ISOTHERMAL KINETICS OF SORPTION IN POROUS MEDIA

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A system of quasi-linear parabolic equations describing nonisothermal sorption kinetics in porous grains is analyzed. Model equations for sorption kinetics with complete derivatives are considered with regard for sorption heat release. The accuracy of different model kinetic equations is estimated. A method is proposed to determine heat transfer coefficients in porous grains. Experimental relationships are obtained describing the dependence of the kinetic curve and mean temperature distribution on time for porous grains of silica gel when benzene vapors are used as sorbate. Experimental relationships are compared with those calculated on an electronic digital computer, their agreement being satisfactory. This proves the application of complete-derivative model equations to be reasonable for practical calculations of nonisothermal sorption kinetics.

The kinetics of sorption in porous grains of sorbent is always accompanied by the generation of heat. The nonisothermal kinetics of sorption in a vacuum and in a gas-carrier stream have been experimentally investigated in a number of studies [1-3]. In the present article we shall consider exact and approximate model equations that can be used to describe the nonisothermal kinetics of sorption in porous grains. The nonisothermal kinetics of sorption is described by the equation of material balance in a porous grain (1), the equation of heat balance for the gas (liquid outside the grain (2), and the equation of heat balance for the solid phase of the porous grain (3), together with the appropriate initial and boundary conditions:

$$\frac{\partial q}{\partial t} = \frac{1}{r^{\nu}} \frac{\partial}{\partial r}\left[r^{\nu} g(c) \frac{\partial c}{\partial r}\right] + \varkappa \frac{1}{r^{\nu}} \frac{\partial}{\partial r}\left[r^{\nu} \frac{\partial T}{\partial r}\right], \quad q = f(c, \overset{*}{T}), \tag{1}$$

$$\frac{\partial T}{\partial t} = \chi \frac{1}{r^{\nu}} \frac{\partial}{\partial r}\left[r^{\nu} \frac{\partial T}{\partial r}\right] + \gamma(\overset{*}{T} - T), \quad 0 \leqslant r \leqslant 1, \tag{2}$$

$$\frac{\partial \overset{*}{T}}{\partial t} = \chi_i \frac{1}{r^{\nu}} \frac{\partial}{\partial r}\left[r^{\nu} \frac{\partial \overset{*}{T}}{\partial r}\right] + \gamma_i (T - \overset{*}{T}) + Q \frac{\partial q}{\partial t}, \tag{3}$$

$$\left(r^{\nu} \frac{\partial c}{\partial r}\right)\Big|_{r=0} = 0, \quad \left(r^{\nu} \frac{\partial \overset{*}{T}}{\partial r}\right)\Big|_{r=0} = 0, \quad \left(r^{\nu} \frac{\partial T}{\partial r}\right)\Big|_{r=0} = 0, \tag{4}$$

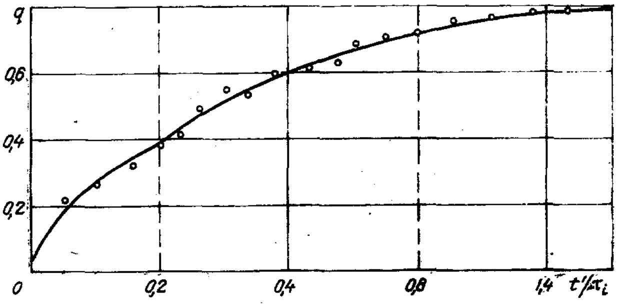

Fig. 1. Kinetic curve ($q_0 = 0.8$; $\tau_i = 9.8$ min): the plotted points represent the experimental data, and the curve represents the calculated function.

