NONLINEAR AND CROSSOVER EFFECTS IN THE DIFFUSION PENETRATION OF HYDROGEN THROUGH A METALLIC MEMBRANE

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The influence is considered of effects due to the nonlinear hydrogen distribution and the interaction of diffusion fluxes of different gas mixture components on the hydrogen permeability of plane metallic membranes.

1. Hydrogen membrane technology (HMT) [1], based on the possibility of obtaining ultrapure hydrogen from gas mixtures by diffusion penetration through metallic membranes has acquired great value in modern engineering. In particular the scales of HMT application in the production of high-quality steels [2] have grown. At present processes of hydrogen penetration have been studied sufficiently extensively ([1-3]; a detailed bibliography of research between 1981-1983 is presented in [4]; out of these later we note [5, 6]), however existing methods of analyzing the penetration process in the diffusion mode are constrained, as a rule, to the case of low hydrogen concentrations when the following two approximations are valid [1, 3]: 1) the assumption about linearity of the stationary hydrogen distribution, and 2) independence of the fluxes of different insertion components from each other is ordinarily assumed in considering hydrogen penetration from gas mixtures. Under these conditions the hydrogen penetration through a membrane (diffusion flux density) is determined by the relationship [1, 3]

$$j_0 = Dc_0/\Omega l \tag{1}$$

which is ordinarily written in the form $P = DL/\ell$ [1, 3], where the hydrogen permeability P can differ from j_0 by a numerical factor while $L \sim c_0$ and is often used to determine the equilibrium solubility L of the hydrogen in the membrane material by means of experimentally established values of P and D.

Meanwhile, as theoretical computations and experimental investigations show, in the general case of arbitrary concentrations the hydrogen distribution over the membrane thickness is substantially nonlinear [7, 8], the effects of mutual influence of their diffusion fluxes [9-11] cannot always be neglected by far during the simultaneous diffusion of several insertion components.

A method of description is elucidated in this paper and the concentration dependence (i.e., the relation with the equilibrium solubility) of the hydrogen permeability is investigated under conditions free of the mentioned constraints. When examining the diffusion of atoms of one component attention is concentrated on the consequences of the nonlinearity of the atom distribution over the membraned, and for the hydrogen diffusion from a gas mixture, on the crossover effects due to the influence of the concentration gradient of the second insertion component on the hydrogen flux. It is assumed that the limiting stage of the penetration process is atom diffusion in the membrane volume. The domain of such temperatures and concentrations is considered when the system is a solid insertion solution. This condition is known to be satisfied in the 500°C temperature range for which industrial filters are exploited to obtain ultrapure hydrogen [2]. It should also be stipulated that the membrane crystal lattice deformations are not taken into account that are associated with the presence of dissolved hydrogen. However, it can be shown [7] that their influence on hydrogen diffusion in the elastic deformation domain reduces mainly to renormalization of the effective interaction energy in (2) but does not alter the form of the expressions utilized below.

2. Let us first examine the rate of hydrogen penetration for arbitrary drops in the concentration (under the mentioned constraint). Membranes based on palladium alloys [1, 2]

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are of greatest practical interest, consequently, we duscuss here the case of hydrogen penetration through a palladium membrane.

The nonlinear distribution of hydrogen over the membrane thickness is due to the dependence of the chemical diffusion coefficient on the concentration, which is in turn associated with the interaction of the diffusing atoms and results in a nonlinear diffusion equation [7]. Correspondingly, the nonlinear effects can be characterized by the deviation of the ratio between the stationary hydrogen flux computed with interatomic interaction j taken into account and the flux j_0 calculated from (1), from one. According to [7], for $c < c_m \approx 0.6$

$$j(x) = -\frac{D}{\Omega}\left[1 + \frac{U}{kT}c\left(1 - \frac{c}{c_m}\right)\right]\frac{dc}{dx}, \tag{2}$$

where $c = c(x)$, $0 \leqq x \leqq \ell$. The following boundary conditions are taken

$$c(0) = c_0 = \text{const}, \ c(l) = 0. \tag{3}$$

We obtain the stationary hydrogen distribution from the condition $j(x) = \text{const}$ or

$$\left[1 - \beta c\left(1 - \frac{c}{c_m}\right)\right]\frac{dc}{dx} = \text{const}. \tag{4}$$

Solving this equation with the boundary conditions (3) we obtain the concentration distribution in the implicit form

$$c - \frac{\beta}{2}c^2 + \frac{\beta}{3c_m}c^3 = g\left(1 - \frac{x}{l}\right), \tag{5}$$

where

$$g = c_0 - \frac{\beta}{2}c_0^2 + \frac{\beta}{3c_m}c_0^3. \tag{6}$$

It follows from (5) that the hydrogen distribution c(x) is nonlinear in the general case $\beta c \neq 0$. Only for $\beta c \to 0$ ($-Uc/kT \to 0$) does the distribution tend to the linear; then $dc/dx = \text{const} = -c_0/\ell$ correspondingly and (2) goes over into (1).

