

The article describes the results of a study of several laws governing the desorption processes in microporous materials, particularly in molecular filters. The sorption characteristics were obtained for model materials which can be used in the structure analysis of microporous materials.

The results of the latest work on desorption of bound moisture in the so-called sorptive porous materials are of particular interest as far as sorptive microporous materials with high sorption energy are concerned, such as various molecular filters.

The laws which have been derived are, in principle, valid for any bound liquid or solvent. But the present article refers only to water, for which the desorption process can be considered identical to the drying process. In the microporous materials under consideration, desorption, and its definition, are not identical to the drying process, because desorption is in this case an independent phenomenon.

Changes in the state diagram of a material are shown in Fig. 1 in $t-X$ coordinates for the desorption process. Changes in the state diagram of a gas (moist air) which is in equilibrium at a certain temperature on the surface of a material (under the assumption that the corresponding amount of material and flowing gas form an adiabatic system) are shown in $\vartheta-x$ coordinates in Fig. 2.

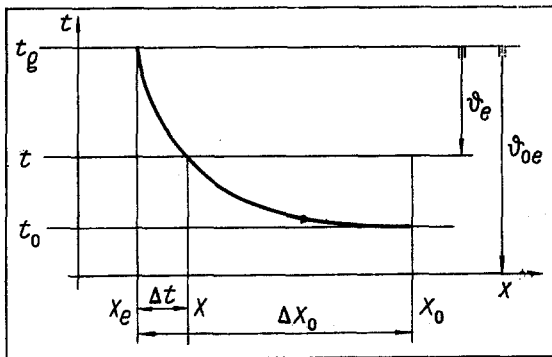


Fig. 1. Development of the state of a material in $t-X$ coordinates.

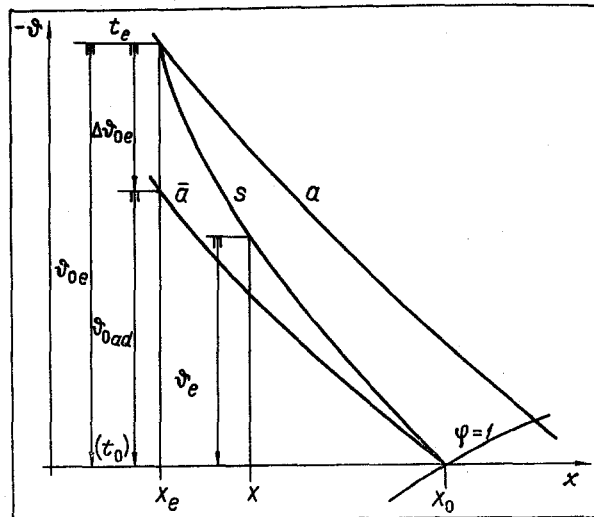


Fig. 2. State of a gas (humid air) in $\vartheta-x$ coordinates.

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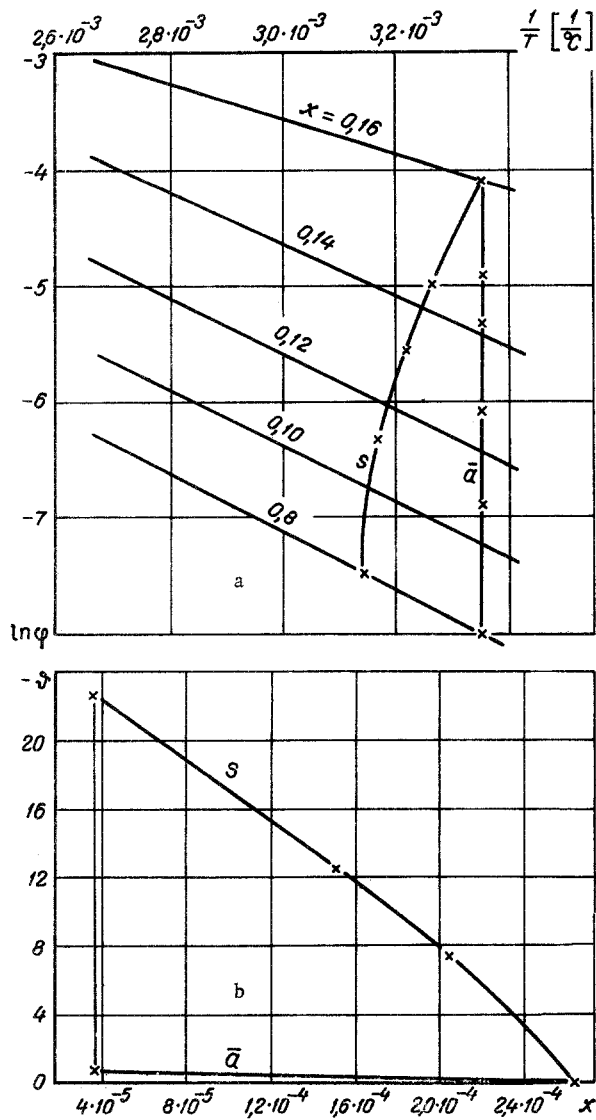


Fig. 3. Change of state of a Linde 5A molecular filter.

