By transforming the results obtained to the processes of structuring capillary-porous materials, it can be concluded that the magnitude of the internal pressure developing during the vaporization of moisture from these materials is dependent on the mobility of the disperse particles (i.e., on the degree of dispersion and, consequently, on the coefficient of shrinkage) and, to a lesser extent, on the intensity of moisture vaporization from the material.

NOTATION

L_σ, capillary (Laplace) pressure, N/m^2; σ, surface tension, N/m; a, width of gap between plates, m; b, diameter of fluid drop held between plates, m; E, modulus of elasticity of membrane material, N/m^2; γ, Poisson coefficient of membrane material; t, temperature in thermohygrostat chamber, °C; φ, relative moisture content of air, %; δ, membrane thickness, m; $W_{(0,0)}$, deflection of center of membrane, m; c, eccentricity of fluid drop relative to membrane, m; d, diameter of membrane, m; j_Σ, intensity of moisture vaporization from slit, kg/m^2·sec; ΔV, increase in drop volume, m^3; S, surface of vaporization of moisture from slit, m^2; τ, duration of process, sec; j_0, intensity of vaporization from free surface of water, kg/m^2·sec; S_0, vaporization surface, m^2.

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FORMATION ON SOLID SURFACES OF A GAS MONOLAYER PROVIDING PROTECTION AGAINST FRICTION IN RAREFIED MEDIA

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UDC 531.43

The dynamics of formation of a monomolecular gas layer on an exposed surface are analyzed on the basis of a solution of the kinetic adsorption equation, with allowance for adsorption, desorption, and the migration of molecules to the free parts of the surface under equilibrium external conditions.

It is known [2, 3] that gas films adsorbed on the surface of rubbing bodies have an important influence on the variation of the friction and wear characteristics. This effect is especially significant in connection with studies of friction processes in a high vacuum, where the use of liquid lubricants and greases is impossible owing to their evaporability. Adsorbed gas films protect the surfaces from "juvenile" contact, thus reducing

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Leningrad Mechanics Institute. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 31, No. 6, pp. 1039-1046, December, 1976. Original article submitted July 23, 1975.

TABLE 1. Depth of Potential Well in the Gas Molecule—Surface Interaction [10]

Gas	H_2	He	CH_4	Ne	N_2	O_2	Ar	CO_2	Kr	Xe
$U \cdot 10^{21}$, J	11,0	1,0	20,3	3,06	11,7	15,3	16,7	41,1	29,3	47,9

the possibility of surface failure. The formation on the friction surface of a gas layer one molecule thick (monolayer) is sufficient to produce qualitative changes in the dry friction process. Hence the importance of studying the process of formation of a protective gas monolayer on friction surfaces in rarefied media and determining the duration of the process.

Let us consider the covering of an exposed surface by an initial layer (monolayer) of gas molecules. The deposition of the molecules on the surface and the rate of formation of the monolayer are determined by the flow regime and the internal state of the gas and by the surface—molecule interaction conditions [9]. On making contact with the surface the gas molecule enters the zone of forces of attraction. If the initial kinetic energy of the molecule is small, it is captured by the surface, and its energy is dissipated into the lattice as vibrational motion. If the initial energy is large, the molecule rebounds and leaves the surface.

If we take as the initial moment of time the deposition of molecules on an absolutely juvenile surface, then for determining the number of molecules adsorbed by the flat surface it is possible to propose [6] the equation

$$\theta(\vec{r}, t) = \int_0^t \{[1 - \sigma\theta(\vec{r}, \tau)][1 - \xi_D(T_w, f, \theta, t, \tau)] \iiint_{u_n<0} |u_n| f(\vec{u}, \vec{r})\, \xi_A(T_w, \vec{u}, \theta)\, du_x du_y du_z\}\, d\tau. \tag{1}$$

The quantity σ in (1) is defined as the surface area occupied by a single molecule, or $\sigma = 1/\nu_0$, where ν_0 [2] is the maximum possible number of molecules in the monolayer per unit area. Thus, $1-\sigma\theta(\vec{r}, \tau)$ is the probability of a gas molecule striking the free part of the surface.

