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THE UNSTEADY MODES OF RADICAL POLYMERIZATION*

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The sets and conditions of bifurcation of three-dimensional structurally stable phase patterns are determined for the system of equations that define unstady processes of radical polymerization in a perfectly stirred flcwing volume. Methods of qualitative analysis of differential equations /1—5/ are used. Integral characteristics of unsteady modes are numerically determined for the conditions of ethylene polymerization under high pressure. Properties of the complete system of equations are compared with those of the previously considered shortened system of equations /6/ which corresponds to the assumption of constancy of monomer concentration.

1. The system of macrokinetic equations for the material and heat balances which define the radical polymerization process in a perfectly stirred flowing volume is of the form

$$\frac{dC_1}{dt} = F_1(C_1, C_2, \theta) = \lambda(C_{10} - C_1) - \alpha C_1 C_2 e^{-\omega/\theta} \tag{1.1}$$

$$\frac{dC_2}{dt} = F_2(C_1, C_2, \theta) = \lambda(C_{20} - C_2) - C_1^m C_2^n e^{-1/\theta} \tag{1.2}$$

$$\frac{d\theta}{dt} = F_3(C_1, C_2, \theta) = \gamma C_1^m C_2^n e^{-1/\theta} - \mu(\theta_0 - \theta) \tag{1.3}$$

$$\theta = \frac{RT}{E_2}, \quad \omega = \frac{E_1}{E_2}, \quad t = k_{02}\tau, \quad \alpha = \frac{k_{01}}{k_{02}}, \quad \lambda = \frac{u}{k_{02}V} = \frac{1}{\mathrm{Da}}, \quad \gamma = \frac{QR}{\rho C_p E_2}$$

$$\mu = \lambda(1+\delta) = \frac{\varkappa F + c_p \rho u}{\rho V k_{02} c_p} = \frac{1}{\mathrm{Se}}, \quad \delta = \frac{\varkappa F}{c_p \rho u}, \quad \theta_0 = \frac{RT_0}{E_2}\frac{1 + \delta T_x/T_0}{1+\delta} = \frac{R}{E_2}\frac{c_p \rho u T_0 + \varkappa F T_x}{c_p \rho u + \varkappa F}$$

on the assumption that the iniciator effectiveness remains constant and that energy absorbed by its decomposition can be neglected /6—9/.

In the above equations R is the universal gas constant, τ is the time, $\varkappa$ is the heat transfer coefficient, F is the surface /area/ of heat exchange, c_p is the medium specific heat at constant pressure, u is the volume flow rate of reagents at the inlet and outlet of the reactor, ρ and V are, respectively, the density and volume of the mixture, Q is the specific heat of the polymerization reaction, E is the activation energy, k_0 is the reaction rate constant, T_0 is the initial temperature of reagents, T_x is the temperature of the heat exchange surface, and C_0 is the concentration of reagents at the reactor inlet. Subscripts 1 and 2 relate to the iniciator or the iniciation reaction, and to the monomer or the polymerization reaction, respectively, $k_{02} = k_*(k_{01}/k_{**})^{1/2}$, where subscripts $*$ and $**$ correspond to the chain reaction growth or termination, respectively, Da is the Damköhler number which is the ratio of time spent in the reactor V/u to the characteristic reaction time $1/k_{02}$, and Se is Semenov's number which is the ratio of the characteristic heat transfer time $\rho V c_p/(\varkappa F + \rho u c_p)$ to the time $1/k_{02}$.

The exponents m and n vary within the limits $n \geqslant 1$ and $0 \leqslant m \leqslant 1$. The values $m = 0.5$ and $n = 1.5$ pertain to ethylene polymerization, and $m = 0.5$ and $n = 1$ to polymerization of styrene /7,9/. When $m = n = 1$ and $\omega = 1$, system (1.1)—(1.3) defines the reaction $A + B \rightarrow D$ previously considered in /10/. When $m = 0$, Eqs. (1.2) and (1.3) define the dynamics of an n-th order reaction in a continuous-flow reactor with perfect stirring /6,11—16/. If variation of the monomer concentration during the reaction is ignored, the system of Eqs. (1.1) -- (1.3) reduces to the shortened system of Eqs. (1.1) and (1.3) /6/.