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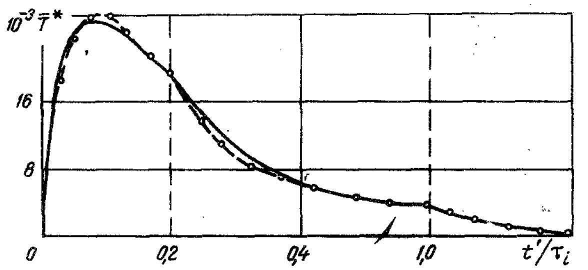

Fig. 2. Distribution of the average temperature in a grain.

$$c|_{r=1}=1,\quad c|_{t=0}=0,\quad T|_{r=1}=0,\quad \overset{*}{T}|_{r=1}=0,\quad T|_{t=0}=0,\quad \overset{*}{T}|_{t=0}=0. \tag{5}$$

Condition (4) corresponds to symmetry at the center of the grain. To integrate the quasilinear system of equations, we must know the numerical parameters (D_i, D_T, k, ν, χ_0, χ_i^0, α, Q_*), which are very difficult to determine experimentally. It is therefore necessary to simplify the system (1)-(5) in such a way that, in the first place, we retain a smaller number of parameters and, in the second place, the system will be a system of equations in total derivatives. Such a model equation for the kinetics in ordinary derivatives can be used for solving problems of sorption dynamics in a gas-carrier stream. Writing

$$\bar{q}=(1+\nu)\int_0^1 r^\nu q\,dr,\quad \bar{T}^*=(1+\nu)\int_0^1 r^\nu \overset{*}{T}\,dr,$$

for g(c) = 1, taking account of the system (1)-(5), we can write the model system of equations for nonisothermal sorption kinetics:

$$\frac{d\bar{q}}{dt}=\beta\omega(\bar{q}/q_0)\,[1-\varphi(\bar{q},\bar{T}^*)],\quad \beta=(1+\nu)(3+\nu), \tag{6}$$

$$\frac{d\bar{T}^*}{dt}=-\rho(\bar{T}^*/\bar{T}_0^*)\,m_3\bar{T}^*+Q\frac{d\bar{q}}{dt},\quad \bar{T}^*|_{t=0}=0,\ \bar{q}|_{t=0}=0, \tag{7}$$

$$q_0=\max(\bar{q}),\ \bar{T}_0^*=\max(\bar{T}^*),\ \bar{q}=f(c,\ \bar{T}^*),\ \varphi=f^{-1}. \tag{8}$$

The functions ω and ρ are found from a numerical solution of the exact quasilinear equations (1)-(5):

$$\omega=\frac{\bar{q}^{j+1}-\bar{q}^{j}}{\beta\tau\left[1-\varphi\left(\bar{q}^{j+\frac{1}{2}},\bar{T}^{*j+\frac{1}{2}}\right)\right]},\quad \bar{q}^{j+\frac{1}{2}}=\frac{1}{2}(\bar{q}^{j}+\bar{q}^{j+1}), \tag{9}$$

$$\rho=\frac{\bar{T}^{*j+1}-\bar{T}^{*j}-Q\bar{q}^{j+1}+Q\bar{q}^{j}}{m_3\tau\bar{T}^{*j+1/2}},\quad \bar{T}^{*j+\frac{1}{2}}=\frac{1}{2}(\bar{T}^{*j}+\bar{T}^{*j+1}). \tag{10}$$

The graphs obtained from Eqs. (9), (10) are processed by the methods of least squares in order to obtain simple analytic functional relationships. From processing of a number of relationships it is found that the most successful analytic form of the functions is the following:

$$\omega(\tilde{q})=(\tilde{q}+\delta)^{-2}\left\{\sum_{n=0}^{3}a_n(\tilde{q}+\delta)^n+a_4\exp[-a_5(1-\tilde{q})]\right\},\ \tilde{q}=q/q_0, \tag{11}$$

$$\rho(\tilde{T})=(\tilde{T}-\delta_0)^{-2}\left\{\sum_{n=0}^{3}b_n(\tilde{T}+\delta_0)^n\right\},\ \tilde{T}=\bar{T}^*/\bar{T}_0. \tag{12}$$

