STATIONARY SYSTEMS OF REACTORS WITH A GRANULAR CATALYST BED

V. G. Levich* and L. M. Pis'men

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Design of reactors with a granular bed of catalyzer is usually made as an approximation of an ideal displacement [1, 2]. The process is described by a system of normal differential equations of the first order or by a system of parabolic equations, and there is always a unique stationary solution for the given kinetic functions $r_i(c_jT)$, unequivocally determining the field of reagent concentrations c_j and temperature T in the reactor. The plurality of systems observed under specific conditions can be caused only by the existence of certain stationary systems of the process in individual grains of the catalyst, leading to ambiguity of the kinetic functions $r_i(c_j, T)$. Possible intermittent transitions between different stationary systems are of a local nature, so that the state of an individual grain is determined only by the conditions of the process at a given point in the bed.

A diffusion model represents an attempt to improve the approximation of ideal displacement and leads to (in a one-dimensional case) equations of the type

$$D^* d^2c_i / dx^2 - w dc_i / dx + r_i(c_j, T) = 0, \tag{1}$$

where $D^* = \frac{1}{2} wl$ is the effective coefficient of linear diffusion, w is the filtration rate of the flow, l is the grain diameter, and x is a coordinate which takes into account the direction of motion of the flow. A similar equation with a coefficient of temperature conductivity $\chi^* = D^*$ is written for the temperature in the bed. Let $L = Nl$ be the characteristic linear scale of the process, so that $dc/dx \sim c/L$ and $d^2c/dx^2 \sim c/L^2$. Then a comparison of the first two terms of Eq.(1), according to the order of magnitude, indicates that the diffusion term is related to the convective term as $1/2N$ and, therefore, where $N \gg 1$, it may be discarded. If these conditions of $N \gg 1$ are not realized, i.e., there is a noticeable change of concentration and temperature at distances comparable with the grain diameter l, then a description of the heterogeneous granular bed by quasi-homogeneous macroscopic equations generally loses meaning, and diffusion equations of type (1) cease to be accurate. Thus, the introduction of a diffusion term is not rational.

A diffusion model formally leads to a non-linear edge problem (very complex for analysis), the solution of which is not ensured. Physically, however, this is unjustified, since in a real granular bed there is no noticeable transfer of material and heat against the flow to macroscopic distances, and an intense mixing of the flow only occurs at distances of the order of l in the empty spaces between grains. This physical picture is well described by the model of a cell of ideal mixing [3, 4]. Further, we will show how the hydrodynamics of the flow affect the conditions of the existence of different systems of the process, by studying the performances of individual cells and comparing them with the systems of a process in an isolated grain of the catalyst.

Equations of the material and thermal balance of a cell of ideal mixing has the form

$$c_{if} - c_{i0} = \beta_i \sigma s (c_{ip} - c_{if}), \tag{2}$$

$$T_f - T_0 = (\alpha / \gamma) \sigma_S (T_p - T_f), \tag{3}$$

$$\beta_i (c_{ip} - c_{if}) = \rho_i (c_{jp}, T_p), \tag{4}$$

$$\alpha (T_p - T_f) = \rho_h (c_{jp}, T_p), \tag{5}$$

*Corresponding Member of Academy of Sciences of the USSR.

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where ρ_i is the rate of formation of i-substance and ρ_h is the rate of heat evolution, related to a unit of external surface of the particles; $s = l/w$; α and β are the coefficients of heat and mass transfer from the center of the flow to a solid surface, γ is the heat capacity of unit volume of the flow, σ is the area of the external surface of the particles in unit volume of the bed: the index p denotes the values of the variables at the grain surface, the index f, inside the cell, and the index 0, at its entrance.

