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# DEVELOPMENT OF THE THEORY AND METHODS FOR CALCULATING THE DYNAMICS OF SORPTION AND DESORPTION

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*A system of equations of heat and mass transfer, phase transformations, and deformation of porous bodies in sorption and desorption are derived and substantiated. Formulas for the area of contact between a liquid and gas in a unit volume of a porous body, for the intensity of phase transition, heat of phase transformations, equilibrium partial vapor pressure, and for the thickness of adsorbate layer on the surfaces of capillaries with allowance for the influence of adsorption forces are presented. The results of a comparison between calculated and experimental data are given.*

***Keywords:*** *heat and mass transfer, phase transformations, deformation, contact area of phases, thickness of adsorbate layer.*

**Introduction**. Development of the theory and methods for calculating sorption and desorption processes in capillary-porous systems is topical for a number of branches of modern technology. In the theories of drying, sorption and desorption, a unified approach to a mathematical description of the processes of heat and mass transfer and of phase transformations in porous bodies has not been developed as yet [1, 2]. Usually, to characterize adsorption processes, a system of equations of heat and mass transfer is used that contains two equations as basic ones — of heat transfer and moisture transfer with a source of the substance being sorbed [2, 3]. The strength of mass sources [2–4] is determined from the approximate empirical relation $\partial\omega/\partial t = \gamma_\omega(\omega_{eq} - \omega)$. This relation does not take account of the influence of the volume concentration of an adsorptive substance (the vapor of the substance being absorbed) $U_v$, which is a function of coordinates and time, and admits the progress of adsorption ($\partial\omega/\partial t > 0$) at $U_v = 0$, which is physically inadmissible.

Investigation and optimization of the dynamics of sorption and desorption of colloid capillary-porous materials are connected with the solution of a combined problem of heat and mass transfer, phase transformations, and deformation in heterogeneous systems.

**Equations of the Dynamics of Sorption and Desorption in Deformable Porous Systems.** We consider a homogeneous isotropic capillary-porous body that can undergo deformation as a result of the advancement of heat and mass transfer and phase transformations processes, and under the action of external forces. The position of an arbitrary point of the body in a certain coordinate system $x_1$, $x_2$, $x_3$ at time $t$ is determined by the radius vector $\mathbf{r}(t) = x_i(t)$ with the components $x_1(t)$, $x_2(t)$, and $x_3(t)$. The displacement of this point in time $t$ as a result of deformation is determined by the displacement vector $\mathbf{u}$ with the components

$$u_i\,[t, x_i(0)] = x_i(t) - x_i(0)\,. \tag{1}$$

The specification of the displacement vector $u_i$, $i = 1, 2, 3$, as a function of time $t$ and of the coordinates for the point at time $t = 0$ entirely determines the body deformation.

In the body considered, at time $t$ we isolate an elementary parallelepiped, whose volume is equal to $\Delta V(t) = \Delta x_1(t)\Delta x_2(t)\Delta x_3(t)$. The relative extensional strain $\varepsilon_{ii}(t)$ along the axis $x_i$ of the parallelepiped edge whose length at the instants of time $t = 0$ and $t$ was equal to $\Delta x_i(0) = x_{iA}(0) - x_{iB}(0)$ and $\Delta x_i(t) = x_{iA}(t) - x_{iB}(t)$, subject to (1), is defined by the relation

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$$\varepsilon_{ii}(t) = \lim_{\Delta x_i \to 0} \frac{[x_{iA}(t) - x_{iB}(t)] - [x_{iA}(0) - x_{iB}(0)]}{[x_{iA}(0) - x_{iB}(0)]} = \lim_{\Delta x_i \to 0} \frac{u_{iA}(t) - u_{iB}(t)}{[x_{iA}(0) - x_{iB}(0)]} = \frac{\partial u_i(t)}{\partial x_i} . \tag{2}$$

In the general case, in the presence of shear stresses and deformations the relationship between the deformation tensor components $\varepsilon_{ij}$ and displacement vector components $u_i$ in Cartesian coordinates in the case of small deformations is defined by the relations [5]

$$\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j} , \quad i, j = 1, 2, 3 . \tag{3}$$

The expression for the relative volume deformation $\varepsilon_V = \Delta V/V$ for the considered elementary parallelepiped, subject to (2), can be written in the form

$$\varepsilon_V(t) = \frac{\Delta V(t) - \Delta V(0)}{\Delta V(0)} = [1 + \varepsilon_{11}(t)]\,[1 + \varepsilon_{22}(t)]\,[1 + \varepsilon_{33}(t)] - 1 . \tag{4}$$

Relations (2) and (4) yield the expression

$$\frac{1}{\Delta V(t)} \frac{\partial \Delta V(t)}{\partial t} = \frac{1}{1 + \varepsilon_V(t)} \frac{\partial \varepsilon_V(t)}{\partial t} = \frac{1}{1 + \varepsilon_{11}} \frac{\partial \varepsilon_{11}}{\partial t} + \frac{1}{1 + \varepsilon_{22}} \frac{\partial \varepsilon_{22}}{\partial t} + \frac{1}{1 + \varepsilon_{33}} \frac{\partial \varepsilon_{33}}{\partial t} . \tag{5}$$

The change in the volume concentration of substance $W$ (energy, mass of the component, momentum) in the isolated elementary parallelepiped with the volume $\Delta V(t) = \Delta x_1(t)\Delta x_2(t)\Delta x_3(t)$ is connected with the processes of heat and mass transfer, deformation, and with the action of the substance sources and sinks.