Differentiating (5) and comparing the result with (2), we find

$$\frac{j}{j_0} = \frac{g}{c_0} = 1 - \beta c_0\left(\frac{1}{2} - \frac{c_0}{3c_m}\right). \tag{7}$$

Because the interaction between the H atoms in Pd is of the anture of attraction ($U < 0$, $\beta > 0$) [7, 12] in the concentration domain $c < c_m$, we have $j < j_0$: the H–H interaction results in diminution of the diffusion flux through the membrane. The greatest deviation of j from j_0 occurs for $c_0 = 3c_m/4$, then $(j/j_0)_{\min} = 1 - 0.1125\beta$. Therefore, neglecting the nonlinearity of the distribution c(x), i.e., extension of the relationship (1) to the domain of arbitrary vlaues of Uc_0/kT is not justified.

The results of computing the quantity j/j_0 by means of (7) for different temperatures and concentrations at the input side are presented in the table (the values $U = -0.36$ eV, $c_m = 06.6$ [7, 12] were taken for the parameters). As is seen from the table, the nonlinearity of the hydrogen distribution due to the interaction (attraction) of the H–H atoms substantial retards the rate of its penetration through the membrane; this effect is magnified when the temperature is lowered.* This deduction is evidently valid for not only palladium but also for all hydride-forming metals where the interaction between the hydrogen atoms is of the nature of attraction. In the case of a repulsion interaction of H–H, the situation would be opposite, i.e., there would be $j > j_0$.

3. Let us now examine the case when a mixture of two diatomic gases is delivered to the input side of the membrane, where one of the gases is hydrogen. Here the question of interest is the influence of mixture composition and degree of interstice population at the input side of the membraned on the rate of hydrogen penetration. As is shown in [9-11], in the case of diffusion of two insertion components with arbitrary concentrations cross-

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*The influences of processes on the membrane surface grow when the temperature is lowered; we do not take the influence of these processes into account here.

TABLE 1. Ratio of Hydrogen Fluxes Through a Palladium Membrane j/j_0 Computed with (j) and Without (j_0) Taking Account of Hydrogen Atom Interaction

Degree of interstice population c_0	Temperature, K				
	600	700	800	900	1000
0,01	0,965	0,970	0,974	0,977	0,979
0,05	0,835	0,859	0,877	0,890	0,901
0,1	0,690	0,735	0,768	0,793	0,814
0,2	0,458	0,536	0,594	0,639	0,675
0,3; 0,6	0,304	0,403	0,478	0,536	0,582
0,4; 0,5	0,226	0,337	0,414	0,484	0,532

over effects occur in the sense that the flux of component 1 is determined by the concentration gradients of both atoms of species 1 and species 2

$$j_1 = -\frac{1}{\Omega}\left(D_{11}\frac{dc_1}{dx} + D_{12}\frac{dc_2}{dx}\right). \tag{8}$$

The influence of the mixture second component on the rate of penetration of the first (hydrogen, here) is characterized by the quantity $j_1(c_2)/j_1(0)$. Further computations were executed in an example of diffusion of inserted atoms over the octahedral interstices of a bcc lattice of a metal—solvent [11]; such a diffusion mechanism can apparently be realized in Nb—O—H and Nb—N—H systems where the oxygen or nitrogen atoms located at the octahedral interstices block out the tetrahedral positions surrounding them and the hydrogen is "displaced" to the octahedral interstices of the Nb lattice [12, Vol. 2, p. 383; 13]. We have for the diffusion mechanism mentioned.

$$D_{11} = D_1[c_1 + (1-c)(1-\beta_1 c_1)]f(c_1, c_2, T), \tag{9}$$

$$D_{12} = D_1 c_1[1-\gamma(1-c)]f(c_1, c_2, T). \tag{10}$$

Furthermore, let us idealize the situation and consider that a stationary distribution is successfully established over the membrane for not only the hydrogen but also for the slightly mobile insertion components (N, O, etc.) because of their diffusion. Taking the same boundary conditions as in the preceding section, $c_i(0) = c_{i0}$, $c_i(\ell) = 0$ $(i = 1, 2)$ and taking into account that $j_1(c_2)$ is independent of x in the stationary case, we obtain from (8)-(10)

$$j_1(c_2) = -\frac{D_1}{\Omega}\left(\frac{dc_1}{dx}\right)_{x=l}. \tag{11}$$

In the absence of a second component $j_1(0)$ and taking into account that this quantity corresponds to the flux j in Sec. 2 (see (2)-(7) for $c_m = 1$), we find from (8) and (9)

$$j_1(0) = -\frac{D_1}{\Omega}(1-\beta_1 c_1 + \beta_1 c_1^2)\frac{dc_1}{dx} = \frac{D_1}{\Omega l}\left(c_{10} - \frac{\beta_1}{2}c_{10}^2 + \frac{\beta_1}{3}c_{10}^3\right). \tag{12}$$