The same reorganization of the system (2)-(5) gives

$$\beta_i^* (c_{ip} - c_{i0}) = \rho_i (c_{ip}, T_p), \tag{6}$$

$$\alpha^* (T_p - T_0) = \rho_h (c_{ip}, T_p), \tag{7}$$

$$c_{if} - c_{i0} = \beta_i^* \sigma s (c_{ip} - c_{i0}), \tag{8}$$

$$T_f - T_0 = (\alpha^*/\gamma) \sigma s (T_p - T_0), \tag{9}$$

where

$$1/\beta_i^* = 1/\beta_i + \sigma s, \quad 1/\alpha^* = 1/\alpha + \sigma s/\gamma. \tag{10}$$

The number of possible performances of the cell under the given determining parameters and conditions at the entrance c_{i0}, T_0 is equal to the number of solutions of the non-linear system of algebraic Eqs. (6), (7). These equations are formally equivalent to the well-investigated equations of the process on an equi-accessible surface of an isolated grain [5, 1] differing from it only by the substitution of the actual coefficients of heat and mass transfer α and β_i for the effective (smaller) values α^* and β_i^* (10). Let us evaluate the relative value of the correction to the coefficient of mass transfer:

$$\beta\sigma s = \frac{\beta}{w} \sigma l = \sigma l \frac{\mathrm{Nu}}{\mathrm{Re} \cdot \mathrm{Pr}} \sim \mathrm{Re}^{-0.4} \mathrm{Pr}^{-2/3}. \tag{11}$$

Here, $\mathrm{Nu} = \beta l/D$ is the Nusselt number; $\mathrm{Re} = wl/\nu$ is the Reynolds number; $\mathrm{Pr} = \nu/D$ is the Prandtl number; D is the molecular diffusion coefficient; ν is the kinetic viscosity. The nondimensional factor of shape σl is a value of the order of unity (for example, for simple cubic packing of spheres $\sigma l = \pi$).

The experimental data of Todos [2] were used for determining the value of Nu. The same determination is obtained for corrections to the coefficient of heat transfer, if we replace β in (11) by α/γ and the diffusion numbers of Nusselt and Prandtl by the thermal numbers. It is evident from (11) that, at normal rate of flow ($\mathrm{Re} \gtrsim 10^2$), the relative correction to the coefficients of transfer is very small, particularly for liquids, and, consequently, mixing of the flow in cells affects the performances of individual grains only to a very small extent.

A reduction in the rate of flow always favors transition of an exothermic process to a higher-temperature system, for example, from a kinetic to an exterior-diffusion system. Since a real granular bed has no true structure, local flow rates ω in different cells, generally speaking, are not the same and do not coincide with the average rate w. A situation may be created here, where, in certain cells (supercritical), the reaction proceeds in a high-temperature system, but in others (subcritical), it proceeds in a low-temperature system, and the question arises about the mutual effect of neighboring cells of different types. Let $\omega^{\neq}$ be the critical rate, so that when $\omega < \omega^{\neq}$, a certain temperature $T_p = T^{\neq}$ is established on the surface of the particles, and when $\omega > \omega^{\neq}$, $T_p \approx T_0$. If $1/a$ is the portion of the flow from a supercritical cell going over to the next cell with $\omega' > \omega^{\neq}$, in which a flow from the subcritical cells occurs with a temperature T_0, then to this cell will enter a flow with a temperature of

$$T_0' = T_0 + \frac{1}{a} \frac{\alpha\sigma s}{\gamma} \frac{\omega}{\omega'} (T^{\neq} - T_0). \tag{12}$$

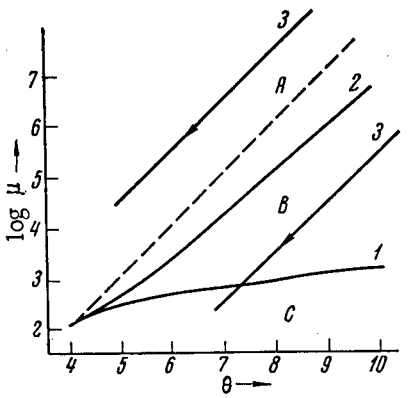

Fig. 1. Diagram of systems of a first order reaction on the external surface of the grains. 1, 2) critical curves, 3) adiabatic path of the process, A) region of kinetic system, B) region of mlutiple systems, C) region of exterior-diffusion system.

