

The equations of motion of nonisothermal dynamics of sorption in porous media are analyzed for the internal diffusion kinetic domain.

Heat liberation occurs during the motion of a mixture of sorbable gases (liquids) through a nondeformable porous medium because of sorption on the developed surface of the porous grains. A considerable quantity of heat can be liberated for high sorbate concentrations, resulting in a rise in the temperature of the solid phase of the porous medium and the gas (liquid) temperature in the flow. The nonisothermal dynamics of sorption in the external diffusion kinetic domain has been examined in [1, 2] without taking account of the longitudinal mixing and without taking account of the heat exchange kinetics. Model equations of nonisothermal dynamics of sorption in a mixed external and internal diffusion kinetic domain are analyzed taking into account the longitudinal mixing of heat-exchange kinetics in this paper; a comparison is made between the output dynamic distribution curves of the sorbate concentration and of the temperature in the stream computed by the model equations and experimentally; it is shown that the model equations under consideration unsatisfactorily describe the nonisothermal dynamics of sorption in porous media.

1. The nonisothermal dynamics of sorption in porous media is described by the system of material balance equations for the concentration taking account of longitudinal mixing, the model equations of sorption kinetics (1), the heat balance equation, the equation of heat-exchange kinetics (2), and the initial and boundary conditions (3):

$$\begin{aligned} \frac{\partial c}{\partial z} + \frac{\partial q}{\partial t} &= \alpha \frac{\partial^2 c}{\partial z^2}, \quad q = f(c, \overset{*}{T}), \quad \varphi = f^{-1}, \quad q_0 = f(c^0 - c_0, \overset{*}{T}), \\ \gamma \frac{\partial q}{\partial t} &= \Omega [q/f(c, \overset{*}{T})][c - \varphi(q, \overset{*}{T})], \quad q_0^0 = f(c^0 - c_0, 0), \end{aligned} \quad (1)$$

$$\Omega(y) = \{b + [\omega(y)]^{-1}\}^{-1}, \quad \alpha + \gamma = 1, \quad 0 \leq z \leq L,$$

$$\frac{\partial T}{\partial t} + \frac{m_3}{m_1} \frac{\partial T}{\partial z} + \frac{m_3 m_2}{m_1} T = Q \frac{\partial q}{\partial t},$$

$$\frac{\partial \overset{*}{T}}{\partial t} = m_3 (T - \overset{*}{T}) + Q \frac{\partial q}{\partial t}, \quad (2)$$

$$c|_{z=0} = c_0 + (c^0 - 2c_0) \exp\left(\frac{z}{2\alpha}\right) \frac{\text{sh} \lambda (L - z)}{\text{sh} \lambda L}, \quad q|_{t=0} = f(c_0, 0),$$

$$\lambda = \frac{1}{2\alpha} \left\{ 1 + \frac{4\alpha}{\gamma} \left[b + \left[\omega \left(\frac{f(c_0, 0)}{q_0^0} \right) \right]^{-1} \right]^{-1} \right\}^{1/2}, \quad c|_{z=L} = c_0, \quad (3)$$

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$$T|_{t=0} = T^*|_{t=0} = T|_{z=0} = 0, c|_{z=0} = F(t), F(0) = c^0 - c_0, \quad (3)$$

$$q|_{z=0} = H(t), T^*|_{z=0} = \Phi(t), H(0) = H_0, \Phi(0) = 0.$$

The functions H and Φ in the boundary conditions are determined from the solution of the ordinary differential equations by the Runge-Kutta method:

$$\gamma \frac{dH}{dt} = \Omega(H/q_0)[F - \varphi(H, \Phi)], \quad \frac{d\Phi}{dt} = -m_3\Phi + Q \frac{dH}{dt}. \quad (4)$$