The amount of substance released or absorbed per unit time in a volume $\Delta V$ is equal to

$$I_V = \int_{\Delta V} I_W dV . \tag{6}$$

The substance flux leaving the volume $\Delta V$ in unit time through its outside surface $\Delta S$ due to diffusive transfer, with allowance for the Ostrogradskii–Gauss theorem, is defined by the expression

$$J^{\mathrm{d}} = \int_{\Delta S} (\mathbf{j}_W d\mathbf{S}) = \int_{\Delta S} (\mathbf{j}_W \cdot \boldsymbol{\delta}_{\mathrm{v}})\, dS = \int_{\Delta V} \mathrm{div}\, \mathbf{j}_W dV . \tag{7}$$

The substance flux outflowing through the surface $\Delta S$ due to convective transfer, with allowance for the Ostrogradskii–Gauss theorem, is given by the relation

$$J^{\mathrm{con}} = \int_{\Delta S} W (\mathbf{w} \cdot \boldsymbol{\delta}_{\mathrm{v}})\, dS = \int_{\Delta V} \mathrm{div}\, (W\mathbf{w})\, dV . \tag{8}$$

The amount of the substance $W$ contained in the volume $\Delta V(t)$ at time $t$ is equal to $W(t)\Delta V(t)$. Its change in unit time with allowance for Eq. (5) is defined as follows:

$$\frac{\partial (W\Delta V)}{\partial t} = \Delta V \frac{\partial W}{\partial t} + W \frac{\partial \Delta V}{\partial t} = \left( \frac{\partial W}{\partial t} + \frac{W}{1 + \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t} \right) \Delta V = \int_{\Delta V} \left( \frac{\partial W}{\partial t} + \frac{W}{1 + \varepsilon_V} \frac{\partial \varepsilon_V}{\partial t} \right) dV . \tag{9}$$

The balance equation of the substance $W$ for the volume $\Delta V(t)$ on the basis of relations (6)–(9) can be presented in the form

$$\int_{\Delta V}\left(\frac{\partial W}{\partial t}+\frac{W}{1+\varepsilon_V}\frac{\partial \varepsilon_V}{\partial t}+\operatorname{div}(W\mathbf{w})+\operatorname{div}\mathbf{j}_W-I_W\right)dV=0\,.$$

This relation, due to the arbitrariness of the volume $\Delta V$, yields the differential equation of substance transfer for a deformable system:

$$\frac{\partial W}{\partial t}+\operatorname{div}(W\mathbf{w})=-\operatorname{div}\mathbf{j}_W+I_W-\frac{W}{1+\varepsilon_V}\frac{\partial \varepsilon_V}{\partial t}\,. \tag{10}$$

Such an equation was obtained for the first time, for a homogeneous body in [6] by a different method, without invoking vector analysis. In the absence of body deformation (at $\varepsilon_V = 0$), Eq. (10) yields an equation sometimes called the Umov equation [7].

Expressions for the components of the displacement vector $u_i$, $i = 1, 2, 3$, can be obtained by solving the equation of thermally induced deformation of concentration [5], which for the case of elastic deformation, when dynamic effects can be neglected, has the form

$$\mu_1\nabla^2\mathbf{u}+(\mu_2+\mu_1)\operatorname{grad}(\operatorname{div}\mathbf{u})-\operatorname{grad}[\mathrm{N}(2\mu_1+3\mu_2)]+\rho F=0\,, \tag{11}$$

where

$$\mathrm{N}=\alpha_T(T-T_0)+\sum_{\beta}\alpha_{i\beta}(\omega_\beta-\omega_{\beta 0})\,;\quad \alpha_T=(\partial x_i/\partial T)/x_i\,;\quad \alpha_{i\beta}=(\partial x_i/\partial\omega_\beta)/x_i\,.$$

For bodies of the simplest shape the solution of the problem of deformation in the course of sorption and desorption can be obtained analytically [6].

Generally, the density of the flux $j_W$ of substance $W$ is composed of the diffusion $j_W^{\mathrm{d}}$ and filtration $j_W^{\mathrm{f}}$ components: $j_W = j_W^{\mathrm{d}} + j_W^{\mathrm{f}}$. Diffusion energy and mass flows of components are proportional to the temperature gradients $T$ and volume concentrations $U_\beta$ of the components $\beta = 1, 2, \ldots, \mathrm{B}$:

$$j_T^{\mathrm{d}}=-\lambda\left(\nabla T+\sum_{\beta=1}^{\mathrm{B}}\delta_{U_\beta}\nabla U_\beta\right),\quad j_{U_\beta}^{\mathrm{d}}=-D\left(\nabla U_\beta+\sum_{\beta=1}^{\mathrm{B}}\delta_{T_\beta}\nabla T\right). \tag{12}$$

The effective diffusion coefficient of a liquid in a porous body $D_{\mathrm{liq}}$ is determined from Nikitenko's formula that follows from the molecular-radiative theory of transfer [5, 8]:

$$D_{\mathrm{liq}}=\gamma_{D_{\mathrm{liq}}}\left[\exp\left(\frac{A}{kT}\right)-1\right]^{-1},\quad \gamma_{D_{\mathrm{liq}}}=\delta^{*2}\varepsilon/3\,. \tag{13}$$

The effective diffusion coefficients of vapor $D_{\mathrm{v}}$ and air $D_{\mathrm{a}}$ in the pores of granules and in transport pores are determined according to the kinetic theory of gases from the formulas

$$D_{\mathrm{v}}=\gamma_{D_{\mathrm{v}}}T^{3/2}/P_{\mathrm{v}}\,,\quad D_{\mathrm{a}}=\gamma_{D_{\mathrm{a}}}T^{3/2}/P_{\mathrm{a}}\,. \tag{14}$$

Here $\gamma_{D_{\mathrm{liq}}}$, $\gamma_{D_{\mathrm{v}}}$, and $\gamma_{D_{\mathrm{a}}}$ are constants.

