability of the membranes to hydrogen. The study made use of a simple model relation D(c) [2] which describes phase transformation in hydride-forming metals [3]. However, it has become evident in recent years that along with a minimum corresponding to phase transformation, the relation D(c) for Pd–H systems has a maximum in the concentration range c = (0.6...0.7)H/Pd [4-7]. In the present study, we discuss the results of calculation of steady-state profiles of hydrogen distribution in palladium membranes and the flow of hydrogen through these membranes with allowance for a relation D(c) that reflects the above features.

In accordance with [7], the concentration dependence of the coefficient of diffusion of H in Pd is approximately described by the relation

$$D(c) = D(0)\left[1-6\,\frac{\beta-1}{\beta}+\left(\frac{\partial\mu_e}{\partial c}-\frac{3\gamma}{2}\,\mathrm{cth}\,\frac{\hbar\omega_\alpha-\gamma c}{2kT}\right)\frac{c(1-c)}{kT}\right], \tag{1}$$

where

$$\beta=\sqrt{1+4\alpha c(1-c)},\quad \alpha=\exp(-w/kT)-1, \tag{2}$$

while the electronic contribution to the chemical potential of the hydrogen subsystem $\mu_e(c)$ is determined from the empirical formula [3, Vol. 2, p. 152]:

$$\mu_e(c)=\sum_{n=1}^{5}(-1)^{n-1}a_n c^n,\quad c<0{,}656, \tag{3}$$

$$\mu_e(c)=b(c-c_1),\qquad c\geqslant 0{,}656.$$

---

Donetsk Polytechnic Institute. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 59, No. 10, pp. 602-606, October, 1990. Original article submitted September 5, 1989.

0022-0841/90/5904-1280$12.50

(3)

In the derivation of (1), use was made of an expression for the configurational contribution to chemical potential [3, Vol. 2, p. 127] that was obtained in a quasi-chemical approximation with allowance for the interaction of nearest-neighbor hydrogen atoms. The vibrational contribution to the chemical potential was calculated in [8].

Let us write out the steady-state solution c(x) of the diffusion equation with diffusion coefficient (1) and boundary conditions $c(0) = c_0$, $c(\ell) = 0$ corresponding to a constant hydrogen pressure on the entry side of the membrane (x = 0) and a zero concentration on the exit side ($x = \ell$). Written in implicit form, this solution appears as follows

$$\frac{x}{l} = 1 - \frac{S(c)}{S(c_0)}, \quad S(c) = \int_0^c \frac{D(c)}{D(0)}\,dc \equiv \sum_{i=1}^{3} S_i(c), \tag{4}$$

where

$$S_1(c) = -5c + \frac{3}{\sqrt{\alpha}}\left\{\arcsin\sqrt{\frac{\alpha}{\alpha+1}} - \arcsin\left[\sqrt{\frac{\alpha}{\alpha+1}}(1-2c)\right]\right\}, \tag{5}$$

$$S_2(c) = \begin{cases} \dfrac{c^2}{kT}\displaystyle\sum_{n=0}^{5}(-1)^n \frac{na_n + (n+1)a_{n+1}}{n+2}\,c^n, & c < 0{,}656, \\ \dfrac{bc^2}{kT}\left(\dfrac{1}{2} - \dfrac{c}{3}\right), & c \geqslant 0{,}656. \end{cases} \tag{6}$$

In the first formula of (6), $a_6 = 0$. The quantity

$$S_3(c) = -\frac{3\gamma}{2kT}\int_0^c c(1-c)\,\mathrm{cth}\,[(\hbar\omega_\alpha - \gamma c)/2kT]\,dc \tag{7}$$

was calculated on a computer by the Simpson method. In calculating $S_1(c)$ for w, we took the relation: w = −33.15 + 0.0112T meV [3, Vol. 2, 143].

We used the relations x(c) to construct graphs of c(x) for temperatures of 800, 525, and 450 K (Fig. 1). With concentrations on the entry side $c_0 < 0.6$, the curves c(x) are close to those calculated in [2] in the Gorsky–Bragg–Williams approximation. The value 525 K was taken as the critical temperature, this value differing from the well-known value $T_c = 565$ K [3, Vol. 2, p. 100]. The difference is due not only to the approximations made in [7, 8] and, accordingly, in the present study (here, we are speaking mainly of the Einstein approximations for the description of the vibration of hydrogen atoms at high concentrations), but also to the sensitivity of the model to small changes in the values of the parameters in the critical region.