The model sorption kinetics equations (1) describe the kinetics in a mixed (external and internal) diffusion kinetic domain. Such a form is convenient in that the kind of equations is identical for the external and internal diffusion kinetic domain [3]. For nonisothermal sorption kinetics the surface coverage function ω can be found as the residual from the solution of the system of parabolic diffusion equations for the concentration and temperature with thermal diffusion taken into account [3-5]. Porous grains having a bidisperse structure (shaped zeolite, ion-exchange resins, etc.) are encountered in practice. The heat and mass transfer processes in such grains must be described separately by a system of differential equations for each "monostructure." In the general case, variable coefficients, dependent not only on the coordinates but also on the force field within the narrow "channels" (pores) of the grains, enter into the heat and mass transfer equations in porous structures. Such a system of equations is not solved successfully in the general case since the parameters and functions in these equations [3] are not known. Hence, it is reasonable to use heat and mass transfer equations containing a smaller number of parameters and describing the heat and mass transfer processes for the grain as a whole, averaged over the grain volume, to analyze the sorption dynamics in porous media. The form of the surface coverage function ω is found as the residual of the kinetics equation in each individual specific case, where the form of the kinetics equation (1) is conserved. In this sense the kinetics equation (1) is universal. The surface coverage functions of monodispersed porous grains for sorption and desorption are, respectively,

$$\begin{aligned} \omega_0(y) &= (y + \delta)^{-2} \left\{ \sum_{n=1}^3 a_n (y + \delta)^n + a_4 \exp[-a_5(1 - y)] \right\}, \\ \omega^0(y) &= (1 - y + \delta_0)^{-2} \left\{ \sum_{n=0}^3 b_n (y - \delta_0)^n + b_4 \exp(-b_5 y) \right\}, \quad y = q/f(c, T^*). \end{aligned} \quad (5)$$

The constants $a_n, b_n, \delta, \delta_0$ can be found from the exact numerical values of ω by least squares. The system (1)-(4) can only be integrated numerically by using an electronic computer for an arbitrary form of the isotherm and arbitrary initial and boundary conditions. Since the coefficients of (1)-(2) are discontinuous in the general case, then a conservative difference scheme in which the through computation converges in the class of discontinuous coefficients must be used for the numerical integration. A conservative, implicit, iteration scheme of second-order accuracy was used; the system of difference equations was solved by the factorization method [6]. It can be shown that the necessary and sufficient condition for stability and convergence of the difference scheme is compliance with the conditions

$$\begin{aligned} \tau_1 &\leq \left\{ \max \left| \left(1 - \frac{\Omega}{2\gamma A_0} \right) (g_1 + g_2) \right| \right\}^{-1}, \quad \tau_2 \leq 2\gamma \left\{ \max \left| \gamma m_3 \left[1 + \right. \right. \right. \\ &+ \left. \left. \frac{a_1}{A_0(1 + a_2)} \right] + Q \left(g_1 + g_2 - \frac{\Omega}{\gamma A_0} \right) \right| \right\}^{-1}, \quad a_1 = \frac{m_1 h}{2(1 + b_1)}, \quad a_2 = \frac{1 - b_1}{1 + b_1}, \\ \tau_3 &\leq 2\gamma \left\{ \max \left| \left(1 - \frac{\Omega}{2\gamma A_0} \right) (\theta g_1 \Omega + Q g_2) \right| \right\}^{-1}, \quad b_1 = 1/4(m_1 + m_2) h, \end{aligned}$$

$$A_0 = \frac{2\alpha}{h^2} + \frac{1}{2\gamma} \Omega(q/f(c, T^*)), \quad g_1 = \Omega \varphi'_q + \frac{\varphi - c}{f} \Omega',$$

$$g_2 = \Omega \varphi'_* - \Omega' q f' f^{-2} (\varphi - c).$$

The time spacing

$$\tau = \min(\tau_1, \tau_2, \tau_3). \quad (6)$$

must be selected for practical computations. In the general case the coefficient of diffusion within porous grains depends on the sorbate concentration. Taking this dependence into account, the exact diffusion equations of kinetics must be integrated [4, 5], and the form of the surface coverage function (5) must be found from the solution. The surface coverage function obtained must later be used in the integration of the sorption dynamics equations. If the dependence of the relative coefficient of diffusion on the sorbate concentration is described by the analytical dependence