The densities of a filtration flux of liquid and gaseous components are defined by the expressions $j_{\mathrm{liq}}^{\mathrm{f}} = U_{\mathrm{liq}}w_{\mathrm{liq}}$, $j_{\mathrm{v}}^{\mathrm{f}} = U_{\mathrm{v}}w_{\mathrm{g}}$, and $j_{\mathrm{a}}^{\mathrm{f}} = U_{\mathrm{a}}w_{\mathrm{g}}$. According to the Darcy law, the velocities of the filtration motion of the liquid $w_{\mathrm{liq}}$ and gaseous $w_{\mathrm{g}}$ phases are proportional to the gradients of their pressures $\nabla P_{\mathrm{liq}}$ and $\nabla P_{\mathrm{g}}$: $w_\zeta = -K_D\nabla P_\zeta/\chi_\zeta$, $\zeta = \mathrm{liq, g}$.

The pressure of the vapor-gas mixture $P_g$ in the body pores is expressed in terms of the volume concentrations of components $U_v$, $U_a$, $U_{liq}$ and temperature $T$ as follows. The volume fractions of the liquid $\Psi_{liq}$ and gas $\Psi_g$ in a porous body are respectively equal to $\Psi_{liq} = U_{liq}/\rho_{liq}$ and $\Psi_g = 1 - \Psi_s - \Psi_{liq}$, where $\rho_{liq}$ is the true density of the liquid. The partial densities of the vapor and air in the pores of the body are defined by the expressions $\rho_v = U_v/\Psi_g$, $\rho_a = U_a/\Psi_g$. The partial pressures of vapor and air are found from the equation of state. For the sorption and desorption processes a vapor-gas mixture can be considered as a mixture of ideal gases. In this case $P_v = \rho_v RT/\mu_v$ and $P_a = \rho_a RT/\mu_a$. The total pressure of the vapor-gas mixture $P_g$ is equal to the sum of the partial pressures of its components.

In [9, 10], on the basis of the laws governing the intensity of spectral radiation of body particles and energy distribution of particles in activation processes, the following formula was obtained for the mass of the condensed body unit volume of particles which in unit time attain the activation energy: $G = \varepsilon\rho_{liq}[\exp(A/kT) - 1]^{-1}$. If a capillary-porous body is an adsorbent, then the force of interaction of a particle of the ambient with the body increases as the particle approaches the body surface, which leads to an increase in the activation energy. In the process of sorption, on the surface of a solid adsorbent a monomolecular condensate layer is formed, whose molecules are the most strongly bound with the adsorbent. The subsequent layers of the bound liquid are held less strongly, and with distance from the adsorbent surface their properties approach those of a free liquid. The interaction of the liquid particles with the adsorbent surface is characterized by the binding energy $E_{ad}$. Since exponential functions are usually used in describing the intermolecular interaction the quantity $E_{ad}$ is represented as follows:

$$E_{ad} = E_{ad0}\left[1 - \left(\frac{\delta - \eta}{\delta^*}\right)^b\right], \tag{15}$$

where $E_{ad0}$ and b are positive constants; $\delta \le \delta^*$. With allowance for the interaction of a liquid particle with a solid body, the expression for the activation energy $A_{ad}$ is written in the form

$$A_{ad} = A + E_{ad0}\left[1 - \left(\frac{\delta - \eta}{\delta^*}\right)^b\right]. \tag{16}$$

The mass of particles that attain the activation energy $A_{ad}$ in unit time in an elementary liquid layer $d\eta$ of unit area located from the sorbent surface at a distance $\eta$ is defined by the expression

$$dG = \varepsilon\rho\left[\exp\left(\frac{A_{ad}}{kT}\right) - 1\right]^{-1} d\eta\,. \tag{17}$$

If $E_{ad0} << kT$, then, according to the Taylor formula, we may write

$$\exp\left\{\frac{E_{ad0}}{kT}\left[1 - \left(\frac{\delta - \eta}{\delta^*}\right)^b\right]\right\} \approx 1 + \frac{E_{ad0}}{kT}\left[1 - \left(\frac{\delta - \eta}{\delta^*}\right)^b\right] \tag{18}$$

and expression (17) can be represented in the form

$$dG \approx \varepsilon\rho\left\{1 - \frac{E_{ad0}}{kT}\left[1 - \left(\frac{\delta - \eta}{\delta^*}\right)^b\right]\right\}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1} d\eta\,. \tag{19}$$

As a result of integration in the interval from 0 to $\delta$ of the product $w_{ev}dG$, where $w_{ev} = \frac{1}{2}\left(1 - \frac{\eta}{\delta^*}\right)$ is the probability of evaporation of an activated particle [9], we find an expression for the intensity of liquid evaporation $I_{ev}$ from a condensate layer of thickness $\delta$ with allowance for its interaction with the porous body walls:

$$I_{\mathrm{ev}} = \varepsilon\rho\delta^{*}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1} \Phi\,(\bar{\delta}, T)\,, \tag{20}$$

$$\Phi\,(\bar{\delta}, T) = \left\{\frac{\bar{\delta}}{2}\left(1 - \frac{\bar{\delta}}{2}\right)\left(1 - \frac{E_{\mathrm{ad0}}}{kT}\right) - \bar{\delta}^{\,b+1}\left[\frac{1}{b+1} - \bar{\delta}\left(\frac{1}{b+1} - \frac{1}{b+2}\right)\right]\frac{E_{\mathrm{ad0}}}{kT}\right\};\ \ \bar{\delta} = \frac{\delta}{\delta^{*}}\,. \tag{21}$$

For the case of evaporation of a thick liquid layer (when $\delta = 1$)

$$\Phi\,(\bar{\delta}, T)\,\big|_{\bar{\delta}=1} = \Phi_0\,(T) = \frac{1}{4} - \frac{E_{\mathrm{ad0}}}{kT}\left(\frac{1}{4} - \frac{1}{b+2}\right). \tag{22}$$

The specific flux of condensing vapor molecules $I_{\mathrm{con}}$ is determined [9] on the basis of the Maxwell law of velocity distribution of molecules:

$$I_{\mathrm{con}} = \frac{f_{\mathrm{con}} m P_{\mathrm{v}}}{\sqrt{2\pi kmT}}\,. \tag{23}$$

