ON THE WORK OF THE POROUS GRAIN OF A CATALYST IN A FRACTIONAL-ORDER REACTION IN THE NONISOTHERMAL STATE

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The quantitative description of the work of the chemical reactor with porous packing is usually based upon the quasihomogeneous approximation. The processes of transport and the rate of the chemical reaction are characterized in this case by a set of effective coefficients. If the individual catalyst grain is porous, then the work of this grain must be considered to calculate the effective reaction rate. First-order reactions in the nonisothermal case have been throughly investigated in a number of theoretical works [1-4]. Fractional-order reactions, with are considered only in the isothermal variation, are distinguished by a very interesting peculiarity, namely, the concentration of the reacting substance and the local reaction rate approach zero at a finite distance from the surface. In view of this, we were interested in investigating the nature of the distribution of the reagent concentration in the presence of an exothermic reaction in the nonisothermal case.

Let us consider a flat catalyst grain with thickness $2l$. Let us assume that the transport of the reagent within the grain is accomplished by diffusion. Then the steady-state distribution of the concentration and temperature will be described by the equations

$$Dc'' - kc^n e^{-E/RT} = 0, \tag{1}$$

$$\lambda T'' + \Delta Q k c^n e^{-E/RT} = 0, \tag{2}$$

where D is the diffusion coefficient; k is the reaction constant; E is the activation energy; R is the gas constant; λ is the coefficient of thermal conductivity; n is the reaction order.

First let us consider the boundary conditions

$$c|_S = c_0, \quad T|_S = T_0. \tag{3}$$

The temperature and concentration at any point, as it follows from (1) and (2), are related by the function [6]

$$c - c_0 = \frac{\lambda}{D\Delta Q}(T_0 - T). \tag{4}$$

Using (4) and introducing the Frank-Kamenetskii [5] transformation to the dimensionless temperature $\theta = (T-T_0)E/RT_0^2$, we obtain from (2)

$$\theta'' = -\left(\frac{\Delta QE}{\lambda RT_0}\right)^{1-n} \frac{ke^{-E/RT_0}}{D^n}(\tilde{\theta} - \theta)^n e^{\theta/(1+\beta\theta)}, \tag{5}$$

where $\beta = RT_0/E, \quad \tilde{\theta} = c_0 D\Delta QE/\lambda RT_0^2.$

From the condition $c \geq 0$ and (4), it follows that the temperature within the grain does not exceed some maximum value $\tilde{\theta}$, since $\theta \geq \tilde{\theta}$; moreover, equality is reached when $c = 0$. Let us consider the most interesting

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case $\beta \ll 1$, and let us assume that $e^{\theta/(1+\beta\theta)} = e^{\theta}$. The boundary conditions of (3), considering the symmetry of the problem, take the form

$$\theta|_{x=0} = 0, \quad \theta'|_{x=l} = 0. \tag{6}$$

Collecting the factors in the right-hand portion of (5) that are independent of θ into one constant A, we obtain

$$\theta'' = -A(\tilde{\theta} - \theta)^n e^{\theta}, \quad 0 \leqslant x \leqslant l. \tag{7}$$

Limiting ourselves to the case $d\theta/dx \neq 0$, let us transform the left-hand portion of equation (7) to

$$\frac{d^2\theta}{dx^2} = \frac{1}{2}\frac{d}{d\theta}\left(\frac{d\theta}{dx}\right)^2.$$

It is especially necessary to consider the case $d\theta/dx = 0$, to which $\theta = \text{const}$ corresponds, which may be realized, as will be shown below, only in fractional-order reactions, where θ may reach the value of $\tilde{\theta}$, and the right-hand portion of (7) will approach zero.

Let us set the temperature in the center of the grain θ_l, which we then find from the boundary conditions. Then

$$\theta' = \left[\int_{\theta}^{\theta_l} 2A(\tilde{\theta} - \theta_2)^n e^{\theta_2} d\theta_2\right]^{1/2}. \tag{8}$$

Performing still another integration, we obtain the temperature distribution in the grain in implicit form

$$x = \int_0^{\theta} \frac{d\theta_1}{\left[2A\int_{\theta_1}^{\theta_l} d\theta_2 (\tilde{\theta} - \theta_2)^n e^{\theta_2}\right]^{1/2}}. \tag{9}$$

In the center of the grain, when $x = l$, $\theta = \theta_l$, i.e.,

$$l = \int_0^{\theta_l} \frac{d\theta_1}{\left[2A\int_{\theta_1}^{\theta_l} d\theta_2 (\tilde{\theta} - \theta_2)^n e^{\theta_2}\right]^{1/2}}. \tag{10}$$

The right-hand portion of equation (10) is a function of θ_l at a known value of the parameter $\tilde{\theta}$, the form of which indicates at what l steady-state systems may be established.