In this formulation the model equations (6)-(8) are inconvenient, since in order to define the functions (9), (10), we must proceed each time to a new numerical integration of the system (1)-(5) for the new parameters (D_i, D_T, $\chi_0\cdot\chi_i$, α, Q_*). It has been shown experimentally that the temperature does not vary very much during the sorption process, and therefore it has been proposed to use the following approximate system of model kinetic equations:

$$\frac{d\bar{q}}{dt}=\beta\omega(\bar{q})\,[1-\varphi(\bar{q},\ \bar{T}^*)], \tag{13}$$

$$\frac{d\bar{T}^*}{dt}=-m_3\bar{T}^*+Q\frac{d\bar{q}}{dt}. \tag{14}$$

We calculate the function ω in Eq. (13), with $\bar{T}^* = 0$, for various types of isotherms, i.e., we essentially determine the function ω for $q_0|_{\bar{T}^*=0} = q_0^0$ and then substitute $q_0|_{\bar{T}^* \neq 0} = q_0$ into the argument of this function.

The most widely used isotherm is the Langmuir isotherm:

$$q = \frac{\tilde{p}c}{1+\tilde{p}c}, \quad \tilde{p} = p \exp\left[-Q_0 \frac{\bar{T}^*}{1+\bar{T}^*}\right], \quad \varphi = \frac{1}{\tilde{p}} \cdot \frac{q}{1-q},$$

$$q_0 = \frac{\tilde{p}}{1+\tilde{p}}, \quad q_0^0 = \frac{p}{1+p}. \tag{15}$$

For the isotherm (15) the form of Eqs. (13)-(14) is convenient, and in a certain sense it is universal. Specifically, once we have calculated the coefficients a_n in (11) numerically, with $\bar{T}^* = 0$, for some Langmuir isotherm parameters p, we can graphically construct the function $a_n = F(p)$, and using this graph, we can easily find the coefficients a_n for any parameters p.

Knowing the coefficients, we can obtain the analytic form of the function $\omega(\bar{q}/\bar{q}_0)$. The linear equation (14) is suitable, since by using this equation we can calculate the coefficients m_3, Q. Taking account of the proposed method, from Eq. (14) we find the first and second principal moments:

$$0 = -m_3\alpha_1(\bar{T}^*) + Q\bar{q}_0, \quad -\alpha_1(\bar{T}^*) = -m_3\alpha_2(\bar{T}^*) + Qt_0\bar{q}_0 - Q\alpha_1(\bar{q}), \tag{16}$$

$$\alpha_1(\bar{T}^*) = \int_0^\infty \bar{T}^* dt, \quad \alpha_1(\bar{q}) = \int_0^\infty \bar{q}\, dt, \quad \alpha_2(\bar{T}^*) = \int_0^\infty t\bar{T}^* dt, \quad \bar{q}_0 = \bar{q}_0(t_0). \tag{17}$$

Solving the algebraic system (16), we obtain

$$m_3 = \alpha_1(\bar{T}^*)A^{-1}, \quad Q = \frac{1}{\bar{q}_0}\alpha_1^2(\bar{T}^*)A^{-1}, \quad A = \alpha_2(\bar{T}^*) + \alpha_1(\bar{T}^*) \times \left[\frac{1}{\bar{q}_0}\alpha_1(\bar{T}^*) - t_0\right]. \tag{18}$$

Making use of the experimental functions $\bar{T}^*(t)$, $\bar{q}(t)$, we calculate the moments from the relations (17), and using these, we find the values of the coefficients m_3, Q from (18).

In order to verify the model equations (13)-(14), we took kinetic curves and temperature curves on a dynamic apparatus. The results are shown in Figs. 1 and 2.