Under the conditions of the thermal equilibrium of the condensed body–gas phase system, the temperature of phases and mass fluxes of evaporating and condensing molecules are the same, i.e., $T_{\mathrm{v}}$ = T and $I_{\mathrm{ev}} = I_{\mathrm{con}}$, and the vapor pressure $P_{\mathrm{v}}$ is equal to the equilibrium vapor pressure $P_{\mathrm{eq}}$. Under these conditions, Eqs. (20) and (23) yield

$$P_{\mathrm{eq}} = \frac{\varepsilon\rho_{\mathrm{liq}}\Phi\,(\bar{\delta}, T)\sqrt{2\pi kmT}}{f_{\mathrm{con}} m}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}. \tag{24}$$

For massive bodies $\bar{\delta} = 1$, Eq. (24) changes to the formula for the saturated vapor pressure:

$$P_{\mathrm{sat}} = \frac{\varepsilon\rho_{\mathrm{liq}}\Phi_0\,(T)\sqrt{2\pi kmT}}{f_{\mathrm{con}} m}\left[\exp\left(\frac{A}{kT}\right) - 1\right]^{-1}. \tag{25}$$

At $E_{\mathrm{ad0}} = 0$ Eq. (25) agrees well with the experimental data of [9] presented in the literature in the form of tables of vapor and liquid at saturation.

On the basis of Eq. (25) and the Clapeyron–Clausius equation, a formula for the phase transition heat was obtained:

$$L = \frac{\varepsilon\rho_{\mathrm{liq}}\Phi\,(\bar{\delta}, T)\sqrt{2\pi kmT}}{f_{\mathrm{con}} m}\,(v'' - v')\left\{\frac{\sqrt{T}}{2}\left[\exp\left(\frac{A}{RT} - 1\right)\right]^{-1} + \frac{A}{R\sqrt{T}}\exp\left(\frac{A}{RT}\right)\left[\exp\left(\frac{A}{RT} - 1\right)\right]^{-2}\right\}^{-2}. \tag{26}$$

As a result of termwise division of Eq. (24) by Eq. (25), we obtain the formula

$$\frac{P_{\mathrm{eq}}}{P_{\mathrm{sat}}} = \varphi_{\delta} = \frac{\Phi\,(\bar{\delta}, T)}{\Phi_0\,(T)}\,. \tag{27}$$

When the forces of interaction between the molecules of the liquid and between the molecules of the liquid and adsorbent coincide, i.e., $E_{\mathrm{ad0}} = 0$, Eq. (27) goes over to the formula given in [9]:

$$\frac{P_{\mathrm{eq}}}{P_{\mathrm{sat}}} = \varphi_{\delta} = \bar{\delta}\,(2 - \bar{\delta})\,. \tag{28}$$

According to Eq. (27), with increase in the mass of the liquid introduced into a closed isothermal cavity, the equilibrium thickness of the condensate layer on the cavity surface increases monotonically until the pressure attains the saturation pressure. A further increase in the amount of the mass of introduced liquid does not lead to a change in $\delta$. In porous systems in the state of equilibrium at prescribed values of temperature and moisture content of the ambient, the thickness of the layer on the walls of the pores is the same and equal to $\delta$ for capillaries of radius $r > \delta$, whereas capillaries of radius $r \le \delta$ are entirely filled by the liquid. Having the function of the sorption isotherm $U = U(\varphi)$, on the basis of Eq. (27) we can determine the relationship between the thickness of the liquid layer $\delta$ in partially fillled pores and its volume concentration $U$: $\delta = \delta(\mathrm{U})$. Provided the hypothesis of local thermodynamic equilibrium used in the thermodynamics of nonequilibrium states is satisfied, this dependence holds also for nonequilibrium processes of moderate intensity. The relative moisture content $\varphi_\delta$, which, according to the sorption isotherm, corresponds to the volume concentration $U$ at the given point of a porous body, will be called the adsorptional moisture content of the body.

The resultant mass flux of adsorbed molecules $I_{\mathrm{am}}$ on the outside surface of the body at different values of the temperature of the body $T$ and ambient medium $T_{\mathrm{am}}$ is equal to

$$I_{\mathrm{am}} = I_{\mathrm{ev}}(T) - I_{\mathrm{con}}(T_{\mathrm{am}}) = \varepsilon \rho_{\mathrm{liq}} \delta^* \left[ \exp\left(\frac{A}{kT}\right) - 1 \right]^{-1} \Phi(\bar{\delta}, T) - \frac{f_{\mathrm{con}} m P_{\mathrm{v}}}{\sqrt{2\pi kmT}} . \tag{29}$$

Equation (29) allows one to calculate the intensity of phase transformations in both sorption and desorption. If the first term on the right-hand side of Eq. (29) exceeds the second term, desorption or drying takes place. Otherwise, the process of sorption occurs.

In a number of cases it is convenient to write Eq. (29) in the form

$$I_{\mathrm{am}} = \varepsilon \rho_{\mathrm{liq}} \delta^* \Phi_0(T_{\mathrm{am}}) \left\{ \varphi_\delta \left[ \exp\left(\frac{A}{kT}\right) - 1 \right] - \varphi_{\mathrm{am}} \left[ \exp\left(\frac{A}{kT_{\mathrm{am}}}\right) - 1 \right] \right\} , \tag{30}$$

where $\varphi_{\mathrm{am}} = P_{\mathrm{v.am}}/P_{\mathrm{eq}}$.

In conformity with (30) and with the condition that the temperatures of phases at each point of the body are identical, the resultant specific flux $I$ of vapor from the liquid to the gaseous phase in a unit volume of a homogeneous porous body can be represented as

$$I = S \varepsilon \rho_{\mathrm{liq}} \delta^* \Phi_0(T_{\mathrm{am}}) \left[ \exp\left(\frac{A}{kT}\right) - 1 \right]^{-1} (\varphi_\delta - \varphi_{\mathrm{am}}) . \tag{31}$$

To find the specific intensity of the phase transition of a liquid component to a vapor in the capillaries of a porous body, we must know the area of contact of the liquid and gaseous phases $S$ in a unit volume of the body and the average thickness of the layer of liquid $\delta$ in partially filled pores. In [11], a method of finding the area of contact between the liquid and gaseous phases is presented on the basis of the differential function $f_V$ of the size distribution of pores. However, the algorithm of its realization presupposes the specification of $f_V$ and is very complex.

