

EXISTENCE AND STABILITY OF STATIONARY REGIMES OF A CHEMICAL REACTION ON A POROUS CATALYST GRANULE

L. M. Pis'men and Yu. I. Kharkats

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Several stationary regimes, some of which are physically unstable, may exist during exothermic reactions on a porous catalyst granule. D. A. Frank-Kamenetskii found two stationary solutions for a zero-order reaction [1]. S. I. Khudyaev recently proved [2] that one of these solutions (the high-temperature regime) is unstable with respect to small perturbations. Three stationary regimes are possible for a single reaction with an order different from zero [3-5]. Numerical solution of the nonstationary equations, as was carried out by Amundson and Raymond [6], proves the instability of the intermediate regime that corresponds to the transition range of the reaction. However, no analytical study on the stability of the stationary regimes has been carried out so far for this and more complex cases.

The method of studying the solutions of nonlinear operator equations near branch points [7], which is well known in functional analysis, is employed in the present investigation; it enables us to determine the criteria necessary for the existence of branching solutions and to prove the instability of some regimes of the process considered.

The set of nonlinear differential equations that describe the process on a porous catalyst granule may be written as a single equation for the vector-function $u = \{c_1, c_2, \dots, c_n, \theta\}$ (c_i are the dimensionless reagent concentrations and θ the dimensionless temperature; the reference values of the variables are so chosen that $u = 0$ on the granule surface):

$$\nabla^2 u + \lambda f(u) = 0. \quad (1)$$

From a physical consideration of the problem it follows that the scalar parameter λ occurring in this equation should be positive. Let λ_0 be a branch point of the solutions of Eq. (1). We shall suppose that $\lambda = \lambda_0 + \varepsilon$, where ε denotes a small parameter, and search for a solution of the following type near the branch point:

$$u = u_0 + \sqrt{\varepsilon} u_1 + \varepsilon u_2 + \dots \quad (2)$$

We shall expand the nonlinear function $f(u)$ into a Taylor series of $u - u_0$:

$$f(u) = f(u_0) + f_1(u_0)(u - u_0) + f_2(u_0)(u - u_0)^2 + \dots, \quad (3)$$

where $f_1 = (\partial f / \partial u)_{u_0}$ denotes the Jacobian matrix of the vector-function $f(u)$, and $f_2 = 1/2 (\partial^2 f / \partial u^2)_{u_0}$ — is a third-rank matrix composed of the second derivatives of $f(u)$. Substituting expansions (2), (3) into (1), we get:

$$\nabla^2 u_0 + \lambda_0 f_0 = 0; \quad (4)$$

$$\nabla^2 u_1 + \lambda_0 f_1 u_1 = 0; \quad (5)$$

$$\nabla^2 u_2 + \lambda_0 f_1 u_2 + f_0 + \lambda_0 f_2 u_1^2 = 0, \quad (6)$$

where $f_0 \equiv f(u_0)$. The $\lambda = \lambda_0$ is a branch point of Eq. (1), if Eq. (5) has a nontrivial solution. Consequently,

$$u_1 = \alpha \varphi_0, \quad (7)$$

where φ_0 is the normalized (with weight f_1) eigenvector-function of Eq. (5) which corresponds to the eigenvalue λ_0 and α a scalar parameter. Equation (6) is solved by means of an expansion into eigenfunctions of Eq. (5). A necessary condition for the solvability of Eq. (6) is that the free term must be orthogonal to the eigenfunction φ_0 :

$$\langle \varphi, f_0 \rangle + \lambda_0 \alpha^2 \langle \varphi_0, f_2 \varphi_0^2 \rangle = 0, \quad (8)$$

where the angular brackets denote integration over the range and convolution over the vector indices. From (8) we derive:

$$\alpha = \pm \sqrt{-\langle \varphi_0, f_0 \rangle / \lambda_0 \langle \varphi_0, f_2 \varphi_0^2 \rangle} \equiv \pm \sqrt{-I_1 / \lambda_0 I_3}. \quad (9)$$

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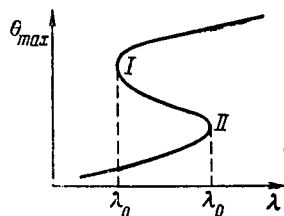


Fig. 1. Plot of the maximum temperature versus λ .

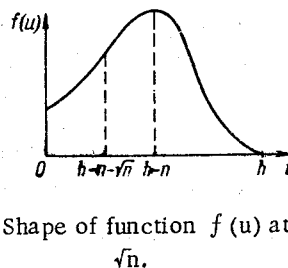


Fig. 2. Shape of function $f(u)$ at $h > n + \sqrt{n}$.

If $I_1/I_3 < 0$, α is real, and there exists a solution if $\varepsilon > 0$, i. e., a pair of solution of Eq. (1) that issue from the branch point and correspond to the two signs of α in formula (9) exist, if $\lambda > \lambda_0$. If $\lambda < \lambda_0$, there are no real solutions in this case. we shall call such a branch point a type I branch point (see Fig. 1). If $I_1/I_3 > 0$, parameter α is purely imaginary, and, consequently, there exists a pair of real solutions, if $\lambda < \lambda_0$ (type II branch point).