If we neglect the dependence of the adsorption probability ξ_A on the velocity vector $\vec{u}$ of the molecules impinging on the surface, which is valid for thermal molecule velocities, then the triple integral in (1) is the mathematical expectation of the number of molecules striking an element of the surface in unit time:

$$\nu = \iiint_{u_n<0} |u_n| f(\vec{u}, \vec{r})\, du_x du_y du_z. \tag{2}$$

Since for Maxwellian molecules the distribution function does not depend on the coordinate [1], Eq. (2) simplifies to

$$\nu = \frac{p}{k} \sqrt{\frac{R}{2\pi\mu T_g}}\, \frac{1}{\text{м}^2 \cdot \text{sec}}\,. \tag{3}$$

With allowance for (3), the kinetic equation of the adsorption layer (1) reduces to

$$\theta(t) = \nu \int_0^t [1 - \sigma\theta(\tau)][1 - \xi_D(T_w, \theta, t, \tau)]\, \xi_A(T_w, \theta)\, d\tau. \tag{4}$$

As a result of energy transfer between the molecule and the lattice (at high surface temperatures) even an adsorbed molecule may acquire sufficient energy to leave the surface (so-called "spontaneous desorption"). To determine the desorption probability ξ_D we use the Frenkel' model [7]:

$$\xi_D = 1 - \exp[1 - \psi(t - \tau)]. \tag{5}$$

The spontaneous desorption coefficient [8]

$$\psi = \tau_0^{-1} \exp\left(-\frac{Q}{kT_w}\right), \tag{6}$$

where, for calculation purposes, the finding energy Q can be taken on the range $(1.5\text{-}3.0) \cdot 10^{-19}$ J; τ_0 is a quantity of the same order as the period of the normal vibrations of the adsorbed atoms (10^{-12}-10^{-13} sec).

Monolayer adsorption is a consequence of: direct impingement of a molecule on the clean part of the surface and impingement of a molecule as a result of ricochet collisions or as a result of migration to the exposed parts of the surface after adsorption in the second layer.

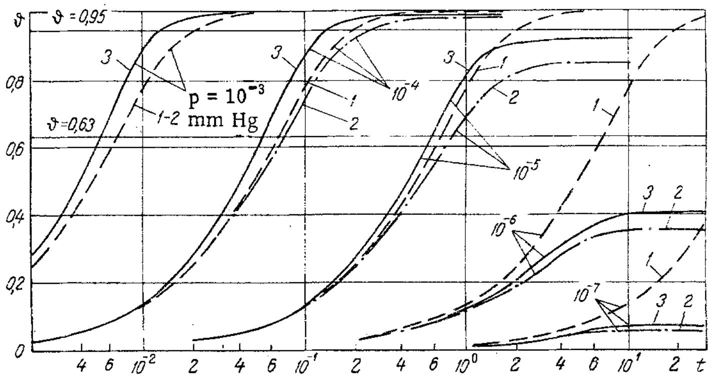

Fig. 1. Effect of desorption and migration processes on the extent and time of deposition of gas molecules (μ = 28 g/mole) on a solid surface (t_w = 460°C; m = 56 g/mole) at various gas pressures (T_g = 293°K): 1) ϑ from Eq. (15); 2) from Eq. (16); 3) from Eq. (12). t, sec.

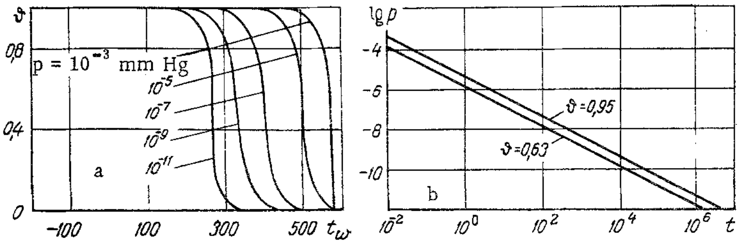

Fig. 2. Effect of gas pressure (T_g = 293°K, μ = 28 g/mole) on the extent of monolayer formation on a solid surface (m = 56 g/mole): a) as a function of surface temperature t_w, °C; b) as a function of time (t_w = 20°C). t, sec; p, mm Hg.