Further, a more simple way of determining the area $S(t)$ on the basis of the desorption isotherm is suggested. It consists in the following. Let for the instant of time $t$ the volume concentration $U$ in the vicinity of a certain point of the body be known. It is required to determine the area of contact $S(t)$ of the liquid with the vapor-gas mixture and the average relative thickness $\bar{\delta}$ of the layer of liquid on the surfaces of partially filled pores of unit volume. The adsorptional moisture content of the body $\varphi_\delta(t)$, which corresponds to the volume concentration of moisture $U(t)$ at the considered point of the porous body, can be determined in accordance with the hypothesis of local equilibrium on the basis of the equation of sorption isotherm and Eq. (27) or (28) as follows. These formulas are solved for $\bar{\delta}$. For the case where $E_{\mathrm{ad0}} << A$, we obtain

$$\delta = \delta^* \bar{\delta} = \delta^* \left(1 - \sqrt{1 - P_{\mathrm{v}}/P_{\mathrm{eq}}}\right) = \delta^* \left(1 - \sqrt{1 - \varphi_\delta}\right) . \tag{32}$$

As a result of differentiation of Eq. (32), we find

$$d\delta = \frac{\delta^* d\varphi_\delta}{2\sqrt{1-\varphi_\delta}} . \tag{33}$$

The volume concentration changes in time $dt$ as

$$dU = \rho_{\text{liq}} S d\delta . \tag{34}$$

As a result of substitution of Eq. (33) into Eq. (34), we obtain the sought expression for the function $S$:

$$S = \frac{2\sqrt{1-\varphi_\delta}}{\rho_{\text{liq}}\delta^*} \frac{\partial U}{\partial \varphi_\delta} . \tag{35}$$

As an example, we give the algorithm of finding the function $S$ for silica gel. Based on the tabulated data presented in [1], the following expression for the sorption isotherm is obtained: $U = U_{\text{max}}\varphi^g$, where $g = 0.542$. Then, for this case

$$\frac{\partial U}{\partial \varphi_\delta} = U_{\text{max}} g \varphi_\delta^{g-1} \quad \text{and} \quad S = \frac{2U_{\text{max}} g}{\rho_{\text{liq}}\delta^*} \varphi_\delta^{g-1}\sqrt{1-\varphi_\delta} . \tag{36}$$

The area $S$ can change from a maximum value $S_{\text{max}}$, corresponding to an absolutely dry adsorbent layer (when $U \to 0$), to a minimum value when $\delta \to \delta^*$.

On the surface of contact between the gaseous and liquid phases a difference in pressures caused by the surface tension force appears; therefore the pressure of liquid $P_{\text{liq}}$ is represented in the form of the sum $P_{\text{liq}} = P_{\text{g}} + P_{\text{cap}}$. The pressure $P_{\text{cap}}$ can be calculated [5, 10] as the average capillary pressure in the body pores:

$$P_{\text{cap}} = 2\sigma(T) \int_{r_{\text{min}}}^{r_{\text{max}}} \frac{\theta}{r} f_V dr \Big/ \int_{r_{\text{min}}}^{r_{\text{max}}} \theta f_V dr = \frac{2\sigma(T)}{r^*} . \tag{37}$$

The characteristic parameter of the dispersity of the sizes of pores $r^*$ lies in the interval between the minimal $r_{\text{min}}$ and maximal $r_{\text{max}}$ radii of capillaries. If there are no data on the function $f_V$, then to find $P_{\text{cap}}$ one can use, in particular, the Kelvin approximate formula $P_{\text{liq}} = P_{\text{sat}} + RT\rho_{\text{liq}} \ln (P_{\text{v}}/P_{\text{liq}})/\mu_{\text{liq}}$.

As a result of the substitution, into the substance transfer equation (10), of the above-given expressions for the diffusion coefficient, volume evaporation intensity, area of contact of the liquid with a vapor-gas mixture, as well as of the relationships between pressures, velocities, and densities of mass fluxes of components and their volume concentrations, a system of equations describing the interrelated processes of heat-and mass transfer and phase transformations in the course of adsorption in capillary-porous bodies is constructed:

$$\frac{\partial U_{\text{liq}}}{\partial t} + \nabla (w_{\text{liq}} U_{\text{liq}}) = \nabla [D_{\text{liq}} (\nabla U_{\text{liq}} + \delta_{\text{liq}} \nabla T)] - SI - \frac{U_{\text{liq}}}{1-\varepsilon_V} \frac{\partial \varepsilon_V}{\partial t} , \tag{38}$$

$$\frac{\partial U_{\text{v}}}{\partial t} + \nabla (w_{\text{v}} U_{\text{v}}) = \nabla [D_{\text{v}} (\nabla U_{\text{v}} + \delta_{\text{v}} \nabla T)] + SI - \frac{U_{\text{v}}}{1-\varepsilon_V} \frac{\partial \varepsilon_V}{\partial t} , \tag{39}$$

$$\frac{\partial U_{\text{a}}}{\partial t} + \nabla (w_{\text{a}} U_{\text{a}}) = \nabla [D_{\text{a}} (\nabla U_{\text{a}} + \delta_{\text{a}} \nabla T)] - \frac{U_{\text{a}}}{1-\varepsilon_V} \frac{\partial \varepsilon_V}{\partial t} , \tag{40}$$

$$c_{\mathrm{ef}}\left(\frac{\partial T}{\partial t}+w_{\mathrm{ef}}\nabla T\right)=\nabla\,(\lambda_{\mathrm{ef}}\nabla T)-\sum c_{\psi}D_{\psi}\,(\nabla U_{\psi}+\delta\nabla T)\,\nabla T-LSI\,, \tag{41}$$

