

agreement of the proposed dependences with the experimental data is good.

The given mathematical model of the absorption of material by a sphere was also used in the analysis of experiments on the sorption of nitrogen by other rocks – sandstone and clay shales. The theoretical curves reflecting the dependence of the total amount of nitrogen absorbed on the sorption time and the experimental data of [3] are shown in Fig. 2. In the calculations, the parameter values assumed for sandstone shale were:  $R = 0.009$  m;  $\varepsilon = 0.15$ ;  $\gamma_V = 0.8 \cdot 10^{-6}$  m<sup>3</sup>/mg;  $\gamma_D = 2.6$  tons/m<sup>3</sup>;  $\alpha = 5.2 \cdot 10^{-4}$  sec<sup>-1</sup>;  $H = 15$  m<sup>-1</sup>;  $\psi = 4 \cdot 10^{-9}$  m<sup>2</sup>/sec;  $\beta = 1.8 \cdot 10^{-4}$  sec<sup>-1</sup>;  $\gamma = 8.8$ ; those assumed for the clay shale were;  $R = 0.009$  m;  $\varepsilon = 0.1$ ;  $\gamma_V = 0.8 \cdot 10^{-6}$  m<sup>3</sup>/mg;  $\gamma_D = 1.9$  ton/m<sup>3</sup>;  $\alpha = 5.2 \cdot 10^{-4}$  sec<sup>-1</sup>;  $H = 15$  m<sup>-1</sup>;  $\psi = 6.7 \cdot 10^{-9}$  m<sup>2</sup>/sec;  $\beta = 2.6 \cdot 10^{-4}$  sec<sup>-1</sup>;  $\gamma = 16.4$ .

The mean-square deviation of the experimental data from the theoretical results after the sorption period and the variation coefficient for sandstone shale were 0.0019 ml/g and 0.4%, while those for clay shale were 0.0053 ml/g and 0.66%.

#### NOTATION

$c$ , adsorbate concentration, mg/m<sup>3</sup>;  $\psi$ , diffusion coefficient, m<sup>2</sup>/sec;  $R$ , radius of sorbent particle, m;  $\beta$ , adsorption coefficient, sec<sup>-1</sup>;  $\gamma$ , Henry coefficient;  $\alpha$ , amount of sorbed material, referred to sorbent mass, mg/m<sup>3</sup>;  $\varepsilon$ , sorbent porosity;  $Bi = HR$ , Biot number;  $c_0(\tau)$ , function expressing change in adsorbate concentration, mg/m<sup>3</sup>;  $\gamma_V$ , specific volume of sorbate, m<sup>3</sup>/mg;  $\gamma_D$ , density of sorbent, ton/m<sup>3</sup>;  $\tau$ , time, sec.

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#### SORPTION ON HYDROPHILIC SWELLING MATERIALS

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A sorption equation for swelling, colloidal, capillary-porous bodies is obtained by the methods of statistical physics. The results of the calculations are in good agreement with experiment.

Vapor and gas absorption by swelling materials may be regarded as a process of mixing of active centers of the sorbent with sorbate molecules [1]. It is assumed that each such center comprises several molecules. In considering pair interactions in solutions, only the nearest neighbors of the active centers need be taken into account. The change in sorbate enthalpy on sorption may be expressed as the product [2]

$$\Delta H \approx -\Delta\omega_{12}p_{12}. \quad (1)$$

The number of contacts averaged over the sorbent volume is

$$p_{12} \approx z_0 n_2 U_1 \approx z_0 n_1 U_2. \quad (2)$$

Each active center may interact locally with some number of sorbate molecules differing from  $z_0$ , but on average over the volume the number of interactions is  $z_0$ . In addition, the probability of a reaction between sorbate molecules and the active centers of the sorbent depends on the volume fraction of the sorbent  $U_2$  in the sorbate–sorbent system.

Substitution of Eq. (2) into Eq. (1) yields

$$\Delta H \approx -\Delta\omega_{12}z_0 n_1 U_2. \quad (3)$$

If the total number of molecules  $n_1$  is replaced in Eq. (3) by Avogadro's number  $N_A$ , then the change in enthalpy  $\Delta H_1$  per mole of sorbate is obtained:

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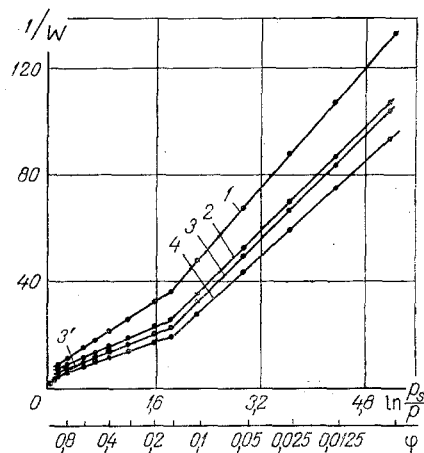


Fig. 1. Isotherms for the sorption of water [6-8] by: 1) cotton, lowland peat; 2) silk, jute; 3) starch, gelatin; 3') gelatin ( $0.6 \leq p/p_s \leq 1$ ); 4) wool.

