Journal of Engineering Physics and Thermophysics, Vol. 66, No. 4, 1994

MODEL OF GAS DIFFUSION THROUGH SOLID AND POROUS MEMBRANES OF FINITE THICKNESS

A. V. Melkikh and V. D. Seleznev

UDC 532.6:539.219.3

The authors suggest a cellular model of a gas-permeable membrane with account for surface diffusion of gas molecules on pore walls. The model is compared to experimental data.

The available theoretical models of diffusion of inert gases in polymer membranes are grouped, as a rule, into two classes that differ substantially in their sets of parameters: 1) Knudsen gas diffusion in channels (pores), in particular, with account for migration over the surface of capillaries and 2) gas diffusion in monolithic (nonporous) polymers. However, recently some experimental works have appeared in which the authors succeed in accomplishing a continuous conversion of monolithic films into porous ones and vice versa by stretching polymer films [1]. In order to describe theoretically the gas permeability of such films, it is necessary to construct a model in which both types of migration could enter as limiting ones.

In considering gas diffusion in monolithic films [2] and in channels of perforated membranes [3] emphasis is placed on the role of surface resistances of membranes, which begins to manifest itself in experiments as the film thickness decreases. However, the mechanisms of occurrence of surface resistance in monolithic and porous membranes differ substantially and it is unclear how they may be combined in a single model.

We suggest a cellular model of a porous membrane that takes into account surface diffusion both on the membrane ends and on pore walls. We also consider a layered model of migration of a gas in a monolithic film. Analysis of the expressions obtained for gas permeability makes it possible to find conditions under which these models produce consistent results.

We consider diffusion in a monolithic membrane representing a single-crystal infinite plate with thickness L.

As is known from experiments and theoretical studies [4], near the surface of a solid the lattice constant decreases, thus causing a change in the heat of dissolution of atoms and their diffusional barriers near the surface. As a rule, only the first layer becomes distorted, and the distortion of the other layers may be neglected. In this case, the potential of interaction of gas atoms with a solid may be represented in the form shown in Fig. 1 (variations in the interaction energy in the plane of the layers are ignored).

The model potential of the membrane (Fig. 1) may be used for any number of layers, including a monolayer.

To simplify consideration of the balance of particles in each potential well (in the i-th layer), we make the following assumptions: the probability of gas adsorption on the surface is equal to 1; the flux of atoms incident on the membrane has a Maxwellian distribution; the time of particle thermalization in each potential well is much shorter than the time of particle residence in it, which permits us to consider distribution of particle in each layer to be equilibrium (the Boltzmann one); the degree of filling of any layer is much less than unity.

Then the system of equations of the layer-by-layer balance of particles may be written as

$$\frac{1}{4} n_a v_t + \frac{1}{4} n_1 v_t \exp\left(-\frac{E_{g1}}{kT}\right) = \frac{1}{4} n_0 v_t \left[\exp\left(-\frac{U_1}{kT}\right) + \exp\left(\frac{Q - E_{g1} - U_1}{kT}\right)\right],$$

$$\frac{1}{4} n_0 v_t \exp\left(\frac{Q - E_{g1} - U_1}{kT}\right) + \frac{1}{4} n_2 v_t \exp\left(-\frac{E}{kT}\right) = \frac{1}{4} n_1 v_t \left[\exp\left(-\frac{E_{g1}}{kT}\right) + \exp\left(-\frac{E}{kT}\right)\right], \quad (1)$$

Ural Polytechnic Institute, Ekaterinburg, Russia. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 66, No. 4, pp. 467-474, April, 1994. Original article submitted March 2, 1992.