Let us investigate the function $f(\theta_l, \tilde{\theta})$, where

$$f(\theta_l, \tilde{\theta}) = \int_0^{\theta_l} \frac{d\theta_1}{\left[\int_{\theta_1}^{\theta_l} (\tilde{\theta} - \theta_2)^n e^{\theta_2} d\theta_2\right]^{1/2}}, \quad 0 < n < 1. \tag{11}$$

This function cannot be directly differentiated with respect to θ_l, since the expressions obtained diverge.

To eliminate these divergences, let us replace the variables $\theta_1 = \theta_l - x$, $\theta_2 = \theta_l - y$. Then

$$f(\theta_l, \theta) = \int_0^{\theta_l} \frac{dx\, e^{-\theta_l/2}}{\int_0^x dy\,(y + \tilde{\theta} - \theta_l)^n e^{-y}}. \tag{12}$$

From (12) it is evident that when $0 \leq n < 1$, f is limited, while when $n \geq 1$, $f(\theta_l, \tilde{\theta})_{\theta_l \to \tilde{\theta}} \to \infty$ and that $f(0, \tilde{\theta}) = 0$ at any n.

The derivative of $f(\theta_l, \tilde{\theta})$ takes the form:

$$\frac{df}{d\theta_l} = \frac{e^{-\theta_l/2}}{\left[\int\limits_0^{\theta_l} dy\, e^{-y} (y + \widetilde{\theta} - \theta_l)^n\right]^{1/2}} - \frac{e^{-\theta_l/2}}{2} \int\limits_0^{\theta_l} \frac{dx}{\left[\int\limits_0^{x} dy\, e^{-y} (y + \widetilde{\theta} - \theta_l)^n\right]^{1/2}}$$

$$+ \frac{e^{-\theta_l/2}}{2} \int\limits_0^{\theta_l} \frac{dx\, n \int\limits_0^{x} dy\, (y + \widetilde{\theta} - \theta_l)^{n-1} e^{-y}}{\left[\int\limits_0^{x} dy\, (y + \widetilde{\theta} - \theta_l)^n e^{-y}\right]^{3/2}}. \tag{13}$$

It is easy to note that $df / d\theta_l|_{\theta_l = 0} = df / d\theta_l|_{\theta_l = \widetilde{\theta}} = \infty$. Thus, $f(\theta_l, \widetilde{\theta})$ may take the form depicted in Fig. 1 at various values of $\widetilde{\theta}$. As can be seen from Fig. 1, the function may be both monotonic (I), and may have a portion with a negative derivative (II, III); in the latter case, the value of $f(\widetilde{\theta}, \widetilde{\theta})$ may be situated differently with respect to the maximum value. It is easy to see that in the cases I and III, the solution is not unique. This question will be analyzed below. Let us note that, in contrast to the case $n \geq 1$, for a fractional-order reaction at certain values of $l = \widetilde{l}$, θ_l may reach the value $\widetilde{\theta}$, which corresponds to an approach to zero of the concentration in the center of the grain. If the dimensions of the grain $2l > 2\widetilde{l}$, then it is necessary to combine the solution given by formula (9) at $0 \leq x \leq \widetilde{l}$, with corresponds in Fig. 1 to the continuation of the graph $f(\theta_l, \theta)$ vertically upward from the point $\widetilde{l}$. Physically, this solution corresponds to a distribution of the process such that the concentration becomes strictly zero within the interval $2(l - \widetilde{l})$.

Let us investigate the possibility of the existence of systems II, III, depicted in Fig. 1. Simple estimates show that when $\widetilde{\theta} << 1$, the first component in (13) is greater than the modulus of the second, and hence of sufficiently small $\widetilde{\theta}$ $df/d\widetilde{\theta} > 0$ and $f(\theta_l, \widetilde{\theta})$ takes the form of I.

A consideration of f when $\theta > 1$ indicates that the value of f when $\theta_l = \widetilde{\theta}$ is less than $e^{-\widetilde{\theta}/2}(2 + \sqrt{2\widetilde{\theta}})$,, i.e., decreases very rapidly with increasing $\widetilde{\theta}$, while the behavior of f at these values of $\widetilde{\theta}$ in the region $\theta_l << 1$ takes the form $2\sqrt{\theta_l} / \widetilde{\theta}^n$. . Beginning with some $\widetilde{\theta} > 1$, the value of the function when $\theta_l = \widetilde{\theta}$ becomes less than its value on the left-hand rising branch, which corresponds to curve III. The intermediate case, when the function contains a portion with a negative derivative, but the maximum is reached in the extreme right-hand point, is depicted by curve II.