The last two processes involve interaction with previously adsorbed molecules. At thermal molecule velocities and relatively low surface temperatures the probability of adsorption on unoccupied parts of the surface is given [6] by

$$\xi_A = \frac{\xi_1}{1 - \beta\sigma\theta}\,. \tag{7}$$

The probability of a molecule reaching the free part of the surface after adsorption on the occupied part and subsequent migration is given by

$$\beta = \frac{1}{1 + \exp\left(-\dfrac{q^2 - q_1}{kT_m}\right)}\,, \tag{8}$$

where $q_2 - q_1$ is the difference between the intermolecular binding energy q_2 and the migration energy $q_1 \simeq 3.23 \cdot 10^{-21}$ J.

The migration probability β is close to unity at low temperatures and at high temperatures tends to 0.5.

The maximum possible probability ξ_1 of a molecule being captured on the clean part of the surface can be determined starting from the potential well model [10]:

$$\xi_1 = 1 - \exp\left[-\frac{2.4\mu^*}{1 - 0.4\mu^* + \mu^{*2}}\left(\frac{U}{k} - T_w\right)\frac{1}{T_g}\right], \tag{9}$$

where μ^* is the ratio of the mass of the gas particles to the mass of a surface atom or $\mu^* = \mu/m$.

Values of U for the molecules of several gases are given in Table 1.

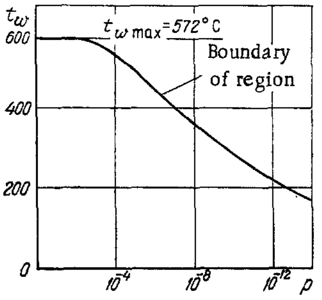

Fig. 3

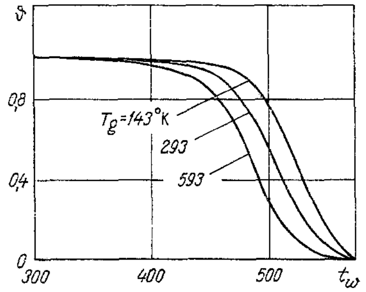

Fig. 4

Fig. 3. Region of formation of a gas monolayer ($T_g = 293$°K) with antifriction properties. $\vartheta > 0.63$. t_W, °C; p, mm Hg.

Fig. 4. Extent of gas monolayer formation as a function of the temperature of the surface and of the medium ($p = 10^{-5}$ mm Hg).

With our previous assumptions and the adsorption and desorption laws derived above, the kinetic equation of the monolayer (4) reduces to the integral equation

$$\theta(t) = \nu\xi_1 \int_{t_0}^{t} \frac{1 - \sigma\theta(\tau)}{1 - \beta\sigma\theta(\tau)} \exp(-\psi t + \psi\tau)\, d\tau + \theta_0 \exp[-\psi(t - t_0)]. \tag{10}$$

Introducing the variable $\vartheta(t) = \sigma\theta(t)$, the relative surface covered by the gas monolayer, and eliminating the integral from (10) and the expression obtained by differentiating it, we reduce (10) to the differential equation

$$\frac{d\vartheta}{dt} = \nu\xi_1\sigma \frac{1 - \vartheta}{1 - \beta\vartheta} - \psi\vartheta \tag{11}$$

with the initial condition: $\vartheta = 0$ at $t = t_0 = 0$.