Since, according to (11), $\alpha\sigma_s/\gamma \ll 1$, the drop in temperature $T_0'-T_0$ always constitutes a small portion of the heat evolved $T^{\neq}-T_0$. If we let $\omega = \omega^{\neq}$ and $\omega' = w$, it is clear that, under average conditions in a given part of the bed, far from critical, the random transition of one cell to a high-temperature system cannot lead to "ignition" of the neighboring cells and it remains local.

Let us examine a reaction of the first order on the external surface of the grains. Then $\rho = -k_p c_p = -k_0 e^{\theta} c_p$, where $\theta = E(T_p-T_0)/RT_0^2$ is the non-dimensional temperature of the surface; k is the rate constant; E is the activation energy; R is the gas constant, and the system (6), (7) becomes one equation [5, 1].

$$\theta(1 + \mu e^{-\theta}) = \Theta, \tag{13}$$

where $\mu = \beta/k_0$; $\Theta = \beta^* hEc_0/\alpha^* RT_0^2$ are the non-dimensional parameters; and h is the thermal effect. When $\Theta > 4$ and

$$\mu < \mu^{\neq} = \frac{1+\sqrt{1-4/\Theta}}{1-\sqrt{1-4/\Theta}} \exp\left[\frac{\Theta}{2}\left(1-\sqrt{1-4/\Theta}\right)\right] \tag{14}$$

(See Fig. 1), the process in the cell changes suddenly to an exterior-diffusion system. It is evident, from the determination of the parameter μ, that when $\beta\sigma s \sim 0.1$, and for normal activation energies, the shift of the transition point caused by mixing in the cell is about 1°.

At larger values of Θ, the surface of the grains in a supercritical cell are heated up to the non-dimensional temperature $\theta \approx \Theta$. Then, according to (12), the process in the cell next to it is determined by the value of the parameter

$$\mu' = \frac{\beta^*(\omega')}{k_0} \exp(-\theta_0') = \frac{\beta^*(\omega')}{k_0} \exp\left(-\frac{1}{a}\frac{\alpha\sigma s}{\gamma}\frac{\omega}{\omega'}\Theta\right). \tag{15}$$

If there is a certain distribution of cells in the granular bed according to local rates of flow ω, and, hence, according to the values of the parameter μ, then that portion of the cell with $\mu < \mu^{\neq}$ will operate as an exterior-diffusion system. For cells with $\mu > \mu^{\neq}$, and $\mu' < \mu^{\neq}$, there will be a certain probability of transition to an exterior-diffusion system under the influence of a neighboring subcritical cell, proportional to a part of the cells that are operating in an exterior-diffusion system.

The conditions for existence of the different systems of the cell, and of the systems of an isolated particle, are local in nature and are determined by the values of concentrations and temperature in a given point of the bed. The latter can be found from solution of the macroscopic equations of the process, written as an approximation of an ideal displacement. For example, in an adiabatic process, the points of transition between systems may be found using phase diagrams of the type shown in Fig. 1.

The case of a process with heat-removal to the wall of the reactor is most interesting. A reaction in a cylindrical apparatus is described in equations

$$D^*\left(\frac{\partial^2 c}{\partial y^2} + \frac{1}{y}\frac{\partial c}{\partial y}\right) - w\frac{\partial c}{\partial x} - r(c, T) = 0, \tag{16}$$

$$\varkappa^*\left(\frac{\partial^2 T}{\partial y^2} + \frac{1}{y}\frac{\partial T}{\partial y}\right) - \gamma w\frac{\partial T}{\partial x} + hr(c, T) = 0, \tag{17}$$

where D^* and $\varkappa^*$ are the effective coefficients of transverse diffusion and thermal conductivity, and $D^* = \varkappa^*/\gamma \approx wl/10$ [2, 6]. The boundary conditions at the reactor wall (when $y = \Lambda$) are

$$\partial c / \partial y = 0, \quad \Lambda \, \partial T / \partial y = -\mathrm{Bi}(T - T_c), \tag{18}$$

where $\mathrm{Bi} = \alpha\Lambda/\varkappa^*$ is the Biot number; T_c is the temperature of the heat carrier, α is the coefficient of heat transfer from the reacting mixture to the heat carrier.