$$g(c) = (1 + \alpha_0)(1 + \alpha_0 c)^{-2}, \quad 0 \leq c \leq 1, \quad \alpha_0 = \text{const}, \quad (7)$$

then it can be shown that the surface coverage function (5) for the thermal Langmuir function with parameter p [7]

$$q = pc(1 + pc)^{-1}, \quad p = p_0 \exp[-Q_0 T^* (1 + T^*)^{-1}]$$

with a variable diffusion coefficient in the form (7) is equivalent to the surface coverage function (5) with a constant diffusion coefficient and a thermal Langmuir function with the equivalent diameter d :

$$q = p(1 + \alpha_0)^{-1} c (1 + dc)^{-1}, \quad d = (p - \alpha_0)(1 + \alpha_0)^{-1}. \quad (8)$$

The coefficients and functions for the sorption and desorption processes are distinct in (1)-(2); for sorption $\gamma \rightarrow \gamma_0$, $\omega \rightarrow \omega_0$, $\varphi \rightarrow \varphi_0$, $f \rightarrow f_0$, while for desorption $\gamma \rightarrow \gamma^0$, $\omega \rightarrow \omega^0$, $\varphi \rightarrow \varphi^0$, $f \rightarrow f^0$. The functions φ and f can be given analytically or in tables, where quadratic or cubic interpolation must be used in the latter case. To determine the conditions under which sorption or desorption will proceed, let us use the inequalities

$$c_i^{(s)j+\frac{1}{2}} > a_0 \varphi(q_i^{(s)j+\frac{1}{2}}, T_i^{*(s)j+\frac{1}{2}}), \quad a c_i^{(s)j+\frac{1}{2}} = \varphi(q_i^{(s)j+\frac{1}{2}}, T_i^{*(s)j+\frac{1}{2}}), \quad (9)$$

$$a^0 c_i^{(s)j+\frac{1}{2}} < \varphi(q_i^{(s)j+\frac{1}{2}}, T_i^{*(s)j+\frac{1}{2}}), \quad a_0, a, a^0 = \text{const}. \quad (10)$$

Sorption proceeds upon compliance with condition (9), and desorption upon compliance with (10). Let us use the conditions

$$q_0^j > a_0 q_0^{j-1}, \quad a q_0^j = q_0^{j-1} \quad (11)$$

$$a^0 q_0^j < q_0^{j-1}, \quad (12)$$

to select the form of the function φ (or f) in (9), (10), where $\varphi \rightarrow \varphi_0$ in (9), (10) upon compliance with (11), and $\varphi \rightarrow \varphi^0$ upon compliance with (12). The values of q_0^j are found from the solutions of (4). The heat transfer coefficients can differ depending on whether heating or cooling of the porous medium by the mixture sorbed occurs. Upon compliance with the conditions

$$T_i^{*(s)j+\frac{1}{2}} > b_0 T_i^{(s)j+\frac{1}{2}}, \quad b T_i^{*(s)j+\frac{1}{2}} = T_i^{(s)j+\frac{1}{2}} \quad (13)$$

heating of the porous medium occurs and $m_1 \rightarrow m_{01}$, $m_3 \rightarrow m_{03}$ must be substituted in (1), (2).