Equation (11) is an equation with separable variables

$$\int_0^{\vartheta} \frac{(1 - \beta\vartheta)\, d\vartheta}{\nu\xi_1\sigma - (\nu\xi_1\sigma + \psi)\vartheta + \beta\psi\vartheta^2} = t. \tag{12}$$

Evaluating the integral, we obtain the solution of (11) in the form

$$\left(\frac{\vartheta - \vartheta_1}{-\vartheta_1}\right)^{\frac{\vartheta_1}{2\psi} - 1} \left(\frac{\vartheta - \vartheta_2}{-\vartheta_2}\right)^{1 - \frac{\vartheta_2}{2\psi}} = \exp\left(-t\sqrt{(\nu\xi_1\sigma + \psi)^2 - 4\beta\psi\nu\xi_1\sigma}\right) \tag{13}$$

when $\psi \neq 0$, where

$$\vartheta_{1,2} = \frac{(\nu\xi_1\sigma + \psi) \pm \sqrt{(\nu\xi_1\sigma + \psi)^2 - 4\beta\psi\nu\xi_1\sigma}}{2\beta\psi},$$

or in the form

$$t = -\frac{1 - \beta}{\nu\xi_1\sigma} \ln(1 - \vartheta) + \frac{\beta}{\nu\xi_1\sigma}\vartheta \tag{14}$$

when $\psi = 0$.

We find $\vartheta(t)$ as the numerical solution of transcendental equation (13) and (14) or by numerical integration of (11).

Particular cases of the solution of Eq. (12) are obtained at $\beta = 0$, which corresponds to Langmuir adsorption. Equation (12) then becomes a linear equation and is solved in closed form:

$$\vartheta = 1 - \exp(-\nu\xi_1\sigma t) \tag{15}$$

when $\psi = 0$ and

$$\vartheta = \frac{1 - \exp\left[-(\nu\xi_1\sigma + \psi)t\right]}{1 + \dfrac{\psi}{\nu\xi_1\sigma}} \tag{16}$$

when $\psi \neq 0$.

Solution (15), without allowance for the dependence of ξ_1 on a number of gas—surface interaction conditions, was used to investigate friction and wear processes in [4].

From (16) as $t \to \infty$ it is easy to obtain the Langmuir isotherms in standard form.

Equation (12) defines the gas molecule deposition process as a function of the nature of the gas and the surface material, the pressure (p), and the gas (T_g) and surface (T_w) temperatures. For a particular state of the medium and the investigated surface material, the temperature of the surface adsorbing the gas molecules, which is determined by the initial conditions and the amount of heat released in the friction process, is unknown. The temperature developed during friction can either be measured experimentally or calculated by the method described in [5], which takes into account both the antifriction properties of the rubbing materials and the friction conditions.

Below we present an analysis of the process of gas monolayer deposition based on a numerical investigation of the expressions obtained using an M-222 computer. In order to analyze the effect of various factors on this process, the calculations were made on the basis of three different adsorption models: 1) Langmuir without allowance for desorption (15); 2) Langmuir with allowance for desorption (16); 3) with allowance for desorption and migration of the molecules (12), on a wide range of parameters of state of the external medium and the surface: pressure $p = 10^{-1}$-10^{-14} mm Hg, $T_g = 143$-593°K, $t_w = -130$- $+600$°C, and for various gases and surface materials.

In accordance with relation (3), the higher the vacuum the fewer the molecules that interact with the surface and the longer the monolayer deposition process. In Fig. 1 we have plotted the deposition curves for nitrogen molecules on an iron surface at various vacuums. If we disregard the desorption process and neglect the interaction of the adsorbed molecules [Eq. (15)], after a certain time a monolayer will form, whatever the state of the medium and the surface (Fig. 1, curves 1). However, even if only the desorption factor is taken into account [Eq. (16)], at a particular gas pressure it is possible to have cases where a monolayer is formed only on part of the surface, which decreases as the vacuum increases (curves 2). When both desorption and migration are taken into account (12), the fraction of the surface occupied by molecules (curves 3) is always somewhat greater than when migration is neglected (curves 2).

From Fig. 1 we may conclude that the lower the pressure, the greater the effect of desorption of monolayer formation (cf. curves 1 and 2) and the less the effect of migration (cf. curves 2 and 3). Conversely, the higher the pressure, the less the effect of desorption and the greater the effect of the interaction of already adsorbed and impinging molecules. This also applies to low-temperature surfaces, since in this case ψ is very close to zero. Thus, even with a relatively high vacuum, the monolayer completely covers the surface (Fig. 2a).

