

INTEGRATION OF NONLINEAR EQUATIONS OF  
EQUILIBRIUM KINETICS OF PHYSICAL SORPTION  
WITH REGARD TO HEAT RELEASE

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The accuracy is analyzed of the equations for a model for anisothermic sorption kinetics in porous granules.

The equilibrium kinetics of physical sorption can be described by means of the quasilinear equations of material balance, the thermal equation of sorption (1), the equation of thermal balance for liquefied gas inside a porous granule (3), the initial conditions (4) and the boundary conditions (5)-(7):

$$\frac{\partial c}{\partial t} + \frac{\partial q}{\partial t} = r^{-\nu} \frac{\partial}{\partial r} \left[ r^{\nu} \frac{\partial c}{\partial r} \right] + \kappa \cdot r^{-\nu} \frac{\partial}{\partial r} \left[ r^{\nu} \frac{\partial T}{\partial r} \right], \quad q = f(c, T^*), \quad (1)$$

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

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

$$c|_{t=0} = c^0, \quad T|_{t=0} = T^*|_{t=0} = 0, \quad (4)$$

$$c|_{r=1} = c_0, \quad T|_{r=1} = T^*|_{r=1} = 0, \quad (5)$$

$$c_0 = \left( c + \alpha_0 \frac{\partial c}{\partial r} \right) \Big|_{r=1} + \alpha_1 \frac{\partial T}{\partial r} \Big|_{r=1}, \quad \left( T + \alpha_2 \frac{\partial T}{\partial r} \right) \Big|_{r=1} = 0, \quad (6)$$

$$\left( T^* + \alpha_3 \frac{\partial T^*}{\partial r} \right) \Big|_{r=1} = 0, \quad (6)$$

$$\left( r^{\nu} \frac{\partial c}{\partial r} \right) \Big|_{r=0} = \left( r^{\nu} \frac{\partial T}{\partial r} \right) \Big|_{r=0} = \left( r^{\nu} \frac{\partial T^*}{\partial r} \right) \Big|_{r=0} = 0. \quad (7)$$

The boundary conditions (5) relate to the internal-diffusion heat and mass exchange, and the conditions (6) to the mixed external and internal diffusion heat and mass exchange.

In the general case the system of equations (1)-(7) can be integrated only numerically with the aid of a digital computer. The disadvantage of such a system lies in that firstly one has to determine experimentally a great number of parameters, ( $\kappa$ ,  $\chi_i$ ,  $\chi$ ,  $\gamma$ ,  $\gamma_i$ ,  $Q$ ) if numerical integration is to be used. It seems, therefore, reasonable that one should try to replace the exact system (1)-(3) by an approximate one though with a smaller number of numerical parameters:

$$\beta \frac{\partial q}{\partial t} + \frac{\beta}{k} \frac{\partial c}{\partial t} = r^{-\nu} \frac{\partial}{\partial r} \left[ r^{\nu} \frac{\partial c}{\partial r} \right], \quad q = f(c, T), \quad t = \frac{t'}{\tau_i}, \quad (8)$$

$$\tau_i = \frac{ka^2}{\beta D_i} [1], \quad (8)$$

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$$\frac{\partial T}{\partial t} = \frac{d^2}{\beta} r^{-\nu} \frac{\partial}{\partial r} \left[ r^\nu \frac{\partial T}{\partial r} \right] + Q \frac{\partial q}{\partial t}, \quad d^2 = \frac{\tau_i}{\tau_T}, \quad \tau_T = \frac{a^2}{\beta D_T},$$

$$\beta = (1 + \nu)(3 + \nu), \quad (9)$$

where T is the characteristic temperature of an elementary volume of a porous granule.

