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Abstract

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ON THE LIMIT OF CHAIN-THERMAL EXPLOSION

In the present work we investigate the influence of slow nonradical reactions on the conditions for the existence of a stable stationary regime of a chain process. Consider a process involving one type of radicals, including three reactions—of first, second, and zeroth order with respect to the radical concentration.

The dimensionless concentrations of radicals η and molecules of the initial substance ξ, and the dimensionless temperature θ in the reaction zone V, are determined by the system of nonlinear equations

$$\begin{gathered} L\eta + \lambda[f(\xi,\theta)\eta + \mu\eta^2 + \varepsilon] = 0, \\ L'\xi - g\lambda f(\xi,\theta)\eta = 0, \\ L^0\theta + h\lambda f(\xi,\theta)\eta = 0, \end{gathered} \tag{1}$$

where L, L', L^0 are second-order differential operators. In the absence of convection $L = \nabla^2$; in a flow reactor $L = \nabla^2 - \mathrm{P}\omega(x)\nabla$, where $\omega(x)$ is the dimensionless (with scale w_0) flow velocity at the point x; $\mathrm{P} = w_0 l/D$ is the Peclet number; l is the linear scale; D is the diffusion coefficient of radicals. The operators L' and L^0 have the same form, but with Peclet numbers $\mathrm{P}' = w_0 l/D'$ and $\mathrm{P}^0 = w_0 l/\chi$, where χ is the coefficient of thermal conductivity and D' is the diffusion coefficient of the molecules.

We shall assume that the temperature dependence of the reaction rate is determined by the Arrhenius equation and that all three reactions proceed via binary collisions. The dimensionless variables ξ and θ are chosen so that the boundary conditions for system (1) are homogeneous: $\xi = (c - c_0)/c_0$, $\theta = E(T - T_0)/RT_0^2$. Then

$$f(\xi,\theta) = (\xi + 1)\exp\frac{\theta}{1 + \frac{RT_0}{E}\theta} \simeq (\xi + 1)e^{\theta},$$

$$h = \frac{1}{\nu}\frac{D}{\chi}\frac{E}{RT_0}\frac{qc_0}{\gamma T_0}, \qquad \lambda = \frac{\nu k_0 c_0 l^2}{D}, \qquad g = \frac{D}{D'\nu}, \qquad \mu = \frac{k_0^{(2)}\nu^{(2)}}{k_0\nu}, \qquad \varepsilon = \frac{\nu^{(0)}k_0^{(0)}c_0}{k_0\nu},$$

where c is concentration; T is temperature; k is the reaction-rate constant; the subscript zero denotes the value at the boundary (taken as the scale); ν is the stoichiometric coefficient of radicals; the superscript in parentheses indicates that the given quantity refers to the reaction of second or zeroth order with respect to the radical concentration; for the main reaction (first order) this index is omitted; γ is the heat capacity per unit volume of the reacting mixture; R is the gas constant; E is the activation energy of the main reaction; q is its thermal effect. The temperature dependence and the thermal effect of the other two reactions, as well as their influence on the consumption of the initial substance and the reverse influence of the latter on their rates, are not taken into account in equations (1), since all these effects do not appear in the approximation sufficient for our purposes.

Since reactions involving only stable molecules proceed much more slowly than reactions of radicals, the quantity ε may be regarded as a small parameter. The unperturbed nonlinear system obtained from (1) for $\varepsilon = 0$ was studied earlier (^{1}). This system always has

trivial solution, stable for $\lambda < \lambda_0$, where λ_0 is the smallest eigenvalue of the operator L in the domain V with the boundary conditions imposed on η. For $\lambda > \lambda_0$ there exists a stable positive solution of the unperturbed system if the inequality

$$a = h\int_V \varphi_0^*(x)\varphi_0(x)\psi_0^0(x)\,dx - g\int_V \varphi_0^*(x)\varphi_0(x)\psi_0'(x)\,dx + \mu\int_V \varphi_0^*(x)\varphi_0^2(x)\,dx < 0, \tag{2}$$

is satisfied, where $\varphi_0(x)$, $\varphi_0^*(x)$ are normalized eigenfunctions of the operator L and of the adjoint operator L^*, corresponding to the eigenvalue λ_0, and

$$\psi_0^0(x) = \lambda_0\int_V K^0(x,\xi)\varphi_0(\xi)\,d\xi, \qquad \psi_0'(x) = \lambda_0\int_V K'(x,\xi)\varphi_0(\xi)\,d\xi, \tag{3}$$

where $K^0(x,\xi)$ and $K'(x,\xi)$ are the Green' s functions of the operators L^0 and L' in the domain V with the boundary conditions for θ and ζ, respectively. If inequality (2) is not satisfied, a positive solution exists for $\lambda < \lambda_0$ and is unstable, while for $\lambda > \lambda_0$ there are no stable stationary solutions (the explosion region).