1062-0125/94/6604-0412$12.50

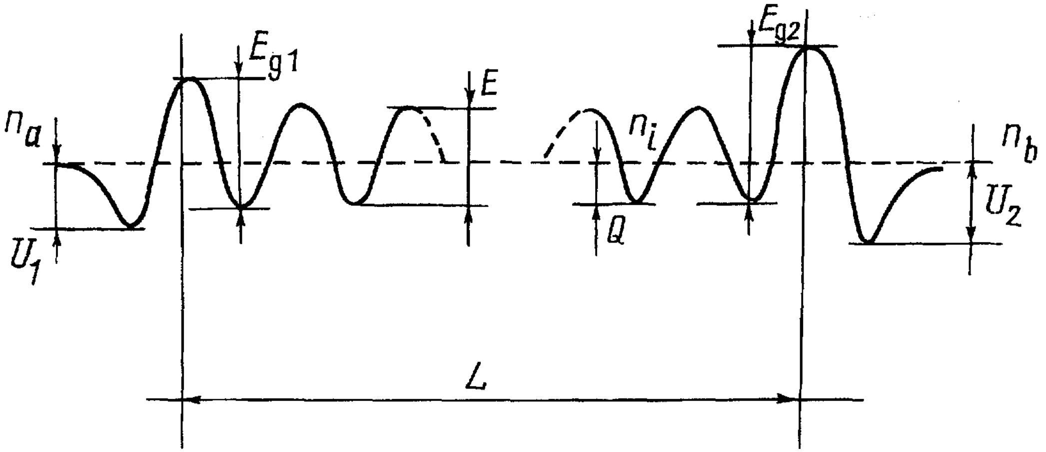

Fig. 1.

. . . .

$$\frac{1}{4}n_b\nu_t + \frac{1}{4}n_{l-1}\nu_t\exp\left(-\frac{E_{g2}}{kT}\right) = \frac{1}{4}n_l\nu_t\left[\exp\left(-\frac{U_2}{kT}\right) + \exp\left(\frac{Q - E_{g2} - U_2}{kT}\right)\right],$$

where l is the number of membrane layers, $l = L/\delta$; δ is the lattice spacing. Each term in system (1) represents the number of particles coming into each potential well per unit area per unit time (the left-hand side of the equations) or leaving it (the right-hand side).

Solving system (1), we obtain for the flux of gas particles per unit area of the membrane

$$j = \frac{1}{4}\nu_t(n_a - n_b) \times \frac{1}{2 + l\exp\left(\frac{E - Q}{kT}\right) + 2\left[\exp\left(\frac{E_g - Q}{kT}\right) - \exp\left(\frac{E - Q}{kT}\right)\right]}. \tag{2}$$

In ref. [2], an analogous (to (2)) formula for the flux through a membrane is obtained, which under the assumptions made and in the notation adopted may be written as

$$j = \frac{1}{4}\nu_t(n_a - n_b)\frac{1}{2 + l\exp\left(\frac{E - Q}{kT}\right) + \alpha_0 + \alpha_l}, \tag{3}$$

where α_0 and α_l are the surface resistances of the membrane. A comparison of (2) and (3) yields

$$\alpha_0 + \alpha_l = 2\left[\exp\left(\frac{E_g - Q}{kT}\right) - \exp\left(\frac{E - Q}{kT}\right)\right].$$

When the surfaces are the same ($\alpha_0 = \alpha_l$):

$$\alpha = \exp\left(\frac{E_g - Q}{kT}\right) - \exp\left(\frac{E - Q}{kT}\right). \tag{4}$$

From the physical meaning of formula (2) it follows that $\exp(E - Q/kT)$ is the resistance of one layer inside the membrane, $\exp(E_g - Q/kT)$ is the resistance of a surface layer. Therefore the term "surface resistance" for α_i is inappropriate since it is a resistance difference between a surface layer and a layer inside the membrane.

Consequently, it is better to rewrite formula (2) in the form

$$j = \frac{1}{4}\nu_t(n_a - n_b)\frac{1}{2\left[1 + \exp\left(\frac{E_g - Q}{kT}\right)\right] + (l - 2)\exp\left(\frac{E - Q}{kT}\right)}. \tag{5}$$

Then in the first brackets the denominator will contain the resistance of an adsorption layer exp $(U - U/kT) = 1$ and of a surface layer exp $(E_g - Q/kT)$, while the second summand pertains to the volume resistance of the membrane.