Solutions of the system of Eqs. (1.1)—(1.3) may be represented in a three-dimensional phase space by trajectories (C_1, C_2, θ). The structure of their totality is determined by the zero surfaces $F_1 = 0, F_2 = 0$ and $F_3 = 0$. Surface $F_1 = 0$ passes across the straight line $C_1 = C_{10}, C_2 = 0$ and monotonically approaches the plane $C_1 = 0$. Surface $F_2 = 0$ passes across the straight lines $\theta = 0,\ C_2 = 1$ and $C_1 = 0,\ \theta = \theta_0$, and monotonically approaches the plane $C_2 = 0$. Surface $F_3 = 0$ passes across the straight lines $C_1 = 0,\ \theta = \theta_0$ and $C_2 = 0,\ \theta = \theta_0$, and at each intersection with the plane $C_2 = \mathrm{const}$ has a maximum and a minimum.

The intersection points of surfaces $F_1 = 0, F_2 = 0, F_3 = 0$ represent the equilibrium positions of system (1.1)—(1.3).

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2. To determine the number of equilibrium positions of system (1.1) — (1.3) we first investigate the possible intersections of surfaces $F_1 = 0$ and $F_3 = 0$, and turn to the lines of intersection of these surfaces and the plane $C_2 = \text{const}$. They are defined, respectively, by the equations

$$\lambda_1 (C_{10} - C_1) - C_1 e^{-\omega/\theta} = 0, \quad \lambda_1 = \frac{\lambda}{\alpha C_2} \tag{2.1}$$

$$C_1^m e^{-1/\theta} + \mu_1 (\theta_0 - \theta) = 0, \quad \mu_1 = \frac{\mu}{\gamma C_2^n} \tag{2.2}$$

These equations define the zero isoclines $dC_1/dt = 0$ and $d\theta/dt = 0$ of the shortened system of equations in the phase plane (C_1, θ) under the condition of constancy of concentration of polymer C_2. The properties of the intersection are determined by their shape and, in particular, by the presence of inflection points.

The isocline (2.1) has one inflection point when $\theta > 0$, since the second derivative $d^2C_2/d\theta^2$ along that line vanishes at the single intersection point of the decreasing function $f_1(\theta) = \lambda_1(\omega - 2\theta)/(\omega + 2\theta)$ and of the increasing function $f_2(\theta) = e^{-\omega/\theta}$. The isocline (2.2) for the most common value $m = 0.5$ has one inflection point between the extrema.

Lines (2.1) and (2.2) can intersect at one, three, and five points. Cases of existence of one and three steady states in the phase plane (C_1, θ) were considered in detail in /6/. It was also shown that five steady states are possible in the comparatively narrow range of parameter variation.

The investigation of isoclines (2.1) and (2.2) shows that five steady state can occur in the phase plane, when the derivative $dC_1/d\theta$ at the inflection point of curve (2.1) is greater than the derivative $dC_1/d\theta$ at the inflection point of curve (2.2). The phase pattern of the shortened system in terms of isoclines shows that in this case the three equilibrium positions (U_1, O, U_2) that lie between the extreme equilibrium positions (O_1, O_2) are unstable (see Fig.1, where arrows indicate regions with positive derivatives).

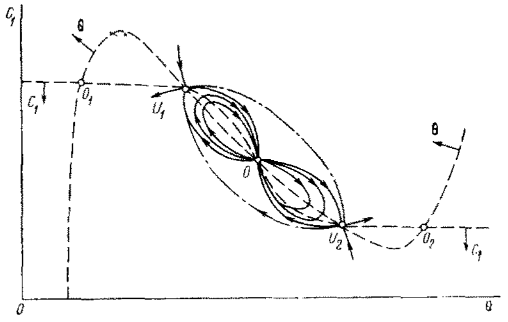

Fig.1

The middle equilibrium position is here a complexe singular point common to two elliptic sectors /15/ located between points U_1, O and O, U_2, while points U_1 and U_2 are of the saddle type. Since all intermediate equilibrium positions are unstable, the process in the reactor defined by Eqs. (1.1) and (1.3), when $C_2 = \text{const}$, as well as in the case of existence of three equilibrium positions (see, e.g., /14/), will approach the equilibrium state in time that corresponds to one of the extreme points of stable equilibrium position, or will approach the stable limit cycle around these equilibrium positions.