TABLE 1. Parameter Values Determining the Form of the Sorption Isotherm

Material	$0,005 \leq p/p_s < 0,15$					$0,15 \leq p/p_s \leq 1$				
	$z_1$	$z_0$	$z_2$	$n$	$a$	$z_1$	$z_0$	$z_2$	$n$	$a$
Wool	4	1	—	20,0	-20,0	4	2 3	4-5 3	8,8	3,3
Starch	4	1	—	25,0	-22,0	4	2 3	4-5 3	10,4	3,9
Silk, jute	4	1	—	25,0	-20,0	4	2 3	4-5 3	10,6	4,0
Cotton, lowland peat	4	1	1	28,1	-20,0	4	2 3	4-5 3	15,2	5,8
Gelatin	4	1	—	25,0	-22,0	4	2 3	4-5 3	10,4	3,9

$0,6 \leq p/p_s \leq 1$   
 $0,15 \leq p/p_s < 0,6$

$$\Delta H_1 \approx -\Delta \omega_{12} z_0 N_a U_2. \quad (4)$$

The following model concepts may be proposed for the calculation of the change in sorbate entropy. The molecules are localized at the active centers of sorbent. Accordingly, the whole space of interactions of sorbate-sorbent type may be divided arbitrarily into cells, each of which has an active center and the associated sorbate molecules. Since the localization of molecules not of ideal gas but of a real, low-molecular, polar sorbate occurs at the active centers, intermolecular reactions of the sorbate molecules may be arbitrarily taken into account, for the purposes of calculating the entropy in the bound state, by means of repeated division of the space of interactions of sorbate-sorbate type into cells, each of which contains a single molecule localized at an active center plus a number of sorbate molecules surrounding and interacting with the first and also localized at these centers. Thus, in such a cell, there would be a number of molecules equal to the coordination number of sorbate in the bound state plus one.

The entropy of sorbate in the free state may also be arbitrarily calculated by dividing the space of interactions of sorbate-sorbate type into cells, each containing one molecule plus a number of molecules equal to the coordination number of the sorbate. Thus, for water in the free state, the coordination number is  $\sim 4$ .

The form of sorption described above corresponds to the real sorption mechanism in porous swelling materials [3, 4].

The sorbate entropy difference may be calculated as follows

$$\Delta S = k \ln \frac{n_1!}{(z_0!)^{z_0} (c_2!)^{c_2}} - k \ln \frac{n_1!}{(c_1!)^{c_1}} \quad (5)$$

The entropy change  $\Delta S_1$  of a mole of sorbate in sorption may be expressed, transforming Eq. (5), as follows

$$\Delta S_1 = -R \left[ \left( \frac{1}{z_0} \ln(z_0!) + \frac{1}{c_2} \ln(c_2!) - \frac{1}{c_1} \ln(c_1!) \right) \right] \quad (6)$$

The change in Gibbs energy in sorption for a mole of sorbate is

$$\Delta G_1 = \Delta H_1 - T\Delta S_1 = RT \ln \frac{p}{p_s} \quad (7)$$

since at equilibrium the change in Gibbs energy for a mole of sorbate and its vapor is the same, and the vapor may be regarded as an ideal gas.

Substituting Eqs. (4) and (6) into Eq. (7) and rearranging gives

$$\frac{1}{W} = n \ln \left( \frac{p_s}{p} \right) + a, \quad (8)$$

where

$$n = \frac{\rho_2}{\rho_1} (1 + m) \frac{kT}{z_0 \Delta \omega_{12}} \quad (9)$$

and

$$a = n \left[ \frac{1}{z_0} \ln(z_0!) + \frac{1}{c_2} \ln(c_2!) - \frac{1}{c_1} \ln(c_1!) \right] \quad (10)$$

An equation similar to Eq. (8) was obtained recently, by different means, in [5].

Isotherms for the sorption of water by swelling materials, taken from [6-8] and plotted in the coordinates of Eq. (8), are shown in Fig. 1. From the given curves, values of  $n$  and  $a$  were calculated for different sections of the graphs, and the coordination number  $z_2$  for the given values  $z_0$  and  $z_1$  was determined from Eqs. (9) and (10). Different versions of the relations between  $z_0$ ,  $z_1$ , and  $z_2$  satisfying the experimental values of  $n$  and  $a$  are given in Table 1.