When the fields are not distorted near the surface ($E_g = E$), we have from (5)

$$j = \frac{1}{4} v_t (n_a - n_b) \frac{1}{2 + l \exp\left(\frac{E - Q}{kT}\right)} . \tag{6}$$

If l exp $(E - Q/kT) << 1$, i.e., the volume resistance of the membrane is much lower than the resistance of adsorption layers, we may obtain a flow through the membrane that is maximum under the given conditions, independent of its thickness, and equal to

$$j_m = \frac{1}{4} v_t \frac{n_a - n_b}{2} \tag{7}$$

We may suggest one more approach to determining the flow through a solid membrane. This approach involves solving of the equation of diffusion inside the membrane. Surface layers are considered as before.

The equation of diffusion inside the membrane is [5]

$$\partial^2 n / \partial x^2 = 0 . \tag{8}$$

Its solution is the function

$$n(x) = a_0 + a_1 x ,$$

where a_0, a_1 are unknown coefficients.

For adsorption layers, we consider the Langmuir mode of adsorption, i.e., we assume that there is a maximum value n_m of n on the surface.

Taking into consideration the boundary conditions at the boundary of the membrane volume and a surface layer (equality of flows and of chemical potentials), we arrive at the system of equations

$$\begin{gathered}
(1 - n_0/n_m) \left[\frac{1}{4} n_a v_t + \frac{1}{4} n_1 v_t \exp\left(- \frac{E_{g1}}{kT} \right) \right] = \\
= \frac{1}{4} n_0 v_t \left[\exp\left(- \frac{U_1}{kT} \right) + \exp\left(\frac{- Q + E_{g1} + U_1}{kT} \right) \right] , \\
\frac{1}{4} n_0 v_t \exp\left(\frac{- Q + E_{g1} + U_1}{kT} \right) = \frac{1}{4} n_1 v_t \exp\left(- \frac{E_{g1}}{kT} \right) (1 - n_0/n_m) - a_1 D , \\
n_1 = a_0 + a_1 \delta , \\
\frac{1}{4} n_l v_t \exp\left(- \frac{U_2 - E_{g2} - Q}{kT} \right) = \frac{1}{4} v_t n_{l-1} \exp\left(- \frac{E_{g2}}{kT} \right) (1 - n_l/n_m) + a_1 D , \\
n_{l-1} = a_0 + a_1 (L - \delta) , \\
(1 - n_l/n_m) \left[\frac{1}{4} n_b v_t + \frac{1}{4} n_{l-1} v_t \exp\left(- \frac{E_{g2}}{kT} \right) \right] = \\
= \frac{1}{4} n_l v_t \left[\exp\left(- \frac{U_2}{kT} \right) + \exp\left(- \frac{U_2 - E_{g2} + Q}{kT} \right) \right] ,
\end{gathered} \tag{9}$$

where D is the volume diffusion coefficient of the gas in the membrane volume.

Solving system (9), we obtain for the flow

$$j = \frac{1}{4} \nu_t (n_a - n_b) \left\{ 2 + \frac{1}{4} \frac{l \nu_t \delta}{D} \exp\left(-\frac{Q}{kT} \right) + 2 \left[\exp\left(\frac{E_g - Q}{kT} \right) - \right.\right.$$

$$\left. - \exp\left(\frac{E - Q}{kT} \right) \right] + \frac{n_a + n_b}{n_m} \exp\left(\frac{U}{kT} \right) + \left[\frac{l \nu_t \delta}{4D} \exp\left(-\frac{Q}{kT} \right) + \right.$$

$$\left.\left. + 2 \exp\left(\frac{E_g - Q}{kT} \right) - 2 \exp\left(\frac{E - Q}{kT} \right) \right] \left[\frac{n_a + n_b}{n_m} \exp\left(\frac{U}{kT} \right) + \frac{n_a n_b}{kT} \exp\left(\frac{2U}{kT} \right) \right] \right\}^{-1}. \tag{10}$$

