HIGH-VACUUM LOW-TEMPERATURE ADSORPTION IN LONG LAYERS OF ADSORBENT

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A continuum approximation is often used to describe diffusion and adsorption in long layers of an adsorbent. This approach simplifies the analysis of the problem considerably. The possibility of using the phenomenological approach is discussed in [1-3]. Both theoretical postulates and experimental data are used to write the corresponding kinetic equations, the former having the form of conservation laws and making it possible to determine the qualitative structure of these equations. The experimental data, along with the determination of specific characteristics of the system, makes it possible to validate the theoretical postulates.

Adsorbents with a developed internal structure are commonly used in industry for low-temperature adsorption [4]. The processes which take place in such adsorbents have specific features which lead to activated diffusion [5], which is important in the case of small amounts of adsorbent. We attempted to experimentally study the process of low-temperature adsorption in long layers of adsorption by the tagged atom method. A description of the experimental unit and some of the results is given in [6]. The tests showed that a characteristic length arises in the layer in the case of relatively small amounts of adsorbent. This length can be regarded as the depth of the layer of adsorbent that participates in adsorption. It is known that in processes described by the diffusion equation (nonlinear in the general case), such a situation is realized when the medium contains distributed sinks of the transported quantity (see [7], for example). Below, we experimentally and theoretically study the possibility of constructing a model of high-vacuum low-temperature adsorption with relatively low surface coverage.

High-vacuum low-temperature adsorption in long layers of adsorbent consists of several important processes differing in their physical nature. We will examine them in chronological order.

1. Movement of Molecules of Adsorbate between Dispersed Particles (Granules) of Adsorbent. In the simplest case — that of planar symmetry with sufficiently low gas pressures — this process can be described by the unidimensional diffusion equation

$$\partial c/\partial t = \partial/\partial x\, D\, \partial c/\partial x. \tag{1}$$

Here, c is the concentration of molecules of adsorbate, x is the coordinate along which, on the average, transport of the substance in the gas phase takes place, t is time; D is the diffusion coefficient, which for the molecular flow regime can be calculated from the formula [8]

$$D = D_0 \frac{\varepsilon}{K_u^2} = \frac{1}{3}\sqrt{\frac{8kT}{\pi m}}\lambda\frac{3}{K_u^2}, \tag{2}$$

where T is the temperature of the adsorbate, k is the Boltzmann constant, m is the mass of a gas molecule, λ is the characteristic size of the free space between the granules of adsorbent, K_u is the sinuosity factor, which accounts for the nonrectilinearity of the motion of the gas, $(1.4 \leqslant K_u \leqslant 2.0)$; $\varepsilon = 1 - \rho^*/\rho$ is porosity, ρ^* and ρ are the apparent and true densities of the adsorbent.

2. Adsorption on Readily Accessible Surfaces of Adsorbent Molecules. The form of the equation describing this process depends on the physical mechanism of adsorption. Estimates of the characteristic time over which equilibrium is established at the given concentration in the gas phase shows [9, 10] that equilibrium is established almost instantaneously in the situations that will be of interest to us. Thus, under conditions which are close to isothermal,

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$$a^* = \Gamma(c)$$

[$\Gamma(c)$ is the corresponding adsorption isotherm; a^* is the quantity of adsorbed gas per unit surface of a granule of adsorbent].

3. Diffusion of Adsorbate Molecules Inside Granules and Adsorption in Micropores. A detailed analysis of activated diffusion inside a granule was made in [5] and in other articles presented in the first part of the same book. The main feature of diffusion in these investigations was presumed to be the presence of a potential barrier at the inlet to the micropores. In the case of low degrees of surface coverage, the presence of this barrier leads to a situation whereby the overcoming of the barrier by adsorbate molecules is the main factor limiting the rate of adsorption inside the granule. There is almost no reverse flow of molecules. The latter circumstance can be attributed to the fact that, for low levels of surface coverage, the equilibrium pressure turns out to be small due to the presence of the potential barrier.