where $c_{\mathrm{ef}} = c_{\mathrm{s}}U_{\mathrm{s}}+c_{\mathrm{liq}}U_{\mathrm{liq}}+c_{\mathrm{v}}U_{\mathrm{v}}+c_{\mathrm{a}}U_{\mathrm{a}}$; $\lambda_{\mathrm{ef}} = \lambda_{\mathrm{s}}U_{\mathrm{s}}/\rho_{\mathrm{s}}+\lambda_{\mathrm{liq}}U_{\mathrm{liq}}/\rho_{\mathrm{liq}}+\lambda_{\mathrm{v}}U_{\mathrm{v}}/\rho_{\mathrm{v}}+\lambda_{\mathrm{a}}U_{\mathrm{a}}/\rho_{\mathrm{a}}$; $w_{\mathrm{ef}} = [w_{\mathrm{liq}}U_{\mathrm{liq}}+w_{\mathrm{g}}(U_{\mathrm{v}}+U_{\mathrm{a}})]/c_{\mathrm{ef}}$. The specific evaporation heat of adsorbate $L$ inside a porous material depends on its volume concentration and is composed of the specific heat of evaporation and specific energy of moisture desorption. The second term on the right-hand side of Eq. (41) attributable to energy transfer by diffusion can usually be neglected [1].

For the system of equations (38)–(41), the boundary conditions of heat and mass transfer, provided that the drying agent parameters are prescribed, is formulated as follows:

$$\lambda\left.\frac{\partial T}{\partial \nu}\right|_{\nu=0}=\alpha\,(T_{\mathrm{am}}-T\,|_{\nu=0})-LI_{\mathrm{am}}\,, \tag{42}$$

$$D_{\mathrm{liq}}\left(\left.\frac{\partial U_{\mathrm{liq}}}{\partial \nu}\right|_{\nu=0}+\delta_{\mathrm{liq}}\left.\frac{\partial T}{\partial \nu}\right|_{\nu=0}\right)+j_{\mathrm{liq}}^{\mathrm{f}}\,|_{\nu=0}=I_{\mathrm{am}}\,, \tag{43}$$

$$-D_{\mathrm{v}}\left(\left.\frac{\partial U_{\mathrm{v}}}{\partial \nu}\right|_{\nu=0}+\delta_{\mathrm{v}}\left.\frac{\partial T}{\partial \nu}\right|_{\nu=0}\right)+j_{\mathrm{v}}^{\mathrm{f}}\,|_{\nu=0}=\gamma_{\mathrm{v,am}}\,(U_{\mathrm{v}}\,|_{\nu=0}-\rho_{\mathrm{v,am}}\Psi_{\mathrm{v}})+\gamma_{\mathrm{v,am}}\delta_{\mathrm{v,am}}\Psi_{\mathrm{v}}\,(T\,|_{\nu=0}-T_{\mathrm{am}})\,. \tag{44}$$

The volume concentration of air on the outer boundary is determined from the condition that the vapor-gas mixture pressure at the internal points of the body in the vicinity of this boundary is equal to the ambient pressure, i.e., $P_{\mathrm{g}}\,|_{\nu=0} = P_{\mathrm{v}}\,|_{\nu=0}+P_{\mathrm{a}}\,|_{\nu=0} = P_{\mathrm{am}} = P_{\mathrm{v.am}}+P_{\mathrm{a,am}}$. In this case the boundary condition of mass transfer for air has the form $U_{\mathrm{a}}\,|_{\nu=0} = P_{\mathrm{am}}\Psi_{\mathrm{g}}\mu_{\mathrm{a}}/(RT\,|_{\nu=0}) - U_{\mathrm{v}}\,|_{\nu=0}\mu_{\mathrm{a}}/\mu_{\mathrm{v}}$.

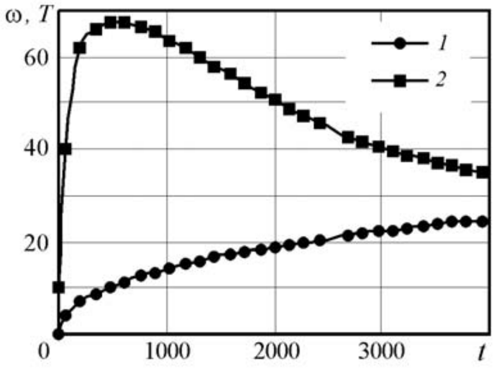
The formulated mathematical model of diffusion-filtration mass transfer in the process of sorption and desorption may be simplified considerably when applied for describing concrete problems. The filtration transfer exerts [9] a substantial influence on the dynamics of adsorption in intensive heating of a body when liquid evaporates at a temperature $T$ exceeding its boiling point or due to the pressure drop between media separated by a porous wall. For the case where the influence of filtration on the progress of heat and mass transfer processes can be neglected, Eq. (40) should be omitted. In this case the vapor-gas mixture pressure is equal to the ambient pressure $P_{\mathrm{am}}$, and the partial air pressure $P_{\mathrm{a}}$ is defined by the expression $P_{\mathrm{a}} = P_{\mathrm{am}}-P_{\mathrm{v}}$. For this case, under conditions (43) and (44) it can be assumed that $j_{\mathrm{liq}}^{\mathrm{ef}} = j_{\mathrm{v}}^{\mathrm{ef}} = 0$.