The boundary-value problem for the quasilinear system (8)-(9), (4)-(7) with an arbitrary function f can be integrated only numerically. However, for a stepwise sorption isotherm,

$$q = \begin{cases} 0, & 0 = c, \\ k, & 0 < c \leq 1, \end{cases} \quad \varphi = \begin{cases} 0, & 0 \leq q < k, \\ 1, & q = k, \end{cases} \quad (10)$$

which is a limit of the convex Langmuir isotherm, the exact solution of Eqs. (8)-(9) can be obtained in an analytic form by reducing our problem to a Stefan problem [2]. In the latter case using the conditions (4) and (5) for  $c_0 = 1$ ,  $c^0 = 0$ ,  $\nu = 0$  we can write

$$\beta \frac{\partial c}{\partial t} = k \frac{\partial^2 c}{\partial r^2}, \quad 0 < c \leq 1, \quad q = k \cdot \eta(r-l), \quad l(t) \leq r \leq 1, \quad c|_{r=1} = 1, \quad (11)$$

$$c|_{r=0} = 0, \quad q = c = 0, \quad 0 \leq r < l(t), \quad l(0) = 1, \quad c(l \pm 0, 0) = \frac{\partial c(l \pm 0, 0)}{\partial r} = 0, \quad (12)$$

$$\frac{\partial T}{\partial t} = \frac{d^2}{\beta} \frac{\partial^2 T}{\partial r^2} + \begin{cases} Q \frac{\partial q}{\partial t}, & 0 \leq t \leq t_1, \\ 0, & t_1 < t < \infty, \end{cases} \quad q(t_1) = 1, \quad (13)$$

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = T|_{r=1} = 0, \quad 0 \leq r \leq 1, \quad k = \max q_{\text{true}} / \max c_{\text{true}}. \quad (14)$$

The solution of Eqs. (11)-(12) is given by

$$c(r, t) = 1 - \operatorname{erf} \left( \frac{1-r}{2 \sqrt{kt/\beta}} \right) [\operatorname{erf}(\alpha/\sqrt{k})]^{-1}, \quad q = k \cdot \eta \left[ \frac{r-l(t)}{2 \sqrt{kt/\beta}} \right],$$

$$l(t) = 1 - 2\alpha \sqrt{\frac{t}{\beta}}. \quad (15)$$

By using the integral form of the first equation in (8) a transcendental equation is obtained for  $\alpha$ :

$$\alpha \sqrt{\pi k} \operatorname{erf}(\alpha/\sqrt{k}) = \exp(-\alpha^2/k),$$

whose solution is  $\alpha = 0.671$  (for  $k = 1$ ),  $\alpha = 0.705$  (for  $k \gg 1$ ). The solution of Eqs. (13)-(14) is found in the form

$$T(r, t) = \begin{cases} \int_0^t \int_0^1 G(r, t, \xi, \tau) Q \frac{\partial q}{\partial \tau}(\xi, \tau) d\xi d\tau, & 0 \leq t \leq t_1, \\ \int_0^1 G(r, t, \xi, 0) T_1(\xi) d\xi, & t_1 \leq t < \infty, \end{cases} \quad (16)$$

$$T_1(r) = T(r, t_1), \quad t_1 = \frac{\beta}{4\alpha^2}, \quad b_n = \frac{\pi}{2} (2n+1),$$

$$G(r, t, \xi, \tau) = 2 \sum_{n=0}^{\infty} \exp \left[ -\frac{d^2 b_n^2}{\beta} (t-\tau) \right] \cos b_n r \cos b_n \xi,$$

where  $G(r, t, \xi, \tau)$  is the Green's function.

By transforming Eq. (16) one obtains

$$T(r, t) = \begin{cases} \sum_{n=0}^{\infty} \cos b_n r H_n(t), & 0 \leq t \leq t_1, \\ \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \cos b_n r F_{n,k}(t), & t_1 \leq t < \infty, \end{cases} \quad (17)$$

$$H_n(t) = \frac{1}{b_n} (-1)^n k Q \exp(\alpha^2/d^2) \exp \left[ -\frac{d^2 b_n^2}{\beta} t \right] (\sqrt{\pi} \alpha/d) \times$$

$$\times \left[ \operatorname{erf} \left( \frac{\alpha}{d} + i d b_n \sqrt{t/\beta} \right) + \operatorname{erf} \left( \frac{\alpha}{d} - i d b_n \sqrt{t/\beta} \right) - 2 \operatorname{erf} \left( \frac{\alpha}{d} \right) \right], \quad (18)$$

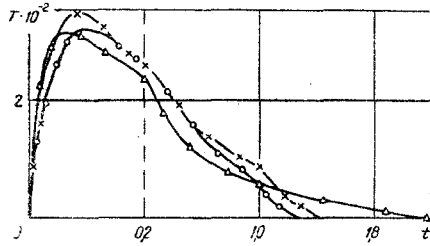


Fig. 1. Mean temperature of a porous granule v. time.

