STEADY MODES OF OPERATION OF CHEMICAL REACTION VESSELS WITH INTERNAL, EXTERNAL, AND COMBINED HEAT TRANSFER

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Steady-state exothermic processes in reaction vessels with internal and external heat transfer are studied for a single reaction with arbitrary kinetics and an exponential temperature dependence of the reaction rate constant. The critical values of the dimensionless parameters characteristic of the process are calculated numerically.

When exothermal processes are carried out under high-temperature conditions, the reaction heat can be used to good advantage for heating the starting mixture. Figure 1 shows the schematic diagrams of several versions of an apparatus for carrying out such processes. The study will be limited to countercurrent systems, assuming that both the reaction vessel and the heat exchanger operate under ideal displacement conditions. This model provides a satisfactory description of the process at high flow rates characteristic of most industrial processes [1, 2]. The problem of designing such systems has been studied in [3–6]; however, no analytical solution with the exception of the external heat exchanger [4] was obtained in these papers, while in reference [5] the investigation of the stability of the steady-state conditions of the process was performed inadequately. An analytical solution to the problem of determining the steady modes of operation of a reaction vessel with internal heat transfer, for a reaction of the zero and first order, has been recently obtained by Zelenyak [7]. The present paper investigates the steady modes of operation of reaction vessels with internal and external heat transfer for an arbitrary relation between the reaction rate and reagent concentration.

I. REACTION VESSELS WITH AN INTERNAL HEAT EXCHANGER

We shall examine a single irreversible exothermic reaction with a kinetic law of the form:

$$r = k(T) f(c) = B \exp(-E/RT)\, f(c),$$

where $f(c)$ is an arbitrary concentration function, which is always greater than 0 when c is greater than 0.* In dimensionless form, the equations of a steady-state process in a countercurrent apparatus have the form:**

*If the starting substances are in nonstoichiometric proportions, this condition is satisfied whenever a deficiency reagent is taken as the key substance.

**The question of the assumptions conventionally used in the derivation of these equations, and the derivation itself, are examined in detail in the literature (see, for example, [2]).

$$\frac{dx}{d\xi} = -\mu e^{\theta} f(x), \tag{1}$$

$$\frac{d\theta}{d\xi} = \delta\mu e^{\theta} f(x) - \alpha(\theta - \tau_1), \tag{2}$$

$$\frac{d\tau_1}{d\xi} = -\alpha(\theta - \tau_1). \tag{3}$$

The boundary conditions are:

$$x(0) = 1, \quad \theta(0) = \tau_1(0), \quad \tau_1(1) = \tau_0. \tag{4}$$

Here, the symbols introduced,

$$\mu = \frac{Vk(T_0) f(c_0)}{v c_0}; \quad \delta = \frac{hc_0 E}{\gamma R T_0^2}; \quad \alpha = \frac{4k_T V}{\gamma v d},$$

are dimensionless parameters.

Frank-Kamenetskii's well-known approximating transformation has been used in the formulation of the temperature dependence of the reaction rate constant. This approximation holds for relatively small values of $\Delta T/T$, i.e., under conditions in which the thermal expansion of the flow need not be taken into account. The system of equations (1)–(3) always has a first integral expressing the energy conservation law:

$$\delta x + \theta - \tau_1 = \delta. \tag{5}$$

By expressing x in (5) through $(\theta - \tau_1)$ and introducing the new variable $y = \theta - \tau_1$, the system can be reduced to one equation:

$$y'' - \left(1 + \frac{f'\left(\frac{\delta - y}{\delta}\right)}{f\left(\frac{\delta - y}{\delta}\right)}\right)(y')^2 + \alpha y y' = 0, \tag{6}$$

with the boundary conditions

$$y(0) = 0, \quad y'(1) = \mu\delta e^{\tau_0} f\left(\frac{\delta - y(1)}{\delta}\right) e^{y(1)}. \tag{7}$$

From an analysis of the initial system of equations, it can be seen that $y = \delta(1 - x)$ is a monotonically increasing function ξ, since $x(\xi)$ decreases monotonically. In this case, by the substitution of variables $y' = z(y)$, Eq. (6) reduces to a quadrature equation.

After performing certain transformations and integrating with allowance for the second boundary condition, we get:

$$\frac{dy}{d\xi} = e^{y} f\left(\frac{\delta - y}{\delta}\right)\left(\lambda + \alpha \int_{y}^{y_0} \frac{s e^{-s}\, ds}{f\left(\frac{\delta - s}{\delta}\right)}\right), \tag{8}$$

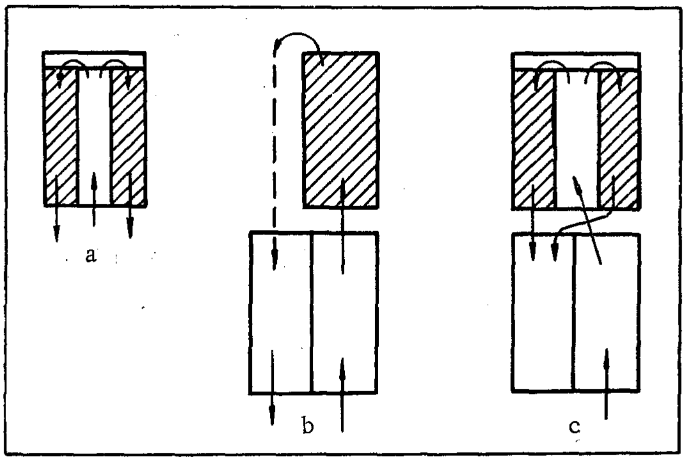

Fig. 1. Schematic diagrams of several reaction vessel versions with a counter-current heat exchanger: a) internal heat exchanger, b) external heat exchanger, c) combined heat exchanger.