**Numerical Method of Calculation and Results of Numerical Experiments.** To solve the system of equations (38)–(41) under given conditions of unambiguity, two grid methods have been developed. The first is applied for solving diffusion problems of sorption and desorption and is based on N. I. Nikitenko's explicit three-layer difference scheme. The second is used for diffusion-convection problems and is based on N. I. Nikitenko's explicit three-layer scaling difference circuit. In Cartesian coordinates $x_1$, $x_2$, and $x_3$ on a uniform difference grid $x_{i,m_i} = m_ih_i$ ($m_i$ = 0, 1, $h_i$ = const, $i$ = 1, 2, 3), $t_n = nl$ ($n$ = 0, 1, ..., $l > 0$) the equation of diffusive transfer of the form $\partial W/\partial t = \nabla[D(\nabla W)]$ is approximated by the difference expression

$$(1+\Theta_W)\,\frac{W^{n+1}-W}{l}-\Theta_W\,\frac{W-W^{n-1}}{l}=\sum_{i=1}^{3}\delta_i\,[D_W\,(\delta_iW)]\,, \tag{45}$$

and the equation of diffusive-convective transfer of the form of $\partial W/\partial t+\nabla(wW) = \nabla[\mathrm{D}(\nabla W)]$, by two difference equations:

$$\frac{\tilde{W}-W}{l}=-\sum_{i=1}^{3}\delta_i\,(w_iW)\,, \tag{46}$$



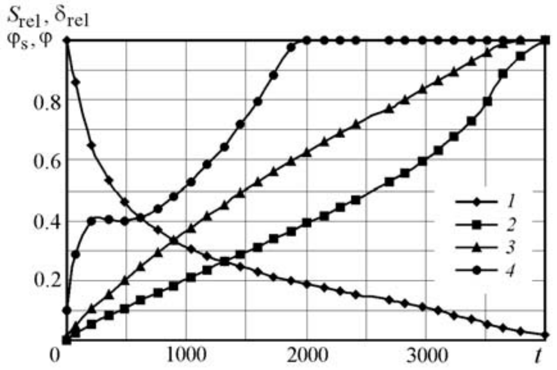


Fig. 1. Kinetics of adsorption in a layer of silica gel immersed in a symmetric flow of the adsorptive vapor: 1) average mass content ω, %; 2) average temperature $T$, $^{\rm o}$C over the layer volume. $t$, s.

Fig. 2. Graphs of change in some unknown functions in the vicinity of the outside surface of the adsorbent layer: 1) relative surface area of the contact $S_{\rm rel} = S/S_{\rm max}$ of the adsorbate with the ambient medium; 2) relative thickness of the condensate layer $\delta_{\rm rel} = \delta/\delta^*$ on the surfaces of partially filled pores; 3) adsorptional moisture content of a body $\varphi_s$; 4) relative humidity of the ambient medium φ. $t$, s.

$$(1+\Theta_W)\,\frac{W^{n+1}-W}{l}-\Theta_W\,\frac{W-W^{n-1}}{l}=-\sum_{i=1}^{3}\delta_i\,(w_i\tilde{W})+\sum_{i=1}^{3}\delta_i\,[D_W\,(\delta_i\tilde{W})]\,. \tag{47}$$

Here, the grid functions for the nodal point $(x_{1,m_1},\ x_{2,m_2},\ x_{3,m_3},\ t_n)$ were written for simplicity without the indices determining the coordinates and time of the point, i.e., $W = W^n_{m_1m_2m_3}$, $\tilde{W} = \tilde{W}^n_{m_1m_2m_3}$, $T = T^n_{m_1m_2m_3}$; $\delta_iW = \dfrac{W^n_{m_{1+1},m_2m_3} - W^n_{m_{1-1},m_2m_3}}{2h_i}$; $\delta_1[D_W(\delta_1 W)] = \dfrac{1}{2h_1^2}\,[(D_{W,m_1+1,m_2m_3} + D_{W,m_1m_2m_3})(W^n_{m_1+1,m_2m_3} - W^n_{m_1m_2m_3})(D_{W,m_1m_2m_3} - D_{W,m_1-1,m_2m_3})(W^n_{m_1m_2m_3} - W^n_{m_1-1,m_2m_3})]$.

The weight parameter of the difference equation $\Theta_W \ge 0$ makes it possible to eliminate the time step limitation connected with diffusion terms. The error of approximation of Eqs. (38)–(41) by difference equations of the form of (45) and (46), (47) has the order $l + h_1^2 + h_2^2 + h_3^2$. The conditions needed for the stability of difference equations of the form of (45) and (46), (47) are determined by the method of conventional assignment of some unknown functions of the system [5]. For Eq. (45) they do not impose limitations on the steps of a spatial grid, with the value of the wight parameter $\Theta_W$ being found from the condition

$$l \le (1+2\Theta_W)\left(2D_W\sum_{i=1}^{3}\frac{1}{h_i^2}\right)^{-1}. \tag{48}$$

For Eqs. (44) and (45) the stability conditions limit only the time step:

$$l \le \min\left[\left(\sum_{i=1}^{3}\frac{w_i}{h_i}\right)^{-1};\ (1+2\Theta_W)\left(2D_W\sum_{i=1}^{3}\frac{1}{h_i^2}\right)^{-1}\right]. \tag{49}$$

Based on the mathematical model and numerical method, the dynamics and kinetics of the adsorption of the layer $0 < x_1 < H$ from a capillary-porous material symmetrically blown by a vapor-gas mixture was calculated. The con-

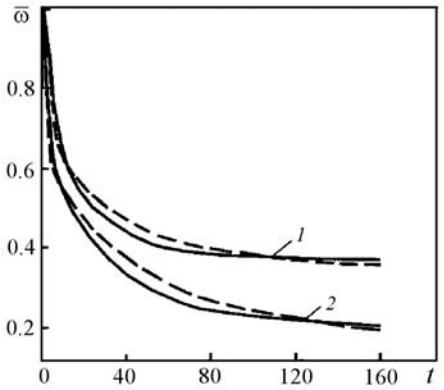


Fig. 3. Graphs of the change in the relative mass content $\overline{\omega} = \omega/\omega_{\max}$ in desorption of water from a layer of zeolite for different temperatures of a heat-conducting surface: 1) $T = 100^{\circ}$C; 2) 150; solid line, predicted data; dashed line, experimental data. $t$, min.

ditions of adsorption were selected such that the influence of filtration and the deformation of the material could be neglected.