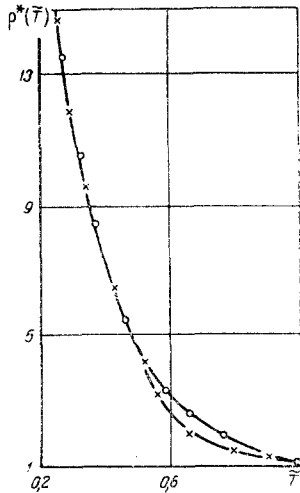


Fig. 2. Heat-exchange function inside a porous granule.

$$F_{n,h}(t) = H_n(t_1) \exp \left[ -\frac{d^2 b_n^2}{\beta} (t - t_1) \right] \left[ \frac{\sin(b_n + b_h)}{(b_n + b_h)} + \frac{\sin(b_n - b_h)}{(b_n - b_h)} \right].$$

For numerical values of  $H_n(t)$  one can make use of the tables in [3, 4]. Having expanded the function  $\text{erf}(x)$  into a series one can write the expressions for the functions  $H_n(t)$  for  $R \gg 1$  as follows:

$$H_n(t) = \frac{1}{b_n} (-1)^n kQ \left\{ \left( \frac{4\alpha}{d} \right) \sum_{k=0}^{\infty} \frac{1}{(2k+1)!!} 2^k R^{k+1/2} \cdot \cos[(2k+1)\varphi_n - 2\alpha b_n \sqrt{t/\beta}] - 2 \left( \frac{\alpha \sqrt{\pi}}{d} \right) \exp[-d^2 b_n^2 t/\beta + \alpha^2 d^{-2}] \text{erf}(\alpha/d) \right\}, \quad (19)$$

$$R = \left[ \frac{\alpha^2}{d^2} + \frac{d^2 b_n^2 t}{\beta} \right]^{1/2},$$

for  $R \gg 1$

$$H_n(t) = \frac{1}{b_n} (-1)^n kQ \left\{ \left[ 2 - 2\text{erf} \left( \frac{\alpha}{d} \right) \right] \frac{\alpha \sqrt{\pi}}{d} \times \right. \\ \times \exp[-d^2 b_n^2 t/\beta + \alpha^2 d^{-2}] - 2 \frac{\alpha}{d} \sum_{k=0}^{\infty} (-1)^k 2^{-k} R^{-k-1/2} (2k+1)!! \times \\ \left. \times \cos[(2k+1)\varphi_n + 2\alpha b_n \sqrt{t/\beta}] \right\}, \quad \varphi_n = \text{arctg}(\alpha^{-1} d^2 b_n \sqrt{t/\beta}). \quad (20)$$

The analytic solutions (15)-(17) are of particular interest when one estimates the error of the approximating model system of equations for anisothermic kinetics of sorption. For concentrations and temperature averaged over a granule one obtains from (8)-(9)

$$\frac{d\bar{q}}{dt} = \frac{(1+\nu)k}{\beta} \frac{\partial c}{\partial r} \Big|_{r=1}, \quad \frac{d\bar{T}}{dt} = \frac{d^2(1+\nu)}{\beta} \frac{\partial T}{\partial r} \Big|_{r=1} + Q \frac{d\bar{q}}{dt}, \quad (21)$$

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

Using Eqs. (21) the model system of equations of anisothermic kinetics can be written as

$$\frac{d\bar{q}}{dt} = \omega(\bar{q}) [1 - \varphi(\bar{q}, \bar{T})], \quad \frac{d\bar{T}}{dt} = \rho(\bar{T}) \bar{T} + Q \frac{d\bar{q}}{dt}, \quad \bar{q} = \frac{\bar{q}}{\max \bar{q}}, \quad (22)$$

$$\omega(\bar{q}) = \frac{(1+\nu)}{\beta} \frac{\partial c}{\partial r} \Big|_{r=1} \cdot [1 - \varphi(\bar{q}, \bar{T})]^{-1}, \quad \rho(\bar{T}) = -\frac{d^2(1+\nu)}{\beta \bar{T}} \frac{\partial T}{\partial r} \Big|_{r=1}, \quad \bar{T} = \frac{\bar{T}}{\max \bar{T}}, \quad (23)$$

where  $\omega(\bar{q})$  is a function of filling the granule with the sorbed substance;  $\rho(\bar{T})$  is the function of heat-exchange inside a porous granule.