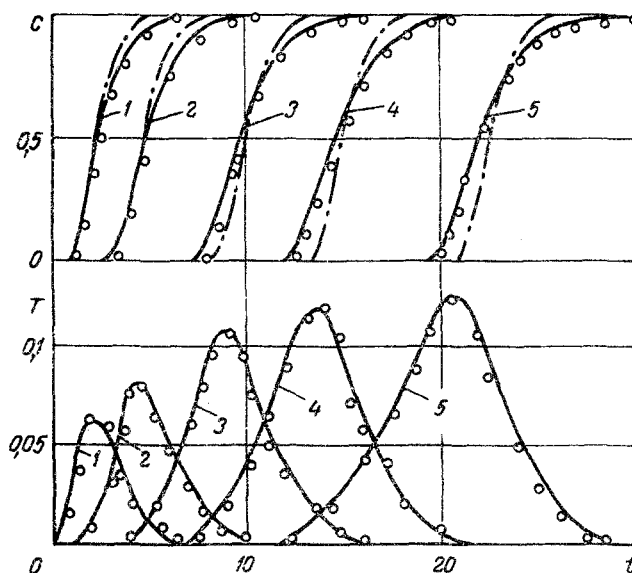


Fig. 1. Output curves of the sorbate concentration and gas-carrier stream temperature distributions for different column lengths.

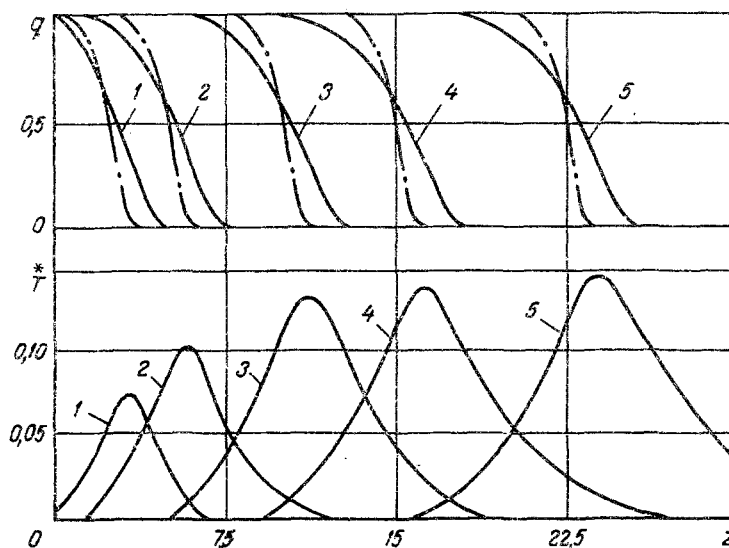


Fig. 2. Distribution of the construction of absorbed substances and the porous grain temperatures along a column for different times.

Upon compliance with the inequalities

$$b^0 T_i^{(s)j + \frac{1}{2}} < T_i^{(s)j + \frac{1}{2}}, \quad b_0, b, b^0 = \text{const} \quad (14)$$

cooling of the porous medium occurs and $m_1 \rightarrow m_1^0$, $m_3 \rightarrow m_3^0$ must be substituted in (1), (2).

The magnitudes of the coefficients of the equations must be known for practical numerical computations using (1), (2), i.e., in substances the inverse problem must be solved under definite conditions. The method of determining the kinetic coefficients for the external and internal diffusion kinetics of sorption has been considered in [8]. The sorption isotherm can be considered linear for very low concentrations and thermal effects can be neglected. The magnitude of the symmetry parameter ν of the porous grains, the porosity σ , and the effective coefficient of longitudinal mixing D

(the longitudinal dispersion) can be found by using the method of statistical moments [9] for low concentrations (linear isotherm region). The heat transfer coefficients m_1, m_2, m_3 can be determined from the solution of the inverse problem of the motion of a thermal perturbation through a porous medium [10]. The output frontal dynamical concentration distribution curves [11] and the temperature in the stream of a gas-carrier were measured for different porous column lengths in order to confirm the model equations (1), (2). The results of the experiment are shown in Figs. 1 and 2 by circles. The porous medium was almost spherical grains of medium-porous silica gel. Benzene at $p/p_s = 0.7$ was used as the sorbate, and purified nitrogen as the gas-carrier. The temperature was measured by using a copper-constantan thermocouple. The heat and mass transfer coefficients in a porous medium were determined experimentally by the method of [8-10], and the dimensionless coefficients in (1), (2) were then computed. The system of equations of nonisothermal sorption dynamics was integrated on the BESM-6 electronic computer by a difference scheme, for known coefficients and with the following parameters: $\alpha = 0.1, \gamma = 0.9, b = 0, \tau_0 = 4.5 \text{ min}, p_0 = 10, \alpha_0 = 1.2, Q = 0.146, Q_0 = 4, m_{01} = 2.4, m_2 = 0.2, m_{03} = 4, m_1^0 = 1.25, m_3^0 = 2.1$. The output curves of the sorbate concentration and the gas-carrier stream temperature are shown by solid lines in Fig. 1 for different column lengths (1, $z = 2.5; 2, 5; 3, 10; 4, 15; 5, 22.5$). The concentration distribution of the absorbed substance and the porous grain temperatures for distinct times along the columns are shown in Fig. 2 (1, $t = 2.5; 2, 5; 3, 10; 4, 15; 5, 22.5$). The dot-dash lines in the figure show the computed curves without heat liberation during sorption. The difference between the experimental and theoretical values of the concentration without taking account of heat liberation can be significant for high values of the initial sorbate concentration.