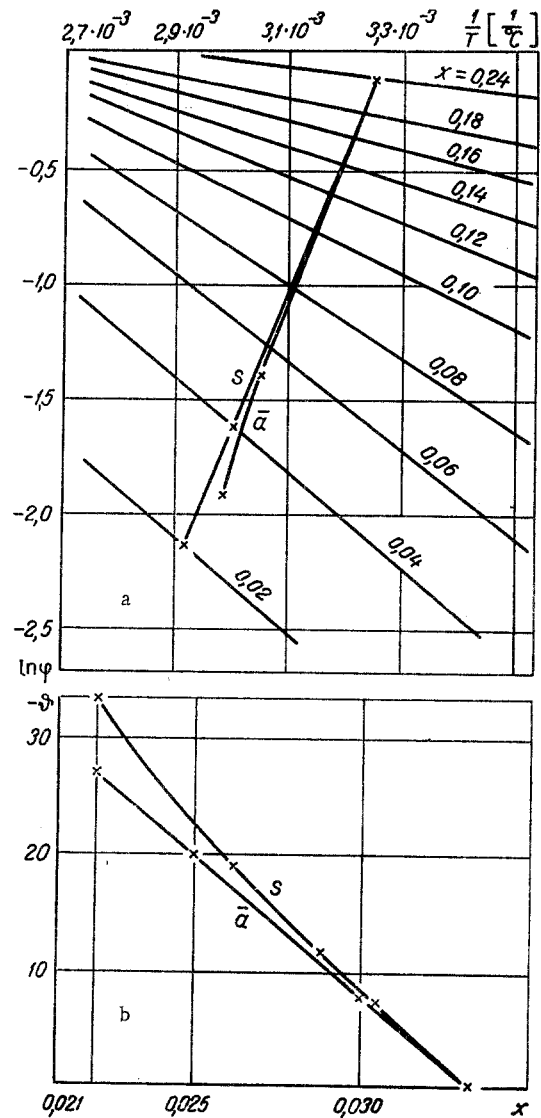


Fig. 4. Change in the state of coal dust.

The state of the material follows curves which start at the point $t_0 X_0$ and end near the t_g isotherm in the $t-X$ diagram (Fig. 1). A temperature between the initial state and the final state of the material is involved and can be calculated with the equation

$$t_0 - t_g = \theta_{0_e} = \frac{R(X_e) + r_{t_0} \Delta X_0}{c_m + 0.46X_0 + 0.54X_e - \frac{c_{n_0}}{\eta_e}}, \quad (1)$$

where

$$\eta_e = \frac{x_0 - x_e}{X_0 - X_e}.$$

The initial values t_0 , x_0 of the desorption process, which correspond to the point 0 , x_0 , are plotted to the abscissa of the $\vartheta-x$ coordinate system (Fig. 2); for the sake of simplicity, the positive direction was assumed for the ϑ coordinate. The point 0 , x_0 is always the intersection of the isotherm of vapor pressure at the temperature t_0 and the phase-boundary curve. This point is therefore also a point of the isostere X_0 . The curve depicting the change in the state s of the material runs from the initial moisture concentration to the final moisture concentration X_e . The vertical section extending from this point to the abscissa axis renders ϑ_{0e} and ϑ_e , respectively (at intermediate points). The adiabatic curve a , which starts at the

TABLE 1

Material	$-\vartheta_{0e}, ^\circ\text{C}$	$-\Delta\vartheta_{0e}, ^\circ\text{C}$	ΔX_0	η_e	S_{A_0}	S_{R_0}	S_0^*
Coal dust.	33,282	5,662	0,22	0,051318	0,995	0,82	0,824
Molecular filter	22,49	21,659	0,08	0,002795	0,0248	0,0257	1,039

same point (the adiabatic curve is not a straight line in the particular coordinate system), intersects the phase-boundary curve at a point which is not identical with the point t_0, x_0 but which is situated to the right of the latter point. The adiabatic curve corresponds to one of the possible changes in the state of the air. This change can occur in the moist phase of the absorbing material and starts at the above-mentioned point. It follows from the figure that the motive forces, which result from desorption of state s due to concentration differences, are smaller than the motive forces resulting from the change in state a .