Thus the dynamics of a system with five equilibrium positions does not substantially differ from the dynamics of a system with three equilibrium positions.

3. In the three-dimensional phase space (C_1, C_2, θ) the points of intersection of surfaces $F_1 = 0$ and $F_3 = 0$ form lines. The points which correspond to the equilibrium position of the shortened system with the lowest temperature form in space one line, while the remaining points form pairwise one or two lines (when the over-all number of equilibrium positions is three or five, respectively) of the parabolic type. The intersection points of these lines with the surface $F_2 = 0$ are nondegenerate equilibrium positions of the system of Eqs. (1.1) — (1.3).

Lines of the parabolic type do not intersect or touch the coordinate surface $C_2 = 0$ (see Fig.2). The number of steady states of the system is, thus, odd and does not exceed the number of steady states of the shortened system.

As shown in /16/, the conditions of the equilibrium position stability can be obtained from the characteristic equation of system (1.1) — (1.3), and the kind of singular points in the three-phase space may be determined by the signs of the free term and of the discriminant of the characteristic equation /17/ using the Sideriades classification /18/.

The intersections of zero surfaces divide the phase space in regions where derivatives are of constant sign (regions of positive derivatives are indicated in Fig.2 by arrows at zero surfaces). Using this it is possible to represent various variants of the system phase pattern. As an example, one of the possible phase patterns of system (1.1) — (1.3) with three equilibrium positions are shown in Fig.2, and in Fig.3 the phase pattern with a single equilibrium position.

We can conclude that the extreme equilibrium positions are of the node-focus type (points $O^{3.0}$, see /2,19/). There are trajectories of different types (Fig.3): *a* and *b* which correspond to an oscillating process around the equilibrium positions; *c* and *d* which correspond to oscillations around the intersection lines of surfaces $F_2 = 0$ and $F_3 = 0$; and *e* and *f* which correspond to a monotonic approach to equilibrium positions inside the spirals *c* and *d*.

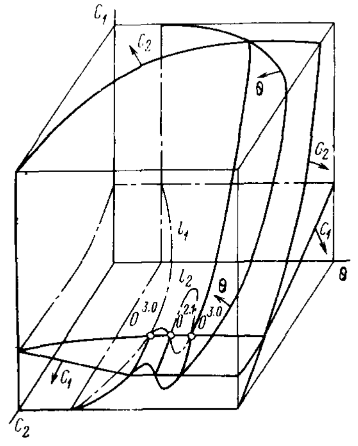

Fig.2

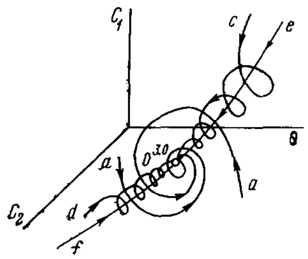

Fig.3

The intermediate equilibrium position is unstable, it is represented by the point $O^{2.1}$ of the saddle type.

The essential difference between the complete system of equations and the shortened one is the existence of oscillatory modes of approach to equilibrium positions accompanied by oscillations of concentration of monomer C_2.

Rapid transitions (thermal explosions) from one extreme steady state to another are possible in a system with several steady states at some changes of parameters. The critical condition of existence of such transitions in a system defined by two first order differential equations is that of tangency of zero isoclines in the phase plane, which corresponds to bifurcation point in the parameter space.