An expression for the diffusion coefficient for models similar to ours is well-known in the literature [5]:

$$D = \frac{\delta^2}{2\tau_0} \exp\left(-\frac{E}{kT} \right), \tag{11}$$

where τ_0 is the oscillation period of a diffusing particle. For our model, $2\delta/\tau_0 = \nu$, and therefore

$$\frac{1}{4} \frac{l \nu_t \delta}{D} = l \exp\left(\frac{E}{kT} \right).$$

Substituting this expression into (10), we obtain

$$j = \frac{1}{4} \nu_t (n_a - n_b) \left\{ 2 + l \exp\left(\frac{E - Q}{kT} \right) + 2 \left[\exp\left(\frac{E_g - Q}{kT} \right) - \right.\right.$$

$$\left. - \exp\left(\frac{E - Q}{kT} \right) \right] + \frac{n_a + n_b}{n_m} \exp\left(\frac{U}{kT} \right) + \left[l \exp\left(\frac{E - Q}{kT} \right) + \right.$$

$$\left. + 2 \exp\left(\frac{E_g - Q}{kT} \right) - 2 \exp\left(\frac{E - Q}{kT} \right) \right] \times$$

$$\left. \times \left[\frac{n_a + n_b}{n_m} \exp\left(\frac{U}{kT} \right) + \frac{n_a n_b}{n_m^2} \exp\left(\frac{2U}{kT} \right) \right] \right\}^{-1}.$$

If $n_a/n_m \exp(U/kT) \ll 1$ (i.e., in the case of slight filling of the surface), we obtain

$$j = \frac{1}{4} \nu_t (n_a - n_b) \times \frac{1}{2 + l \exp\left(\frac{E - Q}{kT} \right) + 2 \left[\exp\left(\frac{E_g - Q}{kT} \right) - \exp\left(\frac{E - Q}{kT} \right) \right]},$$

which coincides completely with (2).

Thus, it may be considered that when the particles are in local equilibrium in each potential well (the time of their thermalization is much shorter than that of their residence in a potential well) both approaches yield the same result. This was to be expected since diffusion equation (8) may be obtained from consideration of random migration of particles in the system of potential wells (Fig. 1).

If local equilibrium does not exist at distances of the order of the dimensions of a well, then a kinetic examination of this system with use of the velocity distribution function of the gas atoms is needed.

In order to illustrate how the above models work and to show the influence of surface defects on the gas flow through a monolithic membrane, we consider the experiment described in [2].

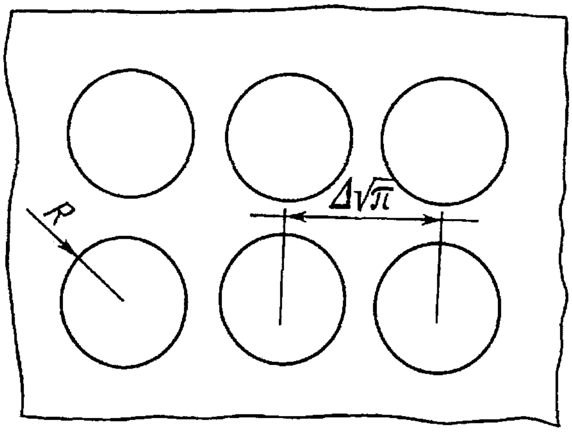

Fig. 2.