2. Upon compliance with the conditions which will be presented below, for a convex sorption isotherm a quasistationary front mode will build up in a porous column after the lapse of a definite time. This mode will correspond to a quasi-invariant solution of the Galilean transport operator [12], $w(\partial/\partial z) - (\partial/\partial t)$ (w is the velocity to be determined). By using group theory methods [13], it can be shown that the quasistationary mode builds up for $m_2 = 0$. In this case, for

$$c_0 = 0, H_0 = 0, F(t) = 1 \quad (15)$$

the system (1), (2) is

$$c - \omega q = \alpha \frac{dc}{dy}, \quad -\gamma \omega \frac{dq}{dy} = \Omega [q/f(c, T^*)][c - \varphi(q, T^*)], \quad (16)$$

$$T^* - aT = Qq, \quad \frac{dT^*}{dy} = -\frac{m_3}{\omega} (T - T^*) + Q \frac{dq}{dy},$$

$$a = \frac{m_3}{m_1 \omega}, \quad y = z - \omega t, \quad \omega = c_*/q_*, \quad q^* = q_*(1 - a)^{-1}, \quad (17)$$

$$T_* = \max T = \max T^*, \quad c_* = \max c, \quad q_* = \max q \text{ (in the wavefront)}$$

$$T_* = Qq^*, \quad q_* = f(c_*, T_*), \quad c(y_0) = c_*, \quad q(y_0) = q_*, \quad (18)$$

$$T(y^*) = T^*(y_*) = T_*, \quad c(+\infty) = q(\infty) = T(\infty) = T^*(\infty) = 0.$$

The quantity q_* is found from the integral form of the material balance equation. The values of c_*, T_* are determined from the solution of a transcendental system of algebraic equations $q_* = f(c_*, T_*)$, $T_* = Qq^*$. The constants y_0, y_* are found from the integral form of (1), (2):

$$y_0 = -\frac{1}{q_*} \int_{y_0}^{\infty} q(y) dy + \alpha \left[1 - \frac{c(0)}{c_*} \right], \quad y_* + \frac{1}{T_*} \int_{y_*}^{\infty} T^*(y) dy = y_0 + \frac{1}{q_*} \int_{y_0}^{\infty} q(y) dy. \quad (19)$$

The system (16), (17) can be reduced to a second-order and first-order equation and the system obtained can be integrated by the factorization method. It follows from physical considerations for the conditions (18) that the functions q , c should decrease monotonely as y increases. Taking this into account, we find from (16), (17)

$$\omega q > c > \varphi(q, T^*). \quad (20)$$

The thermal functions for which it is impossible to draw a tangent from the point $[c_0, f(c_0, 0)]$ to the curve (c, T) and for which condition (20) is satisfied, will be called convex.