In a three-dimensional phase space a new condition, viz. the tangency of intersection lines of three zero surfaces, correspond to the bifurcation point. It is defined by the equation

$$C_1^2 \beta_1 + C_1 C_{10} \beta_2 + C_{10}^2 \beta_3 = 0, \quad \beta_1 = \omega + \frac{\theta^2}{\theta - \theta_0}\left(1 + C_{20}\frac{\alpha}{\lambda} e^{-\omega/\theta}\right) \tag{3.1}$$

$$\beta_2 = \frac{1}{m} - 2\omega - \frac{\theta^2}{\theta - \theta_0}\left[2 + \frac{1-n}{m} + \left(1 - \frac{n}{m}\right) C_{20}\frac{\alpha}{\lambda} e^{-\omega/\theta}\right], \quad \beta_3 = \omega - \frac{1}{m} + \frac{\theta^2}{\theta - \theta_0}\left(1 + \frac{1-n}{m}\right)$$

from which it is possible to eliminate concentration C_1 which at the intersection point of zero surfaces is determined by formula

$$C_1 = C_{10}\left[1 + \frac{\alpha}{\lambda} e^{-\omega/\theta}\left(C_{20} - \mu\frac{\theta - \theta_0}{\gamma\lambda}\right)\right] \tag{3.2}$$

The roots of Eq. (3.1) in conformity with Eq. (3.2) define the critical temperature of the reacting mixture when $C_1 = C_1(\theta)$. The critical temperature corresponds to the bifurcation point of merging of two singular points $O^{3.0} + O^{2.1} \rightarrow \varnothing$ /1,2/.

When $n = 0$ and $m = 0$ Eqs. (3.1) and (3.2) become the Semenov's formula for critical temperature of mixture ignition /20/.

The condition of tangency of intersection lines of zero surfaces (3.1) is based on the following theorem.

Theorem. If at the common point of three zero surfaces $F_1 = 0$, $F_2 = 0$, and $F_3 = 0$ the derivatives of any of the phase space coordinates with respect to any other coordinate of that space along two intersection lines of surfaces are equal, the three lines of intersection of surfaces at the common point of the latter are tangent to each other.

Proof. The equations of intersection of surfaces are defined by the equalities

$$F_i(C_1, C_2, \theta) = 0, \quad F_j(C_1, C_2, \theta) = 0; \; i \neq j, \; i, j = 1, 2, 3 \tag{3.3}$$

By specifying these lines in parametric form $C_1 = C_1^{(i,j)}(z)$, $C_2 = C_2^{(i,j)}(z)$ and $\theta = \theta^{(i,j)}(z)$, where the superscripts (i,j) indicate the intersection lines of surfaces F_i and F_j, we find that Eqs. (3.3) are identically satisfied. Consequently the equalities

$$\frac{\partial F_i}{\partial C_1} dC_1^{(i,j)} + \frac{\partial F_i}{\partial C_2} dC_2^{(i,j)} + \frac{\partial F_i}{\partial \theta} d\theta^{(i,j)} = 0, \quad \frac{\partial F_j}{\partial C_1} dC_1^{(i,j)} + \frac{\partial F_j}{\partial C_2} dC_2^{(i,j)} + \frac{\partial F_i}{\partial \theta} d\theta^{(i,j)} = 0 \qquad (3.4)$$

are valid.

Solving the system of Eqs. (3.4) for $(dC_1 / d\theta)^{(i,j)} \cdot (dC_2 / d\theta)^{(i,j)}$ and taking into account the partial derivatives at the equilibrium positions, we obtain

$$\left(\frac{dC_1}{d\theta}\right)^{(1,2)} = \frac{C_1}{\theta^2}\left[\omega\left(\frac{A}{C_2 - A} + n\right) - 1\right]\left[m - \frac{C_{10}}{C_{10} - C_1}\left(\frac{A}{C_{20} - A} + n\right)\right]^{-1}$$

$$\left(\frac{dC_2}{d\theta}\right)^{(1,2)} = \frac{1}{\theta^2}\left[\omega B + C_{10}\left(\frac{1}{m} - \omega\right)\right] \times \left[\frac{\alpha}{\lambda} Be^{-\omega/\theta} - \frac{C_{10}}{m}\left(\frac{1}{C_{20} - C_2} + \frac{n}{C_2}\right)\right]^{-1}$$

$$\left(\frac{dC_1}{d\theta}\right)^{(1,3)} = \frac{C_1}{\theta^2}\left(n\omega - 1 + \frac{\theta^2}{\theta - \theta_0}\right)\left(m - n\frac{C_{10}}{C_{10} - C_1}\right)^{-1}$$