TABLE 1. Results of Processing of Experimental Data in [2]

Quantity	Gas		
	O_2	N_2	CO_2
$\sigma_{ef}\cdot 10^5$ mole/(m$^3\cdot$Pa)	19	12	225
$\alpha_0+\alpha_l$	$4\cdot 10^6$	$7\cdot 10^6$	$3\cdot 10^5$
$D\cdot 10^{10}$ m^2/sec	1.9	1.8	1.6

TABLE 2. Parameters of Gas Diffusion in a Membrane

Quantity (kcal/mole)	Gas		
	O_2	N_2	CO_2
Q	-0.46	-0.73	1.00
E	3.07	3.14	3.08
E_g-Q	8.64	8.97	7.09
$E-Q$	3.53	3.87	2.07

In the experiment, the permeability of a polymer membrane was measured for different gases. The membrane was made of polyarylensulfonoxide-polydimethylsiloxane block copolymer (PSS). In [2], processing of the experimental data yielded $\alpha_0 + \alpha_l$, the effective dissolution σ_{ef}, and the diffusion coefficients D for different gases (Table 1). In our model

$$\sigma_{ef} = \frac{1}{RT} \exp\left(\frac{Q}{kT}\right), \tag{12}$$

$$D = \frac{1}{4} \nu_t \delta \exp\left(-\frac{E}{kT}\right). \tag{13}$$

Assuming δ (the length of the jump of a molecule) to be equal to approximately 3 Å, we may determine E and Q for different gases by formulas (12) and (13). Moreover, using (4) we may find $E_g - Q$, which characterizes the surface resistance of the polymer for different gases. This surface resistance may be associated both with a decrease in the lattice constant [4] and with polymer inhomogeneity. Calculation results are listed in Table 2.

The experimental data show that even for sufficiently high l the influence of surface resistances may be significant at high E_g.

We now consider gas diffusion in a perforated membrane with account for surface migration of atoms on the membrane ends and the channel walls (Fig. 2). In the cellular model, a membrane of thickness L is permeated with channels of diameter $2R$ so that the mean distance ($\Delta\sqrt{\pi}$) between the centers of neighboring channels is the same.

Since all the cells are assumed to be the same, we consider a single cell, instead of the whole membrane, with the corresponding conditions at its boundary. For simplicity we substitute a circular cell with radius Δ for the square cell.

Next, we write a system of surface diffusion equations for a single cell:

$$-D_1\,\Delta\sigma_1 = \kappa_1 - \frac{\sigma_1}{\tau_1}, \quad -D_2\,\Delta\sigma_2 = 0, \quad -D_3\,\Delta\sigma_3 = \kappa_3 - \frac{\sigma_3}{\tau_3}, \tag{14}$$

where σ_i is the surface density of particles; τ_i is the lifetime of a particle on the surface; $\kappa_i = p_i/\sqrt{2\pi mkT}$ is the number of gas particles incident on unit area of the membrane end in one second.

The first equation in system (14) pertains to the left-hand end face, the second equation is for channel walls, and the third equation pertains to the right-hand end face. We assume that σ_i is much less than the maximum density on the surface σ_m.

The boundary conditions for this system are as follows:

$$\left.\frac{\partial\sigma_1}{\partial r}\right|_{r=\Delta} = 0; \quad \left.\frac{\partial\sigma_3}{\partial r}\right|_{r=\Delta} = 0, \quad \mu_1|_{r=R} = \mu_2|_{x=0}; \quad \mu_3|_{r=R} = \mu_2|_{x=L},$$

$$D_1\left.\frac{\partial\sigma_1}{\partial r}\right|_{r=R} = D_2\left.\frac{\partial\sigma_2}{\partial x}\right|_{x=0}; \quad -D_3\left.\frac{\partial\sigma_3}{\partial r}\right|_{r=R} = D_2\left.\frac{\partial\sigma_2}{\partial x}\right|_{x=L}, \tag{15}$$

where $\mu_i = U_i + kT\ln\sigma_i$ and U_i are the chemical potential and the heat of adsorption of gas atoms on the surface.