As in [2], at $T < T_c$ the functions c(x) are multivalued. In an earlier study [2], we interpreted the multivalued region as a region characterized by the unstable coexistence of the hydride phase and the solid solution. Here, we make a different interpretation: we will assume that the branch of the curve c(x) which is realized is that for which the free energy of the hydrogen subsystem, concentrated in a small region Δx, is lower than for other branches.* This assumption is valid within the framework of the local equilibrium approximation used in the derivation of Eq. (1). As has been shown by specific calculations, the concentration dependences of both the Helmholtz free energy and the Gibbs free energy (thermodynamic potential) are such that the convex envelopes [9, Vol. 1, 340-343] of both functions increase monotonically at moderately low hydrogen concentrations. Thus, in the multivalued region, we should neglect the branches corresponding to large concentrations.

It follows in particular from this interpretation that at T = 450 K and $a_0 = 0.25$ (the lower dot-dash curve in Fig. 1) the concentration in the volume of the specimen is considerably less than the concentration in the thin surface layer: in going from the surface to the bulk, concentration decreases from $c_0 = 0.25$ to $c_0 \sim 0.06$, i.e., by a factor of four. It should be emphasized that this effect –(which becomes stronger with a decrease in temperature) is due to the effective interaction (attraction) of hydrogen atoms in the volume of the membrane. The stated effect leads to decomposition of Me–H alloys into two phases [2] and bears no relationship to the features of the thermodynamics and kinetics of hydro-

---

*This interpretation was suggested by S. I. Masharov.

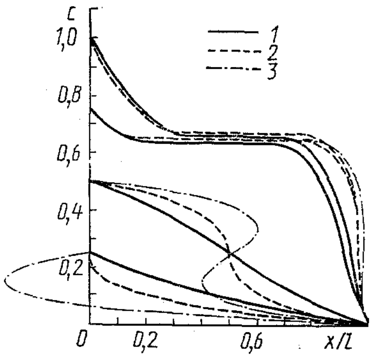

Fig. 1. Steady-state profiles of hydrogen distribution in palladium membranes: 1) T = 800 K; 2) 525; 3) 450.

gen in its interaction with the surface [10]. These features were not considered in the present study. The authors of [2, 11, 12] empirically observed hydrogen enrichment of the surface layer of hydride-forming metals at $T < T_c$. The authors of [12], using the method of galvanostatic desorption from a polycrystalline Pd electrode in a solution of $H_2SO_4$, established that hydrogen spontaneously accumulates in a surface layer from 160 to 700 Å thick at T = 25°C. Here, the surface concentration of hydrogen exceeds the bulk concentration by a factor of 20-60. If the results obtained in the present study do not completely explain these experiments, they at least agree well with them.

It is evident from the figure that at concentrations on the entry side $c_0 < 0.3$, the largest concentration gradients and, thus, the largest stresses may be seen near the same side. At $c_0 > 0.6$, the largest concentrations and stresses occur near the exit side. Meanwhile, in the last case there are nearly horizontal sections of c(x) in the middle part of the membrane. On these sections, the concentrations are close to the values $c_m$ at which the diffusion coefficient (1) is maximal.

It is interesting to examine the effect of the above-described features of the hydrogen distribution on the diffusion flux j (and, accordingly, hydrogen permeability) through the membrane [1]. Under steady-state conditions (j(x) = const):

$$j = -\frac{D(c)}{\Omega}\frac{dc}{dx} = -\frac{D(0)}{\Omega l\,(dz/dc)_{c=0}}. \tag{8}$$