$$\left(\frac{dC_2}{d\theta}\right)^{(1,3)} = \frac{1}{\theta^2}\left[\omega D - C_{10}\omega - \frac{C_{10}}{m}\left(\frac{\theta^2}{\theta - \theta_0} - 1\right)\right] \times \left(\frac{\alpha}{\lambda} De^{-\omega/\theta} - \frac{C_{10}}{C_2}\frac{n}{m}\right)^{-1}$$

$$\left(\frac{dC_1}{d\theta}\right)^{(2,3)} = \frac{C_1}{m}\left[\frac{n}{\theta - \theta_0}\frac{C_{20}C_1}{C_{10} - C_1} - \frac{\alpha}{\lambda}e^{-\omega/\theta} + \frac{1 - n}{\theta - \theta_0} - \frac{1}{\theta^2}\right], \quad \left(\frac{dC_2}{d\theta}\right)^{(2,3)} = -\mu\frac{\theta - \theta_0}{\gamma\lambda}$$

$$A = \frac{C_{10} - C_1}{\alpha C_1}\lambda e^{\omega/\theta}, \quad B = \left(\frac{C_{20} - C_2}{C_2^{\,n}}\lambda e^{1/\theta}\right)^{1/m}, \quad D = \left(\mu\frac{\theta - \theta_0}{\gamma C_2^{\,n}}e^{1/\theta}\right)^{1/m}$$

Let us consider the equalities

$$\left(\frac{dC_1}{d\theta}\right)^{(1,2)} = \left(\frac{dC_1}{d\theta}\right)^{(1,3)} = \left(\frac{dC_1}{d\theta}\right)^{(2,3)}, \quad \left(\frac{dC_2}{d\theta}\right)^{(1,2)} = \left(\frac{dC_2}{d\theta}\right)^{(1,3)} = \left(\frac{dC_2}{d\theta}\right)^{(2,3)} \qquad (3.5)$$

at the point of intersection of the three zero surfaces. Taking into account that by virtue of equations $F_1 = 0$, $F_2 = 0$, and $F_3 = 0$ the equalities

$$B = D = C_1, \quad A = G^{1/n} = C_2 \quad \left(G = \mu\frac{\theta - \theta_0}{\gamma C_1^{\,m}}e^{1/\theta}\right)$$

are satisfied at that point, it is possible to show that all Eqs. (3.5) reduce (without loss of roots) to one and the same Eq. (3.1). This shows that when one of equalities (3.5) is satisfied, all of the remaining three equalities are satisfied.

This proves the theorem, since when along the three lines at their common point all derivatives of space coordinates with respect every other coordinate are equal, these lines are tangent to each other (osculation of first order lines).

4. Numerical investigations of the system of Eqs. (1.1) — (1.3) were carried out for the ethylene polymerization process ($m = 0.5$, $n = 1.5$) with the characteristic parameters selected close to value used in projected and actual experimental and industrial polymerization reactors of the autoclave type. The qualitative analysis has shown the existence of one or two stable steady states approached by the reactor process, hence the parameters and stability of such states were, first of all, determined. The use of the graphic method for determining the solutions in the φ, θ plane, where $\varphi = 1 - C_2 / C_{20}$ is the depth of polymer transformation, proved to be expedient for the determination of parameters and number of steady states.

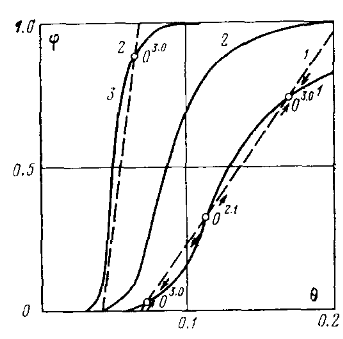

Fig.4

It should be pointed out that conditions of existence of five steady states of the ethylene polymerization reaction are not realized in practice.