The solution of the diffusion equation of system (14) in cylindrical coordinates is

$$\sigma_i(r) = C_{1i}K_0\left(\frac{r}{\sqrt{D_i\tau_i}}\right) + C_{2i}I_0\left(\frac{r}{\sqrt{D_i\tau_i}}\right),$$

where $i = 1, 2$ is the left-hand and right-hand end; K_0, I_0 are Bessel functions.

Solving system (14) with boundary conditions (15), we arrive at an expression for the density of particle flow through the membrane:

$$j = (\kappa_1 - \kappa_3)\frac{D_2\tau_2}{\Delta^2} \times \left\{ \frac{L}{2R} + \frac{\sqrt{D_1\tau_1}}{2R}\,\frac{D_2}{D_1}\,\frac{I_0\left(\frac{R}{\sqrt{D_1\tau_1}}\right) - I_1\left(\frac{\Delta}{\sqrt{D_1\tau_1}}\right)\frac{K_0(R/\sqrt{D_1\tau_1})}{K_1(\Delta/\sqrt{D_1\tau_1})}}{I_1\left(\frac{R}{\sqrt{D_1\tau_1}}\right) - I_1\left(\frac{\Delta}{\sqrt{D_1\tau_1}}\right)\frac{K_1(R/\sqrt{D_1\tau_1})}{K_1(\Delta/\sqrt{D_1\tau_1})}} + \right.$$

$$\left. + \frac{\sqrt{D_3\tau_3}}{2R}\,\frac{D_2}{D_3}\,\frac{I_0\left(\frac{R}{\sqrt{D_3\tau_3}}\right) - I_1\left(\frac{\Delta}{\sqrt{D_3\tau_3}}\right)\frac{K_0(R/\sqrt{D_3\tau_3})}{K_1(\Delta/\sqrt{D_3\tau_3})}}{I_1\left(\frac{R}{\sqrt{D_3\tau_3}}\right) - I_1\left(\frac{\Delta}{\sqrt{D_3\tau_3}}\right)\frac{K_0(R/\sqrt{D_3\tau_3})}{K_1(\Delta/\sqrt{D_3\tau_3})}} \right\}^{-1} + \frac{J_\mathrm{v}}{\pi\Delta^2}, \tag{16}$$

where J_v is the volume flow of particles through a channel.

The first summand in (16) characterizes the flux density due to surface diffusion, and the second summand due to volume diffusion. We consider the case where the volume flow may be neglected compared to the surface flow. It may be inferred from expression (16) that the terms standing after $L/(2R)$ are responsible for the influence of the end faces on the flow. Apparently, they may be interpreted as the surface resistances of the end faces. Without loss of generality, it may be considered that $D_1 = D_3$ and $\tau_1 = \tau_3$ since the expressions responsible for the contribution of both ends are summands (their contributions are additive). In the case where the ends are the same, we have

$$j = (\kappa_1 - \kappa_3)\,(D_2\tau_2/\Delta^2) \times \left\{ \frac{L}{2R} + \frac{\sqrt{D\tau}}{R}\,\frac{D_2}{D}\, \frac{I_0\left(\frac{R}{\sqrt{D\tau}}\right) - I_1\left(\frac{\Delta}{\sqrt{D\tau}}\right)\frac{K_0(R/\sqrt{D\tau})}{K_1(\Delta/\sqrt{D\tau})}}{I_1\left(\frac{R}{\sqrt{D\tau}}\right) - I_1\left(\frac{\Delta}{\sqrt{D\tau}}\right)\frac{K_1(R/\sqrt{D\tau})}{K_1(\Delta/\sqrt{D\tau})}} \right\}^{-1} \tag{17}$$

We now consider two limiting cases of expression (17).

1. The migration length of atoms on the end faces is much less than the cell dimension $\sqrt{D\tau} \ll \Delta$, i.e., the channels are independent of each other and between them there is a large undisturbed region with a uniform surface density. In this case

$$j = (\kappa_1 - \kappa_3)\, \frac{D_2\tau_2/\Delta^2}{\frac{L}{2R} + \frac{\sqrt{D\tau}}{R}\,\frac{D_2}{D}\,\frac{K_0(R/\sqrt{D\tau})}{K_1(R/\sqrt{D\tau})}} = \frac{1}{\pi\Delta^2} J_k,$$

where J_k is the flow through one channel in the membrane, provided no other channels exist.