Figures 1 and 2 present the results of calculation of the dynamics and kinetics of the adsorption of steam supplied to a 15 mm-thick silica gel layer. The concentration of the adsorbate in the adsorbent at the initial time instant is equal to zero, with the adsorptive concentration near the layer surfaces being constant. The adsorption heat is spent on heating the adsorbate and is partially removed through its outside surface.

On the basis of the given mathematical model, also the dynamics and kinetics of water desorption from a layer of zeolite under the conditions of vacuum with conductive supply of heat were calculated. The layer thickness was $H = 10$ mm, and the initial temperature amounted to $T_0 = 20^{\circ}$C. The heating surface temperature was assigned equal to 100 and 150$^{\circ}$C. Figure 3 presents graphs of the change in the average relative moisture content $\omega/\omega_0$ obtained for a zeolite layer experimentally [2] and by calculation, which agree satisfactorily.

**Conclusions.** A mathematical model of heat and mass transfer, phase transformations, and deformation in porous bodies in the course of sorption and desorption has been constructed.

Formulas for the area of contact between a liquid and a gas in a unit volume of a porous body, for the intensity of evaporation and vapor condensation on the surfaces of contact between liquid and gaseous phases, and for the phase change heat with allowance for adsorption forces, equilibrium partial pressure of the vapor phase, and thickness of the adsorbate layer on the surfaces of capillaries have been obtained.

Grid methods of calculation of sorption and desorption in diffusive and diffusive-filtration transfer of a substance have been developed. The results of comparison of theoretical and experimental data point to the adequacy of the mathematical model developed and efficiency of the method of its realization. The mathematical model and calculation method can be used for the calculation and optimization of the regimes of sorption and desorption.

## NOTATION

$A$, activation energy of molecules; $c$, specific isobaric heat capacity; $D$, diffusion coefficient; $E_{\rm ad}$, energy of coupling of the particles of liquid with adsorbent; $f_{\rm con}$, condensation coefficient; $f_V$, differential function of volume distribution of pores; $F$, mass force; $G$, mass of particles in a unit volume that attain the activation energy in unit time; $h$, $l$, size of the steps of the difference grid over the spatial coordinate and time; $H$, thickness; $I_{\rm am}$, intensity of phase transformations of liquid into vapor on the boundary surface of the body; $I$, intensity of evaporation in a unit volume of a porous body; $I_W$, strength of sources and sinks of a substance $W$; $j$, density of diffusive flux of a substance; $j^{\rm d}$, $j^{\rm c}$, diffusive and convective fluxes of a substance; $k$, Boltzmann constant; $K_D$, permeability coefficient; $L$, specific heat of phase transition of liquid into vapor; $m$, mass of a molecule; $P$, pressure; $P_{\rm cap}$, capillary pressure; $\mathbf{r}$ , radius vector; $r^*$, characteristic parameter of the dispersity of pore sizes; $R$, universal gas constant; $S$, area; $t$, time; $T$, temperature; $u_i$, component of displacement vector, $i = 1, 2, 3$; $\mathbf{u}$, displacement vector; $U$, volume concentration of bound vapor at saturation; $U_{\max}$, maximum hygroscopic volume concentration; $v'$, $v''$, specific volumes of liquid and vapor at saturation; $V$, volume; $\Delta V$, volume of elementary parallelepiped; $w$, velocity of filtration motion of a phase; $\mathbf{w}$, velocity vector; $w_{\text{ev}}$, probability of evaporation of a particle; $W$, volume concentration of a substance; $x_1$, $x_2$, $x_3$, spatial coordinates; $\alpha$, heat transfer coefficient; $\alpha_T$, $\alpha_{x\beta}$, coefficient of linear thermal expansion and linear shrinkage; $\delta$, thickness of a layer of liquid where evaporation occurs; $\delta^*$, mean length of diffusion jump; $\delta_\nu$, unit vector directed along the normal $\nu$ to the outside surface; $\delta_\psi$, relative coefficient of thermal diffusion; $\overline{\delta}$, relative thickness of a layer of condensed body; $\varepsilon$, averaged coefficient of the radiation intensity of the particles of liquid; $\varepsilon_{ij}$, component of strain tensor, $i$, $j$ = 1, 2, 3; $\varepsilon_V$, relative volume deformation; $\eta$, coordinate of the point reckoned from the free surface of the layer of liquid along its internal normal; $\theta(\mathrm{r})$, fraction of the volume of capillaries of radius r filled by liquid; $\Theta$, weight parameter of difference equation; $\lambda$, thermal conductivity; $\mu$, molecular mass of substance; $\mu_1$, $\mu_2$, Lamé coefficients; N, thermoconcentrational function; $\rho$, partial density of a component; $\sigma$, surface tension; $\varphi$, relative humidity of a gas; $\varphi_\delta$, absorptional moisture content of a body; $\chi$, dynamic coefficient of viscosity; $\Psi$, volumetric fraction of a porous system occupied by the phase component; $\omega$, specific mass content; $\nabla$, Hamiltonian operator. Subscripts and superscripts: A, B, points of the beginning and end of the edge of an elementary parallelepiped; a, air; ad, adsorption; am, ambient; c, convective; cap, parameters inside a capillary; con, condensation; d, diffusion; ef, effective parameters; eq, equilibrium state; ev, evaporation; f, filtration; g, gas; $i$, $j$ = 1, 2, 3; liq, liquid; m, n, cardinal numbers of difference grid steps for axes $x$ and $t$; min, max, minimal and maximal values of a parameter; s, solid porous body; sat, saturated state of vapor; v, vapor; v.am, partial pressure of vapor in the ambient medium; $W$, substance; $\beta$, cardinal number of the bound substance component, $\beta$ = 1, 2, ..., B; $\nu$, normal to the external boundary of a body; 0, initial value.

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