By plotting the lines $\varphi_1 = (\theta)$ (solid lines in Fig.4: $1 - \Omega_2 = 10^2$, $2 - \Omega_2 = 10^3$, and $3 - \Omega_2 = 10^5$), and equating to zero the derivatives, from Eqs. (1.1) and (1.2), and $\varphi_2(\theta)$ (the dash lines in Fig.4: $1 - \Omega_3 = 7.4$ and $2 - \Omega_3 = 40$) and from Eqs. (1.4) and (1.3) it is possible to determine the parameters at points of intersection of lines that correspond to steady states of system (1.1) — (1.3).

The lines of $\varphi_1(\theta)$ and $\varphi_2(\theta)$ in Fig.4 show the possibility of existence of one of three intersections, i.e. the system has one to three steady states.

Numerical determination of the type of steady points in conformity with the Sideriades's classification, showed that the extreme with respect to temperature points in the case of three intersections and the single point in that of a single intersection are stable and of the $0^{3.0}$ type. This is in agreement with the qualitative determination of the type of singular points of steady states.

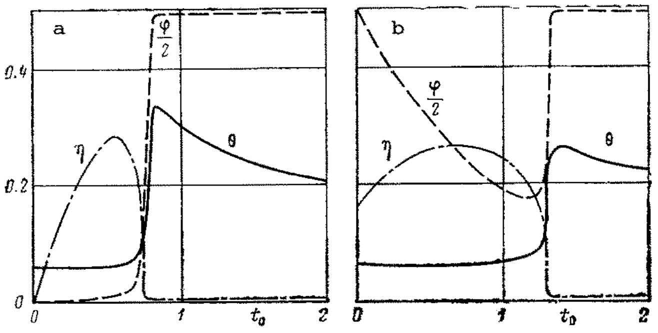

Fig.5

The following conclusions can be drawn from the analysis of line intersections that correspond to steady states of system (1.1) — (1.3) in the φ, θ plane.

1) The variation in a wide range of the determining parameters

$$\Omega_1 = (C_{20}\alpha\,\mathrm{Da})^{-1} = \frac{u}{C_{20}k_{01}V}\ ,\quad \Omega_2 = \left(C_{10}\frac{\mathrm{Da}}{\alpha}\right)^{1/2} = \left(\frac{C_{10}V}{k_{01}u}\right)^{1/2} k_{02},\quad \Omega_3 = \frac{\mathrm{Da}}{C_{20}\gamma\,\mathrm{Se}} = \frac{\varkappa F + \rho c_p u}{uRC_{20}Q}E_2$$

does not substantially affect the depth of transformation of φ and the temperature θ of the low-temperature steady state;

2) a greater depth of transformation for the high-temperature steady state, which is recommended in practice, can be obtained at high values of Ω_2 and Ω_3 ($\Omega_2 \gg 10^3$, $\Omega_3 \gg 10$).

The unsteady process modes in a polymerization reactor were determined by the method of numerical integration of system (1.1) — (1.3) on a computer using the Runge—Kutta method. As a whole, these calculations had confirmed the results of the qualitative analysis. The approach of the reactor process to the steady mode is accompanied by parameter oscillations. When the high-temperature steady state is approached, a sharp, explosion-like, increase of temperature θ and of transformation depth of φ occurs, after which θ and φ slowly decrease to their steady values. It should be pointed out that the calculations were based on the assumption of constancy of parameters at the reactor intake and their independence of parameter variation in the reaction volume.

As an example, the dependence of φ, θ and η on the dimensionless time $t_0 = t\lambda = \tau u / V$ for $\alpha = 5\cdot10^5\ \lambda$, $\gamma = 3\cdot10^5\ \lambda$, $\mu = 2\lambda\ (\delta = 1)$, $\omega = 0.8$, and $\beta = (C_{10}C_{20})^{1/2} = 10^6\,\lambda$, is shown in Fig.5. In this case $\Omega_2 = 1430$, $\Omega_3 = 6.67$ and when $\theta_0 = 0.06$ there is a single steady state in which $\varphi = 0.9875$, $\theta = 0.2081$ and $\eta = 0.0074$. The trajectories of d and a in Fig.3 correspond, respectively, to Figs. 5,a and b.

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