Taking (4) into account, it is not hard to obtain the formula

$$j = \frac{D(0)\,S(c_0)}{\Omega l}. \tag{9}$$

Figure 2 shows the dependence of the dimensionless quantity $j\Omega\ell/D(0) = S(c_0)$, proportional to the flux, on the entry-side concentration (this dependence can be referred to as the concentration-flux characteristic or CFC). If we ignore the concentration dependence of the diffusion coefficient, we obtain a linear CFC $S9c_0) = c_0$. A linear dependence of the flux on concentration on the entry side $c_0$ (or, with allowance for Sieverts' law $c_0 \sim \sqrt{p_0}$, a linear dependence on $\sqrt{p_0}$ — where $p_0$ is the hydrogen pressure on the entry side of the membrane) is seen experimentally in the region of low concentrations bounded below by the effect of surface phenomena [10] and above by the validity of Sieverts' law in the two-phase region [1, 3, 6]. According to Fig. 2, at $c_0 < c_m \approx 0.65$-$0.70$, allowing for the concentration dependence D(c) with Eq. (1) leads to a reduction in hydrogen permeability compared to the linear case. At $c_0 > c_m$, making such an allowance leads to a sharp increase in hydrogen permeability. For $c_0 < c_m$, with a decrease in temperature the relation $S(c_0)$ becomes increasingly weak and, with the transition past $T_c$, sections with a negative slope appear on it (N-shaped characteristic). At $T \lesssim 300$ K, for values of $c_0$ in a certain neighborhood of $c_0 = 0.25$ it turns out that $S(c_0) < 0$, i.e., at these values of $c_0$ hydrogen does not penetrate the membrane (although there always remains the possibility of diffusion along grain boundaries and other lattice defects — a possibility that is not discussed here).

We were not able to find experimental data in the literature to substantiate or refute the above features of the CFC. This evidently has to do with the difficulty of conducting

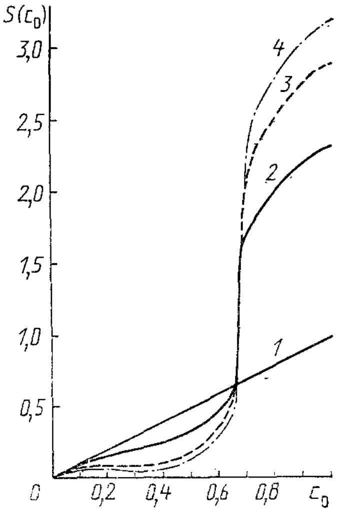

Fig. 2. Concentration-flux characteristics for H in Pd: 1) without allowance for the relation D(c); 2) T = 800 K; 3) 525 K; 4) 450 K.

experiments with high hydrogen concentrations within a broad range of temperatures. Progress in this area might be made by saturating the surface layer of a specimen with hydrogen by an electrochemical method rather than from the gas phase. In analyzing experimental results, it should be kept in mind that the predicted sharp increase (by a factor of 5-10) in the flux with the transition through the value $c_0 \approx c_m$ is due partly not to physical reasons, but to a discontinuity in empirical relation (3) for $\mu_e(c)$ at the point 0.656. This discontinuity causes the derivative $\partial\mu_e/\partial_c$ in the basic formulas to increase suddenly at this point. Thus, it should be expected that the actual increase in the flux with the transition past $c_m$ will be somewhat less than that indicated in Fig. 2, and it may also be more diffuse. Nevertheless, even the qualitative agreement between the experimental CFC's and the theoretical characteristics is indirect proof of the above-predicted (see Fig. 1) features of hydrogen distribution in palladium membranes.

## NOTATION

c(x), hydrogen concentration determined in relation to the number of interstices occupied by hydrogen (for H in Pd, this is equal to the ratio of the number of H atoms to the number of Pd atoms); D(c), coefficient of diffusion of H in Pd; D(0), coefficient of diffusion of H in Pd at $c \to 0$; $\mu_e$, electronic contribution to the chemical potential of the hydrogen subsystem; $\gamma = 0.0147$ eV [7, 8] is a parameter which accounts for the concentration dependence of the frequency of local vibrations of hydrogen atoms; $h\omega_\alpha = 0.066$ eV [3, Vol. 1, p. 100], energy of local vibrations of hydrogen atoms at $c \to 0$; k, Boltzmann constant; T, temperature; $T_c$, critical temperature; w, energy of interaction of a pair of H atoms at adjacent interstices ($w < 0$); $a_1 = 0.06079$ eV; $a_2 = 0.30755$ eV; $a_3 = 1.86118$ eV; $a_4 = 3.60170$ eV; $a_5 = 3.05337$ eV; b = 0.93468 eV; $c_1 = 0.492$ [3, Vol. 2, p. 152]; x, coordinate; $\ell$, thickness of membrane; $z = x/\ell$; $c_0$, hydrogen concentration on the entry side of the membrane; $c_m$, hydrogen concentration at which the diffusion coefficient has a maximum; j, diffusion flux of hydrogen passing through the membrane; Ω, volume occupied by one interstice; CFC, concentration-flux characteristic.