Following [11], we determine the flow of molecules into a micropore:

$$q_1 = 2\pi r_0 \beta(r_0) c_*. \tag{3}$$

Here, c_* is the concentration of molecules near the mouth of the micropore, r_0 is the characteristic radius of the micropore, $\beta = \sqrt{RT/m}\exp[-Q(r)/kT]$ is the probability of a molecule being inside a micropore, $Q(r)$ is the potential barrier at the inlet of the micropore. It is natural to assume that $c_* \sim a^*$. Then

$$q_1 = \eta\Gamma(c) \tag{4}$$

(η is a proportionality factor determined by the physicochemical properties of the adsorbent and adsorbate).

Equation (4) shows that, under certain conditions, the flux of molecules undergoing adsorption inside a granule depends only on the concentration of adsorbate molecules in the gas phase. A relation of type (4) exists if the penetration of adsorbate into micropores inside a granule is impeded [12]. With allowance for (4), we write Eq. (1) in the form

$$\partial c/\partial t = \partial/\partial x D \partial c/\partial x - q, \tag{5}$$

where q is the capacity of the distributed sink. It follows from the above relations that

$$q = \langle\eta\rangle N\Gamma(c)$$

(the brackets denote averaging over the volume, while N is the number of micropores participating in adsorption per unit volume of adsorbent). Thus, the capacity of the sink q in (5) depends on the physicochemical properties and geometry of the adsorbent molecules, the species of gas being adsorbed, the concentration of gas, and the degree of saturation of the adsorbent.

A specific value can be found for q in (5) only by experiment. With this as a goal, we determined the rate of adsorption in a layer of adsorbent.

Figure 1 shows the layer of adsorbent in the ampul (a diagram of the unit was presented in [6]) (1 is a glass ampul, 2 is the layer of adsorbent, and 3 is copper powder). We use xenon Xe and nitrogen N_2 as the adsorbate, while activated chacoal SKT-4 and zeolite SaEN-4V were used as the adsorbent. The arrow shows the direction of motion of the gas being adsorbed. The mass of the adsorbent was determined by weighing. The thickness of the layer of adsorbent ℓ was measured with a ruler, gas flow rate was determined with a buret, and pressure above the surface of the adsorbent was determined with three lamps (PMI-2, PMI-10-2, and LM-3-2). The instrument error of the flow-rate determination was 5%, while the error for the pressure determination was about 30%. Measurements of flow rate and pressure were made every 15 min over an extended period of time (4-7 h). Here, pressure and flow rate remained nearly constant, providing evidence of the steady-state nature of the process).

The experimental data thus obtained, averaged over the time of the experiment, is shown in Fig. 2 in the form of the dependence of the flow rate of the gas Q ($m^3Pa \cdot sec^{-1}$) on pressure P (Pa) above the surface of the SaEN-4V adsorbent (1 — xenon; 2 — nitrogen; $\ell = 10^{-2}$ m). The choice of xenon was dictated by considerations of convenience regarding the use of its radioisotope Xe-133. Similar experiments were conducted with $\ell = 0.2$ m.

Analysis of the results (Fig. 2) shows that a good approximation for the relation Q(P) is the power relation $Q = AP^m$ ($A, m = \text{const} > 0$). Thus, in Eq. (5) we can put $q = \gamma c^\alpha$.

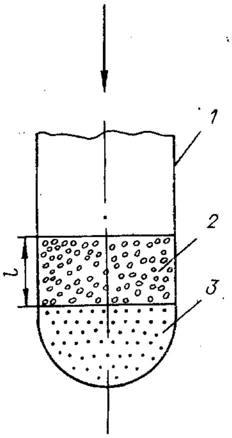

Fig. 1

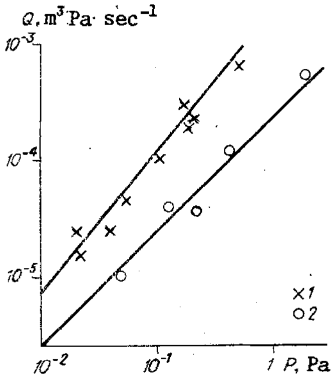

Fig. 2

Taking as the characteristic quantities c_0 (the concentration of gas above the surface of adsorbent), $L = [D/\gamma c_0^{\alpha-1}]^{1/2}$ (length), and $t_0 = \gamma^{-1}c_0^{1-\alpha}$ (time), we can write Eq. (5) in dimensionless form