The sorbent used was spherical fine-grained silica gel with a grain diameter of 2.5 mm. For the sorbate we used benzene vapors with $p/p_s = 0.3$; $Q_0 = +4$; $Q = 0.19$; $m_3 = 12.8$; $T_0^\circ = 293$°K. The isotherm for such benzene vapors can be described by a Langmuir curve with parameter p = 4. The temperature was measured by means of a copper—Constantan thermocouple (0.02 mm thick). As the average temperature of the grain, we took the tentative arithmetic-mean temperature at the center of the grain and near its periphery. The theoretical functions $\bar{q}(t)$, $\bar{T}^*(t)$ were calculated as follows. The quasilinear equation (1) with $g(c) = 1$, $\varkappa = 0$ was numerically integrated on the BÉSM-6 computer. From Eq. (9) we found the form of the function $\omega(\bar{q}/q_0^0)$ and then the function $\omega(\bar{q}/q_0)$. The coefficients m_3, Q were found by the method indicated above, i.e., from Eqs. (17), (18), and the quantities Q_*, Q_0 were found by using Q, which had already been determined. The thermal effect of the sorption, Q_*, was found to be the same by the proposed method as by the method of graphical processing of isosteres [4]. The known values of m_3 and Q were used for numerically integrating Eqs. (13), (14) on the computer by the Runge—Kutta method. The small differences between the experimental and calculated results are explained by the fact that in Eq. (14) $\rho = 1$.

To get more exact calculations for $\bar{T}^*(t)$, the system (6), (7) must be used instead of (13), (14), but the method of determining m_3, Q must be the same as was used for the system (13), (14). The form of the function ρ may be selected in various ways. Experience indicates that the most successful way is to choose ρ in a manner analogous to ω. Analysis shows that for $\rho \neq 1$ the interval for time τ in the numerical integration is reduced by a factor of almost 10 (and the computation time is proportionally increased). Since the experimental $\bar{T}^*$ results do not differ much from those calculated by Eq. (14), using Eqs. (13), (14) for calculating the nonisothermal kinetics and dynamics of sorption is a reasonable procedure, since this saves a considerable amount of computer time.

NOTATION

c	is the concentration of sorbate material within a porous grain of sorbent;
q	is the concentration of absorbed material;
$g(c)$	is the coefficient for taking account of the variation of the diffusion coefficient as a function of concentration;
D_i	is the effective diffusivity within a porous grain;
ν	is the symmetry parameter ($\nu = 2$ for a spherical grain of radius a, $\nu = 1$ for a cylindrical grain of radius a, $\nu = 0$ for grains which have the shape of plates with thickness $2a$);
χ_0	is the thermal conductivity of the gas (liquid) within the grain;
D_T,	is the coefficient of thermal diffusion of the gas (liquid) within the grain;
α	is the coefficient of heat exchange of the gas (liquid) with the solid phase of the porous grain;
ρ	is the density of the gas (liquid);
c	is the thermal capacity of the gas (liquid);
χ_i^0	is the thermal conductivity of the solid phase of the porous grain;
c_T	is the thermal capacity of the solid phase of the porous grain;
ρ_T	is the density of the solid phase of the porous grain;
Q_*	is the thermal effect of adsorption;
T_u, T_u^*	are the true temperatures in °K of the gas (liquid) and the solid phase of the porous grain, respectively;
T_0^0	is the temperature of the surrounding medium in °K;
R	is the gas constant.

$t = t'D_i/ka^2$;

$k = dq(0)/dc$;

$r = r'/a$;

$\chi = k\chi_0/D_i$;

$\varkappa = kD_T/D_i$;

$\gamma = \alpha k/a^2 c\rho D_i$;

$\chi_i = \chi_i^0 k/D_i$;

$\gamma_i = \alpha k/a^2 C_T \rho_T D_i$;

$Q = Q_*/C_T \rho_T T_0^0$;

$Q_0 = Q_*/RT_0$;

$T_u = T_0^0 (1 + T)$;

$T_u^* = T_0^0 (1 + T)$;

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