For a stepwise isotherm we find with the aid of the solutions (15)-(17)

$$\bar{q} = \frac{2(1+\nu)\sqrt{k}}{\text{erf}(\alpha\sqrt{k})} \sqrt{\frac{t}{\pi\beta}}, \quad \omega(\bar{q}) = \frac{1}{\bar{q}} \left\{ \frac{2(1+\nu)}{\pi k(3+\nu) [\text{erf}(\alpha\sqrt{k})]^2} \right\}, \quad (24)$$

$$\bar{T}(t) = \begin{cases} \sum_{n=0}^{\infty} \frac{1}{b_n} (-1)^n H_n(t), & 0 \leq t \leq t_1, \\ \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} \frac{1}{b_n} (-1)^n F_{n,h}(t), & t_1 \leq t < \infty, \end{cases} \quad (25)$$

$$\left. \frac{\partial T}{\partial r} \right|_{r=1} = - \begin{cases} \sum_{n=0}^{\infty} (-1)^n b_n H_n(t), & 0 \leq t \leq t_1, \\ \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} (-1)^n b_n F_{n,k}(t), & t_1 \leq t < \infty. \end{cases} \quad (26)$$

The limiting value of the function  $\rho(\bar{T})$  with  $t \rightarrow \infty$  is

$$\rho_0 = d^2 b_0^2 / (\nu + 3). \quad (27)$$

Using Eq. (25) the values of the function  $\bar{T}(t)$  were calculated, to provide an example, with  $\nu = 0$ ,  $kQ = 0.23$ ,  $d^2 = 5$ ; they are indicated in Fig. 1 by small circles. If one regards  $\rho(\bar{T})$  as the error of the second equation in (22) the values are calculated of the quantity  $\rho^* = \rho(\bar{T})/\rho_0$  with the aid of the solutions (25) and (26); they are shown in Fig. 2 by small circles. To determine the asymptotic of  $\rho^*(\bar{T})$  for  $\bar{T} \rightarrow 0$  (or for  $t \rightarrow 0$  respectively) one writes down

$$\begin{aligned} \rho^*(\bar{T}) &= \frac{(1-\nu) d^2}{\rho_0} \left[ \sum_{n=0}^{\infty} \exp(-d^2 b_n^2 t / \beta) \right] \left[ \sum_{n=0}^{\infty} b_n^{-2} \exp(-d^2 b_n^2 t / \beta) \right]^{-1} \approx \\ &\approx \frac{(1-\nu) d^2 b_0^2}{\rho_0} \left[ \int_1^{\infty} \exp(-d^2 b_0^2 t x^2 / \beta) dx \right] \left[ \int_1^{\infty} x^{-2} \exp(-d^2 b_0^2 t x^2 / \beta) dx \right]^{-1} = \\ &= \frac{\beta}{2\rho_0 t}. \end{aligned} \quad (28)$$

since for  $t \rightarrow 0$  one has

$$\bar{T} = \frac{4\alpha^2 k Q}{\beta} \sum_{n=0}^{\infty} \exp(-d^2 b_n^2 t / \beta) \approx \frac{2\alpha^2}{db_0} \frac{\pi k Q}{\beta} \sqrt{t}, \quad (29)$$

therefore

$$\rho^*(\bar{T}) = \frac{2\pi\alpha^2 k^2 Q^2}{d^2 \rho_0 b_0^2} (\bar{T})^{-2} = A (\bar{T})^{-2}, \quad A = \text{const.} \quad (30)$$

The expression (30) for  $A = 1.1$  on the ascending portion of  $\bar{T}(t)$  ( $0 \leq \bar{T} \leq \max \bar{T}$ ) is shown in Fig. 2 by small crosses. For the descending portion of  $\bar{T}(t)$  ( $\max \bar{T} \leq \bar{T} \leq 0$ ) the quantity  $\rho^*(\bar{T})$  varies between 1.1 and 1, that is, it can be assumed that  $\rho^* \approx 1$  in that portion of the curve  $\bar{T}(t)$ .