$$\partial c/\partial t = \partial^2 c/\partial x^2 - c^{\alpha}. \tag{6}$$

Having augmented Eq. (6) by boundary conditions corresponding to the conditions of the experiment (see Fig. 1), we have

$$c = 1 \text{ at } x = 0,\ \partial c/\partial x = 0 \text{ at } x = l/L. \tag{7}$$

As already noted, adsorption occurred nearly steadily during the experiment. Thus, here it is expedient to rewrite out only the steady-state solutions of Eq. (6) which satisfy conditions (7) for two limiting cases: a thin layer of adsorbent $\ell \gg L$, and a thick layer $\ell \ll L$. At $\ell \ll L$, $c_1 = 1$. Gas flow rate in the layer of adsorbent is determined only by the capacity of the sink: $Q_1 = \gamma c_0^{\alpha} V$ (V is the volume of adsorbent). Henceforth, it is convenient to write this relation in the form

$$Q_1 = \gamma(P/KT)^{\alpha} M \tag{8}$$

(M is the mass of adsorbent). At $\ell \gg L$

$$c_2 = \left[1 + \sqrt{\frac{2}{\alpha+1}}\frac{\alpha-1}{2}x\right]^{-2/(\alpha-1)} \quad (\alpha > 1). \tag{9}$$

Here, the subscripts 1 and 2 correspond to the case of thin and thick layers of adsorbent. Gas flow rate in the thick layer of adsorbent

$$Q_2 = -SD\left.\frac{dc_2}{dx}\right|_{x=0}$$

(S is the cross-sectional area of the adsorbent layer). We will rewrite the last relation in the form

$$Q_2 = \sqrt{\gamma D}\,(P/kT)^{(1+\alpha)/2} S[-dc(0)/dx],$$

where from (9) $dc(0)/dx = -[-2/(\alpha+1)]^{1/2}$.

Figure 3 shows results of measurement of the relative intensity of radiation of the isotope Xe-133 [$\xi = I(x)/I(0)$; $I(x)$ is the intensity of radiation of the isotope Xe-133 minus the background intensity] used to label the xenon. The intensity distribution is shown through the depth of the layer of asorbent for different saturation times τ (1-4 – τ = 2, 5, 8, 11 h, respectively). Radiation intensity of the surface of the adsorbent x = 0 was taken as unity. The layer of adsorbent was deliberately made thick. It can be seen that if $\ell = 10^{-2}$ m, then such a layer of SaEN-4V can be considered thin. If ℓ = 0.2 m, then the layer can be considered thick.

Experimental data on the relation $Q_1 = Q_1(P)$ obtained by the above method was analyzed by the least squares method using the power relation $Q_1 = A_2P^{m_1}/kT$. It follows from a comparison with (8) that $\alpha = m_1$. Here, if the experimental data for a thick layer is also approximated by the power relation $Q_2 = A_2P^{m_2}/kT$, then it is consistent with the proposed theoretical model with $m_2 = (1 + m_1)/2$. The constant A was determined by the least squares method. The chosen correlation coefficient for A_2 was at least 0.85 in all cases.