At the beginning of the sorption process ( $p/p_s < 0.15$ ), each active center of the sorbent interacts, on the average, with one sorbate molecule in such a way that these molecules do not form a continuous phase. When  $p/p_s \geq 0.15$ , the amount of sorbed material increases so much that each active center interacts indirectly with two or three molecules (this is the first hydrate layer around the sorption center) and a sorbate phase appears, with a definite coordination number  $z_2$ .

Note that the sorbent solid-phase volume  $V_2$  appearing in the parameter  $n$  of Eq. (8) is a constant and, of course, the sorbent solid-phase density  $\rho_2 = \text{const}$ , while  $\rho_1$  and  $\Delta \omega_{12}$  are evidently not constant. It is suggested that at low moisture content the density of sorbed material must differ from the sorbate density in the free state, since the individual sorbate molecules are distributed over the active centers of the sorbent, and do not form a continuous phase. The change in density of water on sorption in biopolymers is shown qualitatively in [9].

The binding energy of the sorbate molecule with the active center of the sorbent may decrease, since other molecules exert an influence on the sorbate molecules bound by active centers as a result of the intermolecular forces, and therefore, in comparing experimental curves and the theoretical result in Eq. (8), constancy of  $n$  on definite sections of the isotherms may be achieved by proportional changes in the numerator and denominator of Eq. (9).

The isotherm of water sorption by gelatin when  $0.6 \geq p/p_s \geq 1$  may be described by an equation taking the passing of some of the molecules into solution and their coagulation into clumps into account for sorbents

swelling without limit. As a result of this, some of the functional groups of sorbent become inaccessible to sorbate molecules, and  $z_0$  may be of the order of 1-2, as reflected in Table 1.

The form of the curve describing the isotherm for water sorption by gelatin when  $0.6 \leq p/p_S \leq 1$  may also be explained by the significant change in the ratio of the number of active centers of sorbent and the number of sorbate molecules associated with the total solution of the sorbent (gelatin). In this case, the change in entropy per mole of sorbate is

$$\Delta S_1 = -R \left[ \frac{\alpha}{z_0} \ln(z_0!) + \frac{1}{c_2} \ln(c_2!) - \frac{1}{c_1} \ln(c_1!) \right], \quad (11)$$

where  $\alpha$  is the number of sorbate molecules localized directly at active centers of the sorbent, expressed as a fraction of the total number of sorbed molecules. Substituting the factor  $\alpha$  into the numerator of the power index  $n_1/z_0$  of the factor  $(z_0!)$  in the first term of Eq. (5) leads to Eq. (11). Calculations show that, with rise in  $p/p_S$  in the range  $0.6 \leq p/p_S \leq 1$ , there is a sharp fall in  $\alpha$ . Thus, for example, if  $z_1 \approx z_2$  and  $z_0 = 3$ ,  $\alpha = 1/3$  when  $p/p_S = 0.8$  and  $\alpha = 1/20$  when  $p/p_S = 0.9$ .

#### NOTATION

G, Gibbs energy; H, enthalpy; T, temperature; S, entropy;  $p_{12}$ , number of contacts between a sorbate molecule and an active center of the sorbent, averaged over the sorbent volume;  $\Delta\omega_{12}$ , change in binding energy when a single contact between a sorbate molecule and an active center of the sorbent is formed;  $z_0$ , number of bonds of a single active center of the sorbent with sorbate molecules;  $z_1, z_2$ , coordination number of the sorbate in the free and bound states, respectively;  $n_1$ , total number of sorbed molecules;  $n_2$ , total number of active centers of sorbent;  $m = V_2/V_1$ , volume ratio of solid phase of porous material and sorbate;  $U_1 = V_1/(V_1 + V_2)$ ,  $U_2 = V_2/(V_2 + V_1)$ , volume fraction of sorbate and sorbent, respectively;  $\rho_1, \rho_2$ , density of sorbate and sorbent, respectively; W, moisture content;  $\varphi = p/p_S$ , relative vapor pressure of sorbate; k, Boltzmann constant; R, universal gas constant;  $N_A$ , Avogadro's number;  $c_1 = z_1 + 1$ ,  $c_2 = z_2 + 1$ , number of molecules in cells in the free and bound state, respectively;  $\alpha$ , number of sorbate molecules localized directly at active centers of the sorbent, expressed as a fraction of the total number of sorbed molecules.

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