Starting from the solution of the unperturbed system, one can compute the solution of system (1) in the form of a series in the small parameter ε. The coefficients of the expansion are determined with the aid of the corresponding equations in variations, and, if the latter are solvable, the solution of system (1), obviously, differs from the solution of the unperturbed system by a quantity of first-order smallness in ε and preserves its stability. In a neighborhood of the bifurcation point $\lambda = \lambda_0$, however, this procedure does not lead to the goal, since the dependence of the solution of system (1) on the parameter ε ceases to be analytic. Here the solution can be found with the aid of an expansion in $\sqrt{\varepsilon}$.

In a neighborhood of the bifurcation point the second and third equations of system (1) always have a unique solution (1): $\zeta = R'\eta$, $\theta = R^0\eta$, where R', R^0 are resolvents, and in the first approximation

$$\zeta = -g\lambda_0 \int_V K(x,\xi)\eta\,d\xi, \qquad \theta = h\lambda_0 \int_V K^0(x,\xi)\eta\,d\xi.$$

Therefore system (1), for λ close to λ_0, can be reduced to a single equation

$$L\eta + \lambda[f(R'\eta, R^0\eta)\eta + \mu\eta^2 + \varepsilon] = 0. \tag{4}$$

Putting $\lambda = \lambda_0(1 + \delta\sqrt{\varepsilon})$, $\eta = \sqrt{\varepsilon}\eta^{(1)} + \varepsilon\eta^{(2)} + \cdots$, and expanding $f(R'\eta, R^0\eta)$ in a Taylor series, we have in the first approximation

$$L\eta^{(1)} + \lambda_0\eta^{(1)} = 0, \tag{5}$$

whence $\eta^{(1)} = \alpha\varphi_0$, $R'\eta^{(1)} = -\alpha g\psi_0'$, $R^0\eta^{(1)} = \alpha h\psi_0^0$. The constant α is determined from the solvability condition for the equation of the second approximation

$$L\eta^{(2)} + \lambda_0\eta^{(2)} + \lambda_0[\eta^{(1)}R'\eta^{(1)} + \eta^{(1)}R^0\eta^{(1)} + \mu(\eta^{(1)})^2 + \delta\eta^{(1)} + 1] = 0. \tag{6}$$

We find

$$\alpha = -\frac{\delta}{2a}\left(1 \pm \sqrt{1 - \frac{4ab}{\delta^2}}\right), \tag{7}$$

where the quantity a is defined by (2) and $b = \int_V \varphi_0^*(x)\,dx$. It follows from (7) that for

$a > 0$ and $\delta < -2\sqrt{ab}$ there are two positive solutions—one decreasing and one increasing with increasing δ. For $a > 0$ and $\delta > -2\sqrt{ab}$

there are no positive solutions. For $a < 0$ both solutions have different signs and change sign at the point $\delta = 0$ (i.e., $\lambda = \lambda_0$), and the positive branch of the function $\alpha(\delta)$ is a smooth curve. Here it is easy to see the qualitative correspondence with the solution of the unperturbed system.

The number λ^* is a branching point ^{2} of the nonlinear equation (4), if the linear equation

$$Ly + \lambda^* \left[\eta \frac{d}{d\eta} f(R'\eta, R^0\eta) + f(R'\eta, R^0\eta) + 2\mu\eta\right] y = 0 \tag{8}$$

has a nontrivial solution. Using the approximate solution found above, $\eta \cong \sqrt{\varepsilon}\eta^{(1)}$, we find, in the first approximation,

$$\lambda^* = \lambda_0(1 - 2\sqrt{ab\varepsilon}). \tag{9}$$

For $a < 0$ there are no branching points. For $a > 0$ the branching point determined by (9) is the explosion limit, above which ($\lambda > \lambda^*$) a stationary regime of the process is impossible. The corresponding limiting concentration of radicals is equal (in the first approximation) to

$$\eta^* = \sqrt{\frac{b\varepsilon}{a}}\, \varphi_0(x). \tag{10}$$

Let us consider a simple example. Let $L = d^2/dx^2$ and $\eta = \xi = \theta = 0$ at $x = 0$ and $x = 1$ (a plane vessel without convection). Then $\lambda_0 = \pi^2$,

$$\varphi_0 = \varphi_0^* = \psi_0' = \psi_0^0 = \sqrt{2}\sin \pi x, \qquad b = \frac{2\sqrt{2}}{\pi}, \qquad a = \frac{8\sqrt{2}}{3\pi}(h - g + \mu),$$

and formulas (9), (10) give

$$\lambda^* = \pi^2 \left(1 - 2.08\sqrt{\varepsilon(h - g + \mu)}\right), \qquad \eta^* = \sqrt{\frac{1.50\varepsilon}{h - g + \mu}}\, \sin \pi x.$$

The results obtained can be easily generalized to the case of a complex process involving different types of radicals and stable substances. The general regularity is as follows. The conditions for the existence of a stable stationary regime of the process are not violated by the introduction of slow nonradical reactions. If the unperturbed system has an explosion region, then under the influence of slow reactions proceeding under the conditions of the bifurcation point of the unperturbed system with a rate of order ε, the explosion limit is shifted by a quantity of order $\sqrt{\varepsilon}$; the limiting pre-explosion concentrations of radicals are of the same order. All these quantities are calculated by formulas analogous to (9), (10), but with altered values of the constants a and b.

The results presented are directly applicable also to nonchain autocatalytic reactions.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.

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