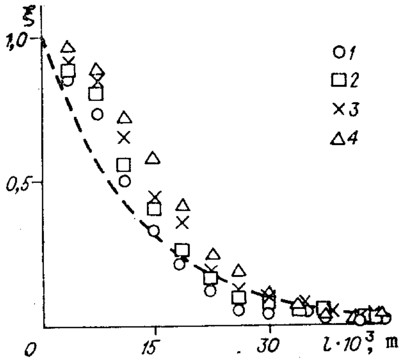

Fig. 3

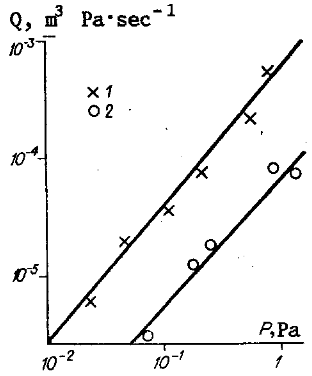

Fig. 4

TABLE 1

Adsorbate	α	γ, $m^{3(\alpha-1)} \times$ $\times sec^{-1}$	$\gamma^* = \gamma c^{\alpha-1}$, sec^{-1}	D_t, $m^2 \cdot sec^{-1}$	D_e, $m^2 \cdot sec^{-1}$
Xe	1,13	$2{,}2 \cdot 10^{-2}$	9,81	$3{,}3 \cdot 10^{-3}$	$2{,}6 \cdot 10^{-3}$
N_2	1,08	$4 \cdot 10^{-2}$	1,704	$7{,}5 \cdot 10^{-3}$	$6{,}8 \cdot 10^{-3}$

TABLE 2

Adorbate	α	γ, $m^{3(\alpha-1)} \cdot sec^{-1}$	$\gamma^* = \gamma c^{\alpha-1}$, sec^{-1}
Xe	1,4	$3{,}8 \cdot 10^{-6}$	393
N_2	1,32	$1{,}05 \cdot 10^{-5}$	27,2

Finally, we calculated the constants γ and D from the formulas

$$\gamma = \frac{A_1 \rho^*}{M} (kT)^{m_1}, \quad D = \frac{A_2}{A_1} \frac{MkT}{\rho^* S} \frac{m_1 + 1}{2}.$$

Table 1 shows data obtained in this manner for Xe and N_2 in the case of adsorption on SaEN-4V ($[\gamma] = m^{3(\alpha-1)} \cdot sec^{-1}]$). The values in the table corresponding to the denominator of D are theoretical values of the diffusion coefficient found from Eq. (2), where $K_u = 1.5$; $\varepsilon = 0.4$; $\lambda = 10^{-3}$ m.

Along with experimental data on the adsorption of Xe and N_2 on adsorbent SaEN-4V, Fig. 2 shows curves obtained with a power approximation of the relation Q(P). Figure 4 shows results for a thickness of adsorbent layer $\ell = 0.2$ m. Figure 3 shows the curve calculated from Eq. (9) for Xe. On the whole, all of the experimental and theoretical data shown in Figs. 2-4 shows that the theoretical and experimental relations agree satisfactorily.

We attempted to perform similar experiments involving adsorption on activated charcoal SKT-4. However, experiments with the radioisotope Xe-133 showed that the thin-layer situation is almost impossible to realize under the given conditions. This is because the length ℓ at $\ell \ll L$ becomes comparable to the dimensions of the adsorbent granules. This makes the continuum approximation invalid. We therefore attempted to conduct tests on a thick layer $\ell \gg L$. The diffusion coefficient was assumed to be equal to its value found for SaEN-4V (the sizes of the SKT-4 and SaEN-4V granules were roughly the same). The results of calculations of the constants α and γ are shown in Table 2.

One of the main postulates of the theory of adsorption in long layers of adsorbent is the near absence of desorption (due to activated diffusion) and redistribution of the adsorbate layer. To substantiate this hypothesis, we experimentally determined the intensity of radiation of the isotope Xe-133 when the adsorbent was held at the nitrogen temperature for a long period of time in a vacuum after the cessation of saturation. Holding the adsorbent under these conditions for 3-5 days did not lead to any appreciable redistribution of the isotope along the layer of adsorbent.

The completed analysis of activated diffusion in long layers of adsorbent accurately describes the effect associated with the manifestation of characteristic length (depth of layer).

The largest deviation from the theoretical relation is seen near the boundary of the layer $x = 0$. This is apparently related to a certain amount of heating the adsorbent undergoes due to the heat released during adsorption.

Thus, despite the sizable instrument errors which generally occur in similar experiments conducted under high-vacuum, low-temperature conditions, it can be considered proven that Eq. (3), with a nonlinear sink, satisfactorily describes activated low-temperature diffusion.

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