Therefore, the influence of the second component of a gas mixture on the rate of hydrogen penetration under the mentioned idealized conditions is described by the expression

$$\frac{j_1(c_2)}{j_1(0)} = -\frac{(dc_1/dz)_{z=1}}{c_{10}\left[1-\beta_1 c_{10}\left(\frac{1}{2}-\frac{c_{10}}{3}\right)\right]}, \tag{13}$$

where the dimensionless coordinate $z = x/\ell$ has been introduced.

The method of calculating the functions $c_1(z)$ and $c_2(z)$ and the respective quantity $(dc_1/dz)_{z=1}$ for arbitrary concentrations when it is impossible to neglect the interaction of the fluxes of components 1 and 2 is presented in [11]. Following the procedure elucidated in [11], we evaluated the values of $j_1(c_2)/j_1(0)$ for different values of the concentration of the second component on the input side of the membrane c_{20} for a given degree of interstice population $c_0 = c_{10} + c_{20}$ under the assumption that $f(c_1, c_2, T) = 1$. The appropriate curves are represented in the figure. It was assumed in the computations that $U_{11} = -0.3$ eV, $U_{12} = -0.5$ eV, which is characteristic for hydrogen (1) and nitrogen or oxygen (2) in niobium [12,

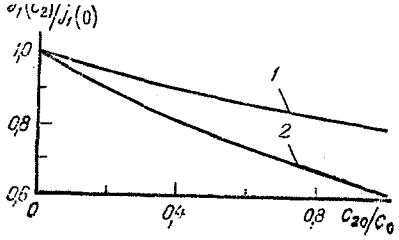

Fig. 1. Dependence of the rate of hydrogen penetration on the relative concentration of the second insertion component: 1) $c_0 = 0.1$; 2) 0.2.

Vol. 2, p. 382]; the value of U_{22} was taken as $U_{22} = -0.3$ eV. The calculations were performed for the temperature T = 800 K. Phase transitions [11] are absent in the system for selected values of the parameters.

It is seen from the figure that the hydrogen flux diminishes monotonically as the fraction of the second component grows at the membrane input, where as the degree of interstice population increases the retarding action of the second component is magnified. These results are qualitatively in agreement with the experimental data [14] obtained for the measurement of the rate of hydrogen penetration through structural materials from nitrogen–hydrogen mixtures.

The case can analogously be considered when a quasistationary distribution of the second component is realized near the input side of the membrane because of its low mobility while the remaining part of the membrane is free of it. Then the hydrogen flux is calculated from (8)-(10) for a given second component distribution. Estimates show that under such conditions the second component atoms act as traps and also diminish the rate of hydrogen penetration.

NOTATION

$c(x)$, hydrogen cocentration determined from the ratio to the quantity of interstices it occupies; c_0, hydrogen concentration at the input side of the membrane; ℓ, membrane thickness; D, hydrogen diffusion coefficient in the membrane material as $c \to 0$; Ω, is the volume per interstice; k, Boltzmann's constant; T, temperature; $\beta = -U/kT$; D_{11} and D_{12}, components of the diffusion coefficient tensor; c_i, concentration of the i-th insertion component (i = 1, 2); $j_1(c_2)$, flux density of the first insertion component in the presence of second component atoms; $c = c_1 + c_2$, probability of occupation of a given interstice by atoms of some component (degree of interstice population); $f(c_1, c_2, T)$, a function whose value is almost one in the domain of c_1, c_2, T, ordinarily under consideration; $z = x/\ell$; U_{ik}, parameters of interaction between atoms of the components i and k; $\beta_1 = -U_{11}/kT$; $\gamma = -U_{12}/kT$.