## LITERATURE CITED

1. L. I. Smirnov and V. A. Gol'tsov, Inzh. Fiz. Zh., 55, No. 3, 397-402 (1988).
2. L. I. Smirnov, V. A. Gol'tsov, B. A. Lobanov, and E. V. Ruzin, Fiz. Met. Metalloved., 60, No. 4, 770-775 (1985).
3. G. Alefeld and I. M. Felkley (eds.), Hydrogen in Metals [Russian translation], Moscow (1981).
4. S. Majorowski and B. Baranowski, J. Phys. Chem. Solids, 43, No. 12, 1119-1127 (1982).

5. A. H. Verbruggen, C. W. Hagen, and R. Griessen, J. Phys. F., 14, No. 6, 1431-1444 (1984).
6. V. A. Gol'tsov, V. V. Latyshev, and L. I. Smirnov, Interaction of Hydrogen with Metals [in Russian], Moscow (1987), pp. 105-113.
7. L. I. Smirnov and S. S. Filonenko, Fiz. Met. Metalloved., 67, No. 2, 240-243 (1989).
8. L. I. Smirnov, E. V. Ruzin, and V. A. Gol'tsov, Ukr. Fiz. Zh., 30, No. 9, 1392-1397 (1985).
9. R. Balesku, Equilibrium and Nonequilibrium Statistical Mechanics, Moscow (1978).
10. I. E. Gabis, T. N. Kompaniets, and A. A. Kurdyumov, Interaction of Hydrogen with Metals [in Russian], Moscow (1987), pp. 177-208.
11. M. Strongin, J. Colbert, G. J. Dienes, and D. O. Welch, Phys. Rev. B, 26, No. 6, 2715-2719 (1982).
12. R. V. Bocur, Surface Coat. Technol., 28, No. 3-4, 413-421 (1986).

---

# RADIATION SLIP IN A HIGHLY POROUS MATERIAL LAYER

N. V. Pavlyukevich

UDC 536.3

Expressions are obtained for the coefficient of radiant heat conductivity and the temperature jumps in the radiation slip mode in a highly porous material layer.

The model of a dust-laden gas [1] is often used as the globular model of a porous body in the theory of transport processes in highly porous media. Its crux is that the highly porous body is simulated by a homogeneous system of spherical particles of identical radius r distributed randomly and fixed in space (see sketch).

If the skeleton of such a porous body is opaque, while its material has the emissivity $\varepsilon$, then radiation transport therein can be described on the basis of an integral equation for the radiation energy emanating from unit volume of the porous body per unit time [3]. Assumptions about the homogeneity of the medium and isotropy of the scattering as well as the approximations of a gray body a and the photon mean free path $\Lambda$ were used in deriving this equation. The radiation wavelength should here be much less than both the sphere diameter and the spacing between them.

The quantity $\Lambda$ per unit volume equals [1]

$$\Lambda = \frac{4\Pi}{S} = \frac{4}{3}\frac{\Pi}{1-\Pi} r,$$

where $S = \dfrac{1-\Pi}{\frac{4}{3}\pi r^3} 4\pi r^2 = \dfrac{3(1-\Pi)}{r}$ is the surface of spheres of radius r.

If $\Lambda$ is considerably less than the thickness of the porous layer L ($\ell = L/\Lambda \gg 1$) and the effective heat conductivity of the highly porous material is low and can be neglected then, the radiation energy transfer process can be considered diffusion. Using the approximation of an optically thick layer [4], the radiation transfer should be described by the heat conduction equation with radiant heat conductivity coefficient $\lambda_R$.

We write the expression for the energy flux density of the intrinsic radiation $q_R$ in the section X in the form

$$q_R = 2\pi \int_0^X \int_0^1 S \frac{\sigma T^4(\xi)}{4\pi} \exp\left(-\frac{X-\xi}{\Lambda\mu}\right) d\mu d\xi -$$

---

A. V. Lykov Institute of Heat and Mass Transfer, Belorussian Academy of Sciences, Minsk.
Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 59, No. 4, pp. 606-609, October, 1990. Original article submitted January 11, 1990.

0022-0841/90/5904-1284$12.50