We shall investigate the stability of the solutions near the branch point. The linearized equation for a small deviation $\tilde{u}$ from the stationary solution u reads

$$\beta \partial \tilde{u} / \partial t = \nabla^2 \tilde{u} + \lambda f_1(u) \tilde{u}, \quad (10)$$

where β denotes the diagonal matrix composed of the inverse coefficients of diffusion and heat conductivity. Assuming $\tilde{u} = e^{\mu t} v$, we find

$$\nabla^2 v + \lambda f_1 v - \mu \beta v = 0. \quad (11)$$

The stationary solution is stable only if Eq. (11) has a nontrivial solution with $\text{Re } \mu < 0$. In the branch point (at $\lambda = \lambda_0$), the spectrum of μ contains the value $\mu = 0$. We shall investigate the change of this eigenvalue near the branch point. Substituting the following series expansion in powers of $\sqrt{\varepsilon}$ into Eq. (11):

$$v = v_0 + \sqrt{\varepsilon} v_1 + \dots, \quad \mu = \sqrt{\varepsilon} \mu_1 + \dots, \quad (12)$$

we get

$$\nabla^2 v_0 + \lambda_0 f_1(u_0) v_0 = 0; \quad (13)$$

$$\nabla^2 v_1 + \lambda_0 f_1(u_0) v_1 + \lambda_0 f_2(u_0) v_0 u_1 - \mu_1 \beta v_0 = 0. \quad (14)$$

From (13) it follows that $v_0 = \varphi_0$ (we omit the arbitrary constant, because it is unessential). Utilizing (7), we find from the solvability condition of Eq. (14) that

$$\mu_1 = \lambda_0 \alpha \langle \varphi_0, f_2 \varphi_0^2 \rangle / \langle \varphi_0, \beta \varphi_0 \rangle \equiv \lambda_0 \alpha I_3 / I_2. \quad (15)$$

From (15) it is evident that the sign of μ_1 differs for solutions corresponding to the two opposite signs of α ; hence it follows that only one of the two solutions leaving the branch point can be stable.

$I_3 = 0$ is a special case. Here, the behavior of the solutions near the branch point has to be analyzed by means of expansions in terms of $\varepsilon^{1/3}$. This brings forward that one real solution exists on the two sides of the branch point, while the sign of μ and, hence, the stability character of the solution remains unaltered in passing through the branch point. Such a degenerated branch point may be interpreted as the coalescence of two branch points of types I and II, respectively.

To study in more detail the conditions for the existence and stability of the solutions, we shall consider a set of chemical reactions without such abnormalities as are autocatalysis and retardation of the reaction by the original substance. In this case all coefficients in the concentration equations in the set (5) are negative. Considering these reactions consecutively, passing from the end of the chain of chemical conversion to the beginning, we may note that the concentration equations in the set (1) have no branch point and can always be solved unambiguously. Consequently, in this case the concentrations of all reagents may be expressed in the temperature by means of some integral operators. In this way, the vector Eq. (1) is reduced to a scalar equation for the temperature function. This equation still has the shape of (1), but now $f(u)$ is a scalar nonlinear operator, and parameter λ may also be interpreted in a different way. The independent variable u in the other equations must now be taken to represent the

temperature function, and f_1 and f_2 denote the first and second derivatives of the Frechet operator $f(u)$ in the point $u = u_0$ of the functional space.

In an exothermic process $f_0 > 0$, and, hence, $I_1 > 0$. From formula (9) it now follows that a type I branch point corresponds to $I_3 < 0$ and a type II branch point to $I_3 > 0$. Since type I and type II branch points must alternate, the maximum possible number of branch points (except degenerated points) exceeds the number of sign alternations of integral I_3 by one. This estimate of the number of branch points may be made more accurate if it is taken into account that the inequality $f_1 > 0$ must hold in a branch point. This follows from the positive value of λ_0 and the theorem that the eigenvalues of the linear Eq. (5) change when function f_1 is altered [8].

We thus arrive at the following conclusion: the number of branch points cannot be larger than twice the number of regions in which the inequalities $I_3 > 0$ and $f_1 > 0$ are fulfilled simultaneously. We note that if the system considered contains a reaction of zero-order, the estimate given for the number of branch points must be diminished by one, since one of the points disappears into infinity.

By way of example we shall now consider a single exothermic reaction of the n -th order. In this case the operator relationship between the concentration and the temperature degenerates into the simple linear relationship [9] and the single temperature equation to which the description of the system is reduced is of shape (1) with the scalar nonlinear function

$$f(u) = e^u(h - u)^n, \quad (16)$$

where parameter h has the meaning of the maximum possible temperature in the system considered: $0 \leq u \leq h$. It is easily proved that the first derivative of this function can be positive in the region $u > 0$ only if $h > n$, and that the second derivative f_2 can be so only if $h > n + \sqrt{n}$. In the range $h > u > h - n$, $f_1 < 0$, so that, although $f_2 > 0$ in the range $h > u > h - n + \sqrt{n}$, there exists only a single region in which $f_2 > 0$ and $f_1 > 0$ are satisfied simultaneously (see Fig. 2). Since the second derivative f_2 must be positive if the inequality $I_3 > 0$ has to be satisfied, we may state that the system considered can have no more than two branch points and, hence, three stationary regimes, while the branch points can appear only if $h > n + \sqrt{n}$. We note that this necessary condition is independent of the geometry of the system.

We shall now analyze the stability of the stationary solutions. Since $I_2 > 0$, it follows from formula (15) that the sign of μ_1 is identical to the sign of α if $I_3 > 0$, i. e., in a type II branch point, whereas μ_1 and α are of opposite sign if $I_3 < 0$ (in a type I branch point). Consequently, the lower temperature regime (corresponding to $\alpha < 0$) is stable in a type I branch point, and the upper regime ($\alpha > 0$) in a type II branch point. In the case of a single reaction the solutions which correspond to loops between the branch points and represent the transition region of the reaction are unstable.

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