By comparing the exact function  $\rho^*(\bar{T})$  with the approximation in (30) one can see that the expression (30) can be used with sufficient accuracy in approximate evaluations of the quantity  $\rho^*(\bar{T})$ . In practice, however, the model equation (22) for  $\rho^*(\bar{T}) = \int_0^1 \rho^*(\bar{T}) d\bar{T} = m = \text{const}$  is more convenient:

$$\frac{d\bar{q}}{dt} = \omega(\bar{q}) [1 - \varphi(\bar{q}, \bar{T})], \quad \frac{d\bar{T}}{dt} = -m\bar{T} - Q \frac{d\bar{q}}{dt}. \quad (31)$$

For a stepwise isotherm the solution (24) for  $\nu = 0$  is

$$\bar{q} = \frac{2\sqrt{k\bar{t}}}{1 + 3\pi \operatorname{erf}(\alpha_1 \sqrt{k})} = k\gamma \sqrt{\bar{t}}, \quad \text{for } k > 1 \quad \gamma \approx 0.815, \quad \bar{q}(t_1) = k \quad (32)$$

and corresponds to the solution of the first equation of (31). By using (32) the solution of the second equation (31) is given by

$$\bar{T}(t) = \begin{cases} \frac{k}{\sqrt{m}} \gamma i Q \exp(-mt) \frac{\sqrt{\pi}}{2} \operatorname{erf}(-i\sqrt{m}t), & 0 \leq t \leq t_1, \\ \bar{T}(t_1) \exp[-m(t-t_1)], & t_1 \leq t < \infty. \end{cases} \quad (33)$$

For  $mt \ll 1$  the numerical values of (33) can be found from the expression

$$\bar{T} = \frac{k\gamma}{\sqrt{m}} Q \sum_{n=0}^{\infty} \frac{2^n (-1)^n}{(2n-1)!!} (mt)^{n+1/2},$$

if the function  $\operatorname{erf}(x)$  is expanded into a series, and for  $mt \gg 1$  from the expression

$$\bar{T} = \frac{\gamma k Q}{2m\sqrt{t}} \sum_{n=0}^{\infty} \frac{(2n-1)!!}{2^n (mt)^n}.$$

For  $m = d^2 b_0^2 = 12.5$  the solution (33) is indicated in Fig. 1 by small crosses. The solutions (24), (25), (32) are obtained for  $\nu = 0$  when the granules are represented by disks. In the majority of cases, however, the granules are of spherical or nearly spherical shape ( $\nu \leq 2$ ). Therefore to be able to compare them the solution of the system (31) for  $\nu = 2$ ,  $m = 12$ ,  $kQ = 0.23$ ,  $q = (pc/1 + pc)$  (the Langmuir function),  $p = p_0 \exp[-Q_0 T(1 + T)^{-1}]$ ,  $Q_0 = 4$ , is indicated in Fig. 1 by triangles.

The filling-up function  $\omega(\tilde{q})$  for the system (31) was obtained by numerical integration of the quasi-linear equation (8) on an electronic computer. The Langmuir function for  $p_0 = 10$  ( $p_0 \gg 1$ ) is nearly step-like. To compare the exact and approximate functions  $T(t)$  (Fig. 1) one notes that the anisothermal kinetics of sorption for porous granules of any form ( $0 < \nu \leq 2$ ) can be described by the approximation model system of equations (31).

#### NOTATION

$q$	is the concentration of absorbed substance;
$c$	is the sorbate concentration inside a porous substance;
$\kappa$	is the relative thermodiffusion coefficient;
$\chi$	is the relative temperature conduction coefficient of gas (fluid) inside a porous granule;
$\gamma$	is the relative heat-exchange coefficient between gas (fluid) and solid phase;
$\chi_i$	is the relative temperature conduction coefficient of solid phase of a porous granule;
$Q$	is the relative coefficient of sorption thermal effect;
$T$	is the relative gas (fluid) temperature inside a porous granule;
$T^*$	is the relative solid-state temperature of a porous granule;
$T_{prop} = T_0^0(1 + T)$ ;	
$T_{prop} = T_0^0(1 + T^*)$ ;	
$T_0^0, K$	are the initial temperature;
$\nu$	is the symmetry parameter.

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