LITERATURE CITED

1. V. A. Gol'tsov, "Hydrogen in metals," in: Atomic-Hydrogen Power and Technooogy [in Russian], No. 1, 193-230 (1978).
2. V. A. Gol'tsov, A. R. Tochinskii, A. S. Minakov, et al., Scientific-Technological Basis of the Production of Especially Pure Hydrogen by a Diffusion Method (Hydrogen Membrane Technology). Dep. in Chermetinformatsii March 19, 1985, No. 3D/2853 (1985).
3. P. V. Gel'd and R. A. Ryabov, Hydrogen in Metals and Alloys [in Russian], Moscow (1974).
4. V. A. Gol'tsov, L. F. Gol'tsova, R. F. Alimova, and V. A. Garkusheva, Fiz-Khim. Mekh. Metalloved., No. 4, 116-121 (1985).
5. N. I. Ionov, Fiz. Tverd. Tela, 27, No. 9, 2545-2548 (1985).
6. M. A. Krykin and S. F. Timashev, Fiz. Tverd. Tela, 27, No. 8, 2549-2556 (1985).
7. L. I. Smirnov, V. A. Gol'tsov, B. A. Lobanov, and É. V. Ruzin, Fiz. Met. Metalloved., 60, No. 4, 770-775 (1985).
8. M. Strongin, J. Colbert, G. J. Dienes, and D. O. Welch, Phys. Rev. B: Condens. Matter 26, No. 6, 2715-2719 (1982).
9. L. I. Smirnov, V. A. Gol'tsov, and B. A. Lobanov, Fiz. Met. Metalloved., 61, No. 5, 837-844 (1986).
10. Yu. A. Buevich, Inzh.-Fiz. Zh., 50, No. 6, 974-979 (1986).
11. V. A. Gol'tsov and L. I. Smirnov, Fiz. Met. Metalloved., 63, No. 2, 238-244 (1987).
12. G. Alefel'da and I. M. Fel'klya (eds.), Hydrogen in Metals [Russian translation], Moscow (1981).

13. S. I. Morozov, V. V. Sumin, A. V. Belushkin, and I. N. Natkanets, Fiz. Tverd. Tela, 27, No. 9, 2751-2754 (1985).
14. V. I. Pokhmurskii, B. F. Kachmar, and V. V. Fedorov, Fiz.-Khim. Mekh. Materialoved., 18, No. 3, 21-25 (1982).

STATISTICAL CALCULATION OF THE SELF-DIFFUSION COEFFICIENTS OF DISORDERED SUBSTITUTIONAL BINARY SOLID SOLUTIONS

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We obtain and analyze approximate analytical expressions for the self-diffusion coefficients of a disordered substitutional binary solid solution.

A topical problem of the theory remains the microcopic justification for the phenomenological values of the transport coefficients including also the diffusion coefficient. All realistic substances are, in practice, solutions, i.e., to some degree, they must contain impurities. It is known [1, 2] that in this case, the diffusion coefficient is determined by the self-diffusion coefficients of the components. Consequently, the above problem reduces in practice to a statistical calculation of the self-diffusion coefficients.

In disordered substitutional binary solid solutions, the dominant mechanism of the diffusion processes is the monovacancy mechanism [3]. Noting the earlier results concerning self-diffusion in pure crystals with vacancies [4] and the structure of binary solid solution with vacancies [5, 6], this fact makes it possible to construct and realize an algorithm for the required statistical mechanical calculation of the self-diffusion coefficients of the components of the disordered substitutional solid solution. The starting premises of this algorithm are contained in the statistical method of conditional distributions [7] and in the random-walk theory in its statistical interpretation [8, 9].

SELF-DIFFUSION COEFFICIENTS OF A BINARY SYSTEM

For a crystalline binary system which consists of components A and B for the case of isotropic cubic lattice the self-diffusion coefficients are [8]

$$D_L = (1/6)\, k_L R^2 \quad (L = A,\ B), \tag{1}$$

where k_L is the jump frequency of atoms of type L, and R is the length of the jump (the nearest neighbor separation in the lattice). The elementary self-diffusion act in the monovacancy mechanism is a jump of an atom from an occupied site to a neighboring vacant site. This jump requires the overcoming of a potential barrier which is associated with the force field of other atoms. Consequently, the elementary acts of self-diffusion of an atom takes place only if the i-th site is filled, the j-th site is vacant and the atom on site i is activated with a sufficiently high kinetic energy which makes it possible for the atom to leave its site. This situation can be described by the probability density of observing in the neighborhood of site i near a point with coordinates q_i^L an atom of type L with momentum in the interval from p_i^L to $p_i^L + dp_i^L$ in the neighborhood of site i near a point with coordinates $F_{ij}(q_i^L, p_i^L)$ under the condition that the neighboring site j is vacant. We denote this probability density by S_{ij}. The self-diffusion process contains contributions only from atoms which reach the boundary S_{ij} between the unit cells containing the filled and empty sites with a positive projection of the momentum p_{iz}^L onto the z axis which passes through the full and empty sites. Therefore, the jump frequency can be written as

$$k_L = (1/M_L) \sum_{j=1}^{z_1} \int_{-\infty}^{\infty} dp_{ix}^L \int_{-\infty}^{\infty} dp_{iy}^L \int_{0}^{\infty} dp_{iz}^L \int_{S_{ij}} dq_i^L\, p_{iz}^L F_{ij}(q_i^L,\ p_i^L), \tag{2}$$

where M_L is the mass of an atom of type L, and z_1 is the number of nearest neighbors.

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