The general solution of the inhomogeneous system (17) is

$$\begin{aligned} \frac{T}{T_*} &= B \exp(\mu y) + m_1 Q \exp(\mu y) \int q(y) \exp(-\mu y) dy, \quad \mu = -m_1(1-a), \\ \frac{T^*}{T_*} &= aB \exp(\mu y) + Qq + am_1 Q \exp(\mu y) \int q(y) \exp(-\mu y) dy, \quad B = \text{const}. \end{aligned} \quad (21)$$

For boundedness of the solution (21) we have $\mu < 0$. Hence,

$$\omega > m_3/m_1. \quad (22)$$

Upon compliance with condition (22) and $m_2 = 0$ a quasi-invariant solution of the quasi-stationary front type (a traveling wave) exists for a convex thermal function. The solution of the system (16), (17) can be found in analytic form for a step-thermal function and an approximate surface coverage function

$$\omega(y) = b/y. \quad (23)$$

After manipulation, we write the approximate solution in this case as

$$\begin{aligned} \frac{q}{q_*} &= \begin{cases} 1, & y \leq y_0, \\ \frac{1}{2} + \frac{b\alpha}{\gamma} - \frac{b}{\gamma} y, & y_0 \leq y \leq y_2, \\ 0, & y \geq y_2, \end{cases} \quad \frac{c}{c_*} = \begin{cases} 1, & y \leq y^0, \\ \frac{1}{2} - \frac{b}{\gamma} y, & y^0 \leq y \leq y_1, \\ 0, & y \geq y_1, \end{cases} \\ y^0 &= -\gamma/(2b), \quad y_1 = \gamma/(2b), \quad y_0 = \alpha + y^0, \quad y_2 = \alpha + y_1, \\ \frac{T}{T_*} &= \begin{cases} 1, & y \leq y^*, \\ -\frac{m_1}{\mu} \left(\frac{1}{2} + \frac{b\alpha}{\gamma} - \frac{b}{\gamma} y \right), & y^* \leq y \leq y_2, \\ 0, & y \geq y_2 \end{cases} \\ \frac{T^*}{T_*} &= \begin{cases} 1, & y \leq y_*, \\ \left(1 - \frac{m_1 a}{\mu} \right) \left(\frac{1}{2} + \frac{b\alpha}{\gamma} - \frac{by}{\gamma} \right), & y_* \leq y \leq y_2, \\ 0, & y \geq y_2. \end{cases} \end{aligned} \quad (24)$$

The constants y^* , y_* are found from the equations

$$\left(1 - \frac{m_1 a}{\mu} \right) q(y_*) = 1, \quad -\frac{m_1}{\mu} q(y^*) = 1.$$

The solution (24) can be used to describe the nonisothermal dynamics of sorption for a porous medium consisting of finely-porous silica gels, zeolites, and zeolite-containing sorbents.

NOTATION

c is the sorbate concentration in the stream; q is the concentration of absorbed substance; z and t are the dimensionless coordinate and time; α is the relative longitudinal mixing coefficient; $\alpha = \tau_D(\tau_D + \tau_i)^{-1}$; τ_D is the deceleration time due to longitudinal effective mixing; τ_i is the deceleration time due to the finite rate of internal diffusion mass transfer; $\gamma = \tau_i(\tau_D + \tau_i)^{-1}$, γ is the relative kinetic coefficient; $b_0 = \tau_e/\tau_i$; τ_e is the deceleration time due to finite rate of external diffusion mass transfer; $\omega(y)$ is the surface coverage function of a porous grain; $\hat{T}_{true} = T_0^0(1 + T)$; T_0^0K is the initial temperature; T is the temperature in the gas (liquid) stream; \hat{T}^* is the solid phase temperature of the porous grain; $\hat{T}_{true}^* = T_0^0(1 + \hat{T}^*)$; Q is the thermal effect of sorption; m_1 , m_3 are the kinetic heat transfer coefficients; m_2 is the kinetic heat transfer coefficient from the cylindrical channel wall of a porous medium; τ and h are time and coordinate spacing; $\tau_0 = \tau_D + \tau_i$; $t = t'/\tau_0$; $z = \delta z'/(u\tau_0)$; $g(c) = D(c)/D(c^*)$; t' and z' are the dimensional time and coordinate; $c^* = \max c$.

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