Two limiting systems of heat transfer in the reactor can be isolated: a nearly adiabatic system, when practically all of the heat of reaction goes to heating the reacting flow, and a nearly isothermal system, when the heat of reaction is carried to the wall, and the change of temperature along the length of the reactor is small. In the nearly isothermal system, the term with the linear derivative in (17) is small in comparison with the term with the derivatives according to the transverse coordinate, and in a first approximation can be discarded, and the concentration of the reagent is almost constant over the whole cross-section of the reactor in virtue of the boundary condition (18). The system (16), (17) is reduced to the equations

$$w \, d\bar{c} / dx = \bar{r}(\bar{c}, T), \tag{19}$$

$$\frac{d^2T}{dy^2} + \frac{1}{y}\frac{dT}{dy} + \frac{h}{\varkappa} r(\bar{c}, T) = 0, \tag{20}$$

where the line designates averaging over the cross-section of the reactor. A nearly isothermal system is possible if Eq. (20) is solvable. Otherwise, the process changes to a nearly adiabatic system, which is accompanied by a considerable drop in temperature along the length of the reactor. Thus, if $r = k(T_c)e^{\theta}f(c)$, where $\theta = E(T - T_c)/RT_c^2$, then (20) takes the form $\xi = y/\Lambda$ and $H = Ehk(T_c)f(\bar{c})\Lambda^2/\varkappa^2 RT_c^2)$. Equation (21) is solvable [7] when

$$\frac{d^2\theta}{d\xi^2} + \frac{1}{\xi}\frac{d\theta}{d\xi} + He^{\theta} = 0, \tag{21}$$

($\xi = y/\Lambda$ and $H = Ehk(T_c)f(\bar{c})\Lambda^2/\varkappa^2 RT_c^2$). Equation (21) is solvable [7] when

$$H \leqslant H^{\neq} = \frac{4}{1 + \sqrt{1 + 4/\mathrm{Bi}^2}} \exp\left(-\frac{2}{1 + \mathrm{Bi}/2 + \sqrt{1 + \mathrm{Bi}^2/4}}\right). \tag{22}$$

The limiting cases are: $H^{\neq} = 2$ and $\mathrm{Bi} = \infty$; $H^{\neq}/\mathrm{Bi} = 2/e$ when $\mathrm{Bi} = 0$.

It is apparent from determining the parameter H, that the most dangerous position where the inequality (22) should be proved is at the entrance of the reactor. If $H > H^{\neq}$ at the entrance, than a temperature peak should be found here (the phenomenon is very prevalent in practice). The question about whether or not formation of a peak leads to a change in the process to a new system (for example, from kinetic to exterior-diffusion), depends on whether or not the critical conditions of change are attained before the inequality $H < H^{\neq}$ begins to be fulfilled. For example, in the case of the above examined first order reaction, the equality $H = H^{\neq}$ is represented in Fig. 1 by a straight line parallel to the ordinate axis. If conditions at the entrance correspond to a point to the right of this line, then the path of the process is approximately represented by an adiabatic straight line. The reaction can change into a diffusion system, if the adiabatic path crosses the critical curve 1 before the straight line $H = H^{\neq}$.

LITERATURE CITED

1. I. I. Ioffe and L. M. Pis'men, Engineering Chemistry of Heterogeneous Catalysis [in Russian] (1965).
2. R. Aris, Introduction to the Analysis of Chemical Reactors, New York (1965).
3. H. A. Deans and L. Lapidus, Am. Inst. Chem. Eng. J., 6, 656 (1960).
4. H. Cramers and G. Alberda, Chem. Eng. Sci., 2, 173 (1953).
5. D. A. Frank-Kamenetskii, "Diffusion and Heat Transfer in Chemical Kinetics" [in Russian], Izd. AN SSSR (1947).
6. R. H. Wilhelm, Pure and Appl. Chem., 5, 403 (1962).
7. A. G. Merzhanov and F. I. Dubovitskii, DAN, 120, No. 5 (1958).