In these conditions (e.g., at normal surface temperature) the pressure dependence of the monolayer formation time is linear up to a very high vacuum (Fig. 2b). However, the higher the surface temperature, the smaller the part of the surface on which a protective monolayer is formed at a given pressure.

In Fig. 3 we have indicated the region of state of a rarefied nitrogen medium and a solid iron surface outside which a monolayer is formed on less than 63% of the surface area. The higher the gas temperature the more the curve bounding this region is shifted to the left (Fig. 4), i.e., the higher the gas temperature, the less the possibility of a monolayer being formed.

The rate of formation of the gas monolayer also depends on the material forming the deposition surface. The molecules are adsorbed most rapidly on an aluminum surface. The heavier the material, the slower the adsorption. For example, depending on the state of the gas and the surface, monolayer formation takes 1.3 to 2.8 times longer on a gold than on an iron surface. The monolayer is also formed more slowly on a graphite than on an aluminum surface.

The molecules of different gases are adsorbed at different rates, the rate depending not only on the molecular weight of the gas, but also on the depth of the potential well in the gas—surface interaction [10] and the size of the gas molecules, which determines the value of ν_0 [2]. These three quantities not being related, as they characterize different aspects of the nature of the gas, there is no definite physical relationship between the nature of the gas and the rate of formation of the monolayer. It has been established that the gas molecules are not captured at surface temperatures of above 200°C for helium, 520°C for hydrogen, 830°C for oxygen, and 2700°C for carbon dioxide. At $T_g > 293°K$ hydrogen molecules are adsorbed most slowly, then oxygen and nitrogen. Methane and water vapor molecules have the greatest adsorbability. An increase in gas temperature leads to a greater difference between the rates of monolayer formation for molecules with the greatest adsorbability and poorly adsorbed gas molecules. Correspondingly, the material of the surface and the kind of gas affect the boundary of the region of monolayer formation: The slower the formation of the monolayer, the greater, other things being equal, the leftward shift of the boundary (Fig. 3).

The results obtained can be used for simulating operating conditions in friction studies on various solids in rarefied media. It is possible to calculate whether the pressure in the vacuum chamber is adequate for simulating the effect of some greater degree of rarefaction on the friction processes. If the operating conditions of the friction pair are such that they lie outside the boundary of the region of protective monolayer formation, then no further decrease in pressure can affect the friction and wear characteristics of the material. However, carrying out the friction and wear experiments at a higher pressure considerably simplifies the work in the vacuum chamber.

Moreover, the results of the monolayer dynamics calculations, together with the solution of the thermal contact problem for rubbing parts [5], simplify the design of experiments to investigate the effect of the loading and speed of the rubbing pair on the friction and wear characteristics of materials. The use of these data makes it possible to determine by calculation the maximum friction regimes, corresponding to a sharp decrease in the antifriction properties of the material.

NOTATION

t, τ, variable time and gas-molecule deposition time, respectively, sec; $\theta(\vec{r}, t)$, mathematical expectation of number of molecules captured by surface in neighborhoods of the point $\vec{r}$ at time t; $f(\vec{u}, \vec{r})$, distribution function representing the density of the mathematical expectation of the number of gas molecules at the point $\vec{r}$ possessing velocity $\vec{u}$ at time τ; ξ_A, probability of adsorption of gas molecules; ξ_D, desorption probability; T_g, gas temperature, °K; T_W, t_W, surface temperatures, °K and °C, respectively; μ, molecular weight of gas, g/mole; m, molecular weight of surface material, g/mole; ν, mathematical expectation of number of molecules impinging on an element of surface per unit time, $m^{-2} \cdot sec^{-1}$; σ, area of a single gas molecule; p, ambient pressure, N/m^2 (3) or mm Hg (torr); R, universal gas constant; k, Boltzmann's constant; ψ, spontaneous desorption coefficient; ξ_1, probability of capture of gas molecule on clean surface; β, probability of molecules reaching free part of surface after adsorption on occupied part and subsequent migration; U, depth of potential well in gas—surface interaction, J; ϑ, relative size of surface covered by gas monolayer.

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