It can be shown that the portions with a negative derivative on the graphs II, III are unstable; hence, when the point $l = l_{cr}$ is reached on the side $l < l_{cr}$, the system passes into the second stable state. Here if there is a jump from state 1 to 2, belonging to curve III, then the concentration becomes zero within the region $\widetilde{l} < x < 2l - \widetilde{l}$ (see Fig. 2). The shaded region on the figure corresponds to the distributions that cannot be realized when the parameter l is increased.

Furthermore, let us consider an analogous problem in the case of mixed boundary conditions

$$c|_{x=0} = c_0, \quad dT / dx|_{x=0} = \gamma(T_0 - T_\infty). \tag{14^a}$$

$$dc / dx|_{x=0} = \alpha(c_0 - c_\infty), \quad dT / dx|_{x=0} = \gamma(T_0 - T_\infty). \tag{14^b}$$

Obviously, the solution should take the form (9), (10), where T_0 is determined by the second equation in (14^a):

$$\frac{dT}{dx} = \frac{RT_0^2}{E} \frac{d\theta}{dx} = \gamma(T_0 - T_\infty). \tag{15}$$

Let us substitute into (15) the derivative from (8)

$$\frac{RT_0^2}{E}\left[\int\limits_0^{\theta_l} 2A\,(\widetilde{\theta} - \theta_2)^n e^{\theta_2} d\theta_2\right]^{1/2} = \gamma(T_0 - T_\infty). \tag{16}$$

The left-hand potion of (16) is a function of T_0, which we denote as $\varphi(T_0)$. Let us find an upper estimate for this function:

$$\int\limits_0^{\theta_l} (\widetilde{\theta} - \theta)^n e^{\theta_2} d\theta_2 < e^{\widetilde{\theta}} \frac{\widetilde{\theta}^{n+1}}{n+1}. \tag{17}$$

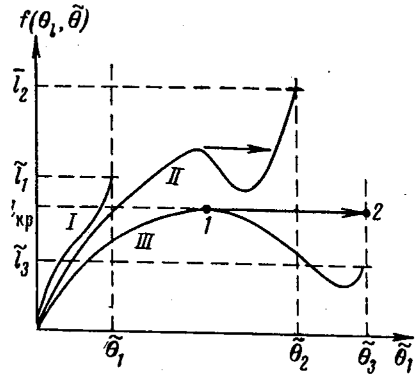

Fig. 1. View of $f(\theta, \tilde{\theta})$ for various values of $\tilde{\theta}$.

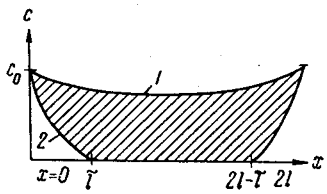

Fig. 2. Distribution of the reagent concentration within the catalyst grain under systems 1 and 2.

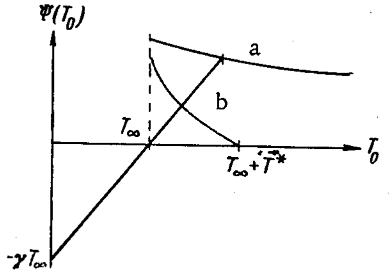

Fig. 3. $\psi(T_0)$—Majorizing function for $\varphi(T_0)$: a) under the boundary conditions (14^a); b) under the boundary conditions (14^b).

Expressing $\tilde{\theta}$ in terms of c_0 and T_0 in (17) and substituting into (16), it is easy to determine that $\varphi(T_0)$ is limited when $T_0 \to \infty$. Thus, for any T_∞ and γ, there is an intersection of $\varphi(T_0)$ (Fig. 3,a) and the straight line $\gamma(T_0-T_\infty)$, and, consequently, there is a steady-state solution. Under the boundary conditions (14^b), from (4) we obtain a relationship of c_0 and T_0

$$c_\infty - c_0 = \lambda\gamma(T_0 - T_\infty) / aD\Delta Q.$$

From the position $c_0 \geq 0$, we find that

$$T_\infty \leqslant T_0 \leqslant T_\infty + T^* = T_\infty + c_\infty aD\Delta Q / \lambda\gamma. \tag{18}$$

The majorant for (16), considering (17) and (18), behaves as shown in Fig. 3. In this case, there should also be a steady-state solution, satisfying the inequality (19). Let us note that since the fractional order of the reaction is replaced by first order at extremely low concentrations, the further drop of the concentration becomes exponential, but the characteristic depth of penetration of the reaction is determined by the value of l.

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