THE STATIONARY OPERATION MODES OF A CONTINUOUS ISOTHERMAL CHEMICAL REACTION

Yu. P. Gupalo and Yu. S. Ryazantsev

The problem of determination of stationary operation modes of a continuous isothermal reactor in one-dimensional approximation with the lengthwise diffusion of the substance taken into consideration reduces to a two-point boundary value problem for the second-order equation [1]

$$\frac{d^2\xi}{dx^2} - U\frac{d\xi}{dx} + R(\xi) = 0 \qquad \left(U = \frac{u}{D}, \quad R(\xi) = \frac{r(\xi)}{D}\right) \tag{1}$$

$$x = 0,\ d\xi/dx = U\xi; \quad x = l,\ d\xi/dx = 0$$

Here ξ is the degree of advancement of the reaction, assumed to be single-step (reversible or irreversible); u is the flow rate; D is the effective coefficient of lengthwise diffusion; and $r(\xi)$ is the reaction rate, with the reactor occupying the region $0 \leq x \leq l$. Except for zero- and first-order reactions, Eq. (1) is not linear, and problem (1) has no analytical solution. Known attempts at numerical solution of this problem [2, 3] do not guarantee the uniqueness of solution. The question of uniqueness is by no means trivial, as shown, e.g., by the fairly recent attempt at a numerical analysis of this problem [4] for the particular case of a heterogeneous catalytic reaction, which had shown the possibility of existence of three stationary modes.

Mathematically, problem (1) is equivalent to the problem of the existence and of the number of stationary operation modes of a continuous adiabatic reactor considered in [5]. In accordance with the results presented there it is possible to state that: 1) if the function $R(\xi)$ is positive and monotonically decreasing, problem (1) always has a unique solution; 2) if, however, the function $R(\xi)$ is positive and nonmonotonic, problem (1) has always (besides certain exceptional cases) an odd number of solutions. In the second case the determination of the number of solutions can be reduced to solving a problem which in certain respects is more convenient for integration than problem (1).

Let us consider certain particular cases.

1. A homogeneous reversible chemical reaction. In this case the function $r(\xi)$ is of the form [1]

$$r(\xi) = k\prod_{j=1}^{N} c_j^{\beta_j} - k'\prod_{j=1}^{N} c_j^{\gamma_j} \quad (c_j = c_{j0} + \alpha_j\xi) \tag{2}$$

Here k and k' are constants of the rates of direct and reverse reactions, respectively; β_j and γ_j are the orders of direct and reverse reactions, respectively; c_j and c_{j0} are, respectively, the concentration and the initial concentration; α_j is the stoichiometric coefficient (subscript j relates to the j-th constituent of the mixture of original substances and of products of reaction), and N is the over-all number of constituents.

Usually (except in cases of autocatalysis) reagents ($\alpha_j < 0$) accelerate a direct reaction ($\beta_j \geq 0$) and retard a reverse one ($\gamma_j \leq 0$), while end products ($\alpha_j > 0$) slow down a direct reaction ($\beta_j \leq 0$) and accelerate a reverse one ($\gamma_j \geq 0$), and not all β_j and γ_j vanish. Hence it follows from (2) that function $r(\xi)$ decreases monotonically and problem (1) has a unique solution. This proves, in particular, that the stationary modes determined by numerical methods in [2] for reactions of various orders are unique. The conclusion about uniqueness of solutions remains, obviously, valid for k' = 0 (irreversible reaction).

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 10, No. 3, pp. 97-98, May-June, 1969. Original article submitted December 10, 1968.

2) The rate of an autocatalytic reaction increases at low degrees of advancement ξ of the reaction and decreases at high ξ [1]. Hence in this case function $R(\xi)$ is nonmonotonic, and problem (1) may have several solutions.

3) The effective rate of a heterogeneous catalytic reaction can depend on the rate of diffusion and adsorption of reagents, desorption of products of reaction, etc. The dependence of the reaction rate on ξ may consequently be of a complicated character and nonmonotonic. For example, the rate of a heterogeneous catalytic reaction can in a number of cases be present in the form

$$r(\xi) = k\frac{(\xi_m - \xi)^{n_1}}{[1 + \lambda(\xi_m - \xi)]^{n_2}} \tag{3}$$

where k, ξ_m, λ, n_1, and n_2 are positive constants. In this case the function $r(\xi)$ for $n_2 > n_1[1 + (\lambda\xi)^{-1}]$ is nonmonotonic, and problem (1) can have several solutions. The latter occurs, e.g., in the case of the reaction of ethylene hydrogenation considered in [4].

LITERATURE CITED

1. R. Aris, Introduction to the Analysis of Chemical Reactors, Prentice-Hall, New Jersey, 1965.
2. L. T. Fan and R. C. Bailie, "Axial diffusion in isothermal tubular flow reactors," Chem. Eng. Sci., vol. 13, no. 1, 1960.
3. H. Hofmann and H. J. Astheimer, "Der Einfluss der Vermischung bei heterogenen Reaktionen in kontinuierlich-betriebenen isotherm arbeitenden Rohrreaktoren," Chem. Eng. Sci., vol. 18, no. 10, 1963.
4. T. Matsuura and M. Kato, "Concentration stability of the isothermal reactor," Chem. Eng. Sci., vol. 22, no. 2, 1967.
5. Yu. P. Gupalo and Yu. S. Ryazantsev, "Stationary operation modes of a continuous adiabatic chemical reactor," PMTF [Journal of Applied Mechanics and Technical Physics], vol. 8, no. 5, 1967.