Adiabatic line \bar{a} , which starts at point x_0, t_0 , divides the vertical section of the straight line ϑ_{0e} (and also vertical section ϑ_e which begins from any point of the curve indicating the change in the state) into two portions. The section above the adiabatic line results from the sorption.

The curve representing the change of the state s between the two final points is given by the equation

$$\vartheta_e = \frac{R(X_e) - R(X) + r_{i_e} \Delta X}{c_m + 0.46X_0 + 0.54X - \frac{C_{x_0}}{\eta_e}} \quad (2)$$

Figure 3 displays curves which represent changes in the state of a Linde 5A molecular filter; Fig. 4 displays similar curves for comparison. The change in the state of the material in $\ln \varphi - 1/T$ coordinates is in both figures denoted by the letter a , whereas the letter b is used to denote the change in the state of humid air which is in equilibrium with the surface of the material ($\vartheta-x$ coordinates).

Substantial variations of the numerical values observed in the sorption process are shown by these figures.

The figures show at the same time that the phase changes are nonadiabatic. This may be a consequence of the fact that desorption requires a higher temperature (at almost the same $X_0 - X_e$ and, correspondingly, $x_0 - x_e$ values) than changes in state \bar{a} from the initial state (or, in accordance with the preceding concept, desorption results in lower ΔX_0 and Δx_0 values, respectively, at the same temperature).

The present article attempts to obtain a more thorough comparison by comparing several new characteristics. The so-called absolute sorption, which is defined as

$$\frac{1}{S_{A_0}} = \frac{R(X_0) + r_{i_0} \Delta X_0}{r_{i_0} \Delta X_0} \quad (3)$$

in the final state of the process, is one of these characteristics. We obtain

$$\vartheta_{0e} = \frac{1}{S_{A_0}} \frac{r_{i_0} \Delta X_0}{C_0} \quad (4)$$

and

$$S_{A_0} = \frac{r_{i_0} \Delta X_0}{C_0 \vartheta_{0e}} = \frac{r_{i_0} \Delta X_0}{\eta_e C_0 \vartheta_{0e}}$$

There exists a striking analogy between this formula and the formula for the Lewis coefficient of moist air. Equation (4) can therefore be considered the equivalent Lewis law for adsorbing porous materials.

The so-called relative sorption is determined (in the final state) in the following way:

$$S_{R_0} = \frac{\vartheta_{0ad}}{\vartheta_{0e}} \quad (5)$$

(the notation agrees with Fig. 2).

Since

$$\vartheta_{0ad} = -\frac{i_{d_e}}{c_{n_0}} \Delta X_0, \quad (6)$$

we obtain with Eqs. (6) and (4):

$$S_{R_0} = -\frac{i_{d_e}}{r_{t_0}} \frac{C_0}{c_{n_0}} \eta_e S_{A_0} = -\frac{i_{d_e} \Delta X_0}{c_{n_0} \vartheta_{0e}} \quad (7)$$

which is another way of expressing the above-mentioned analogy.

Finally, we obtain

$$S_0^* = \frac{S_{R_0}}{S_{A_0}} = -\frac{i_{d_e}}{r_{t_0}} \frac{C_0}{c_{n_0}} \eta_e. \quad (8)$$

Table 1 lists values of these characteristics for model materials.

The reduced S_{A_0} and S_{R_0} values in the case of molecular filters are of particular interest. These values indicate that the sorption energy is high and that the quantity S_0^* is stable.

The above-mentioned characteristics may be useful in calculations of the structure of materials which are characterized by the given properties.

NOTATION

η	is the relative rate of the mass flow of a medium (i. e., of a solid body in relation to a gas);
φ	is the relative humidity of air;
r_t	is the heat of evaporation of a liquid at temperature t ;
i_{d_0} and i_{d_e}	are the entropy of overheated vapor at the temperatures t_0 and t_e , respectively;
x	is the absolute water-vapor concentration in a vapor-air mixture;
x_0	is the absolute moisture concentration in the vapor-air mixture at the temperature t_0 ;
x_e	is the absolute concentration of moisture in the vapor-air mixture in the final equilibrium state of air;
X	is the absolute concentration of moisture in the solid (expressed relative to the dry weight of the solid);
X_0	is the absolute moisture concentration in a solid at the beginning of a nonstationary process;
X_e	is the required moisture concentration in the final equilibrium state of the solid;
$R(X)$	is the integral sorption energy per unit dry weight of the solid;
c_p , c_n , and c_m	are the specific heats of dry air, moist air, and dry solid material, respectively;
$C_0 = c_m + 0.46 X_0 + 0.54 X_e - c_{n_0}/\eta_e$.	

Subscripts

0	denotes the initial state or the beginning of a process;
e	denotes the final state or the equilibrium of the system;
t	denotes a certain temperature t ;
g	denotes some state (e.g., at a certain temperature).