An account for the migration of atoms on the end faces of the membrane leads to a small correction for the channel length in this case.

2. The migration length of atoms on the end faces is much larger than the cell dimension $\sqrt{D\tau} \gg \Delta$:

$$j = (\kappa_1 - \kappa_3)\, \frac{D_2\tau_2/\Delta^2}{\frac{L}{2R} + 2\frac{D_2\tau_2}{\Delta^2}\,\frac{1}{1 - R^2/\Delta^2}}. \tag{18}$$

If we take into account that the membrane accumulates all molecules, including those incident on the channel wells, then R^2/Δ^2 disappears in the denominator. For $R \ll \Delta$, we obtain that the flow through the membrane is the maximum possible in the limit $D_2\tau_2/\Delta^2 \gg L/(2R)$:

$$j = \frac{1}{4} v_t (n_a - n_b) \frac{1}{2},$$

which coincides with the analogous limit for a solid membrane (7).

If we take expression (11) for D_2 and $R \ll D$ in (18), then we arrive at

$$j = \frac{1}{4} v_t (n_a - n_b)\, \frac{1}{2 + \frac{2\Delta^2}{\delta^2} \exp\left(\frac{E - Q}{kT}\right) \frac{L}{2R}}. \tag{19}$$

It is easy to see that formulas (6) and (19) are analogous.

Passage in the limit from a porous to a solid membrane may be performed by taking the cell radius and the pore diameter equal to the lattice spacing and half the lattice spacing, respectively, i.e., $2\Delta = \delta$ and $4R = \delta$. In this case, formulas (6) and (19) coincide completely.

To perform a rigorous passage in the limit without loss of any information, it is necessary to have a unified membrane model that includes the models discussed above as limiting cases. Such a model must be based on the particle distribution functions inside the channels, on the surface of the membrane, and inside it.

NOTATION

L, membrane thickness; U, heat of gas adsorption; Q, heat of gas dissolution in the membrane; E, activation energy of diffusion; E_g, activation energy of diffusion in a near-surface layer; n_a, n_b, n_i, numerical density of gas particles on the both sides of the membrane and in the i-th layer, respectively; v, mean thermal velocity of molecules; l, number of membrane layers; δ, lattice spacing; γ, particle flow density in the membrane; α_0, α_l, surface resistance of the membrane; n_m, maximum gas density on the surface; D, gas diffusion coefficient in the membrane; τ_0, oscillation period of a particle in a potential well; σ_{ef}, effective gas solubility in the membrane; Δ, distance between the centers of neighboring channels; R, channel radius; σ, surface density of particles; τ, particle lifetime on the surface; p, gas pressure; μ, chemical potential of gas atoms; K_0, I_0, Bessel functions; J_v, volume gas flow through a channel; k, Boltzmann constant; T, gas temperature; n_0, n_l, numerical densities of gas particles on the left- and right-hand surfaces of the membrane.

REFERENCES

1. A. Peterlin, Polymer Eng. Sci., **16**, No. 3, 126 (1976).
2. A. A. Ovchinnikov, S. K. Timashev, and A. A. Belyi, Kinetics of Diffusion-Controllable Chemical Processes [in Russian], Moscow (1986).
3. V. V. Ovchinnikov, V. I. Kuznetsov, B. T. Porodnov, et. al., Kolloidn. Zh., **1**, No. 1, 64-69 (1988).
4. A. G. Kotov and V. V. Gromov, Radiation Physics and Chemistry of Heterogeneous Systems [in Russian], Moscow (1988).
5. N. N. Nikolaev, Diffusion in Membranes]in Russian], Moscow (1980).