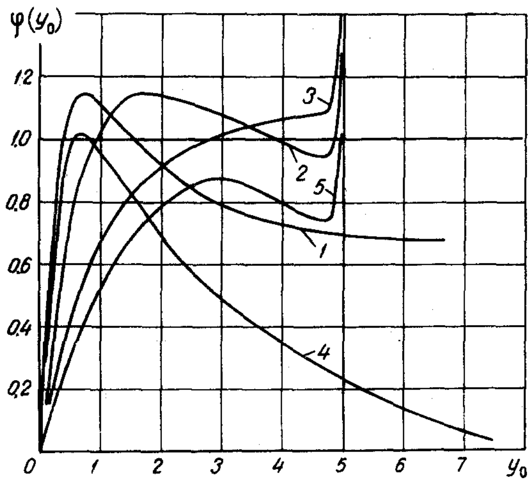

Fig. 2. Curves for determining a steady-state mode of a reaction vessel with an internal (1, 2, 3) and a combined (4, 5) heat exchanger for reactions of various order: 1) zero-order, $\alpha = 2.0$, $\lambda = 0.25$; 2, 3) first-order, $\delta = 5.0$, $\alpha = 0.8$, $\lambda = 0.1$ and $\delta = 5.0$, $\alpha = 0.2$, $\lambda = 0.2$, respectively; 4) zero-order; 5) positive order, $r \geq 1$, $\delta = 5.0$.

where $y_0 = y(1)$; $\lambda = \delta\mu e^{\tau_0}$.

By separating the variables and integrating, we arrive at a transcendental equation

$$\varphi(y_0) = \int_0^{y_0} \frac{e^{-y}dy}{f\left(\frac{\delta - y}{\delta}\right)\left(\lambda + \alpha \int_y^{y_0} \frac{se^{-s}ds}{f\left(\frac{\delta - s}{\delta}\right)}\right)} = 1 \quad (9)$$

for determining y_0. The form of the function $\varphi(y_0)$ will be studied for two possible cases.

1. The function $f((\delta - y)/\delta)$ has no zeros on the right semiaxis,* while at infinity, it does not decrease faster than $\exp[-(1 - \varepsilon)y]$, where $\varepsilon > 0$. In this case, the function $\varphi(y_0)$ is defined over the entire right semiaxis, while for $y_0 \to \infty$ we have:

$$\varphi(y_0) \to A,$$

where

$$A = \int_0^{\infty} \frac{e^{-y}dy}{f\left(\frac{\delta - y}{\delta}\right)\left(\lambda + \alpha \int_y^{\infty} \frac{se^{-s}ds}{f\left(\frac{\delta - s}{\delta}\right)}\right)}. \quad (10)$$

The curve $\varphi(y_0)$ is continuous and must have at least one maximum, since it can be shown that $\varphi'(y_0) < 0$ at sufficiently large y_0. If the function $\varphi(y_0)$ has one maximum, then, as can be seen from Fig. 2, for various values of the parameters α and λ, Eq. (9), and hence the initial system, may have one, two, or no solutions.**

2. The function $f((\delta - y)/\delta)$ has a zero of p-th order for $y = \delta$ and has no zeros for $y < \delta$. In this case, function $\varphi(y_0)$ has a logarithmic singularity at the point $y_0 = \delta$ for $p \geq 1$, and has no singularity for $p < 1$. Depending on the form of the function $f((\delta - y)/\delta)$ over the interval $0 \leq y \leq \delta$ and on the values of the parameters λ, δ, and α, the function $\varphi(y_0)$ can be expressed by either curve (curves 2 and 3) in Fig. 2. It should be noted that in this case, for all parameter values except some critical ones, the function $\varphi'(y_0)$ must have an even number of zeros, while Eq. (9) must have an odd number of solutions. The uniqueness of a solution is assured if function $\varphi(y_0)$ increases monotonically. At least one solution to Eq. (9) will always exist. It should be noted that a solution which corresponds to the descending segment of the curve $\varphi(y_0)$ is unstable from physical considerations (5). The assumption concerning the stability of the solutions that correspond to the ascending segment does not disagree with physical considerations.

Numerical calculations were performed for several specific types of kinetic function.

a) Zero-order reaction. In this case $f(x) = 1$ and

$$\varphi(y_0) = \int_0^{y_0} \frac{e^{-y}dy}{\lambda + \alpha(1+y)e^{-y} - \alpha(1+y_0)e^{-y_0}}. \quad (11)$$

Figure 2 shows the curves of function $\varphi(y_0)$ for the parameter values $\alpha = 2.0$ and $\lambda = 0.25$. In Fig. 3a, the critical curves for α and λ are plotted in the parameter plane on the basis of numerical results. They are determined from the condition:

$$\varphi_{\max}(\lambda_{cr}^{(1)}) = 1; \quad A = \lim_{y_0 \to \infty} \varphi(y_0, \lambda_{cr}^{(2)}) = 1.$$

For $\lambda_{cr}^{(1)} < \lambda$, Eq. (9) has no solutions; for $\lambda_{cr}^{(2)} \leq \lambda \leq \lambda_{cr}^{(1)}$ there exist two solutions, while for $\lambda < \lambda_{cr}^{(2)}$, there exists a unique solution.

b) First-order reaction. In this case $f(x) = x$ and

$$\varphi(y_0) = \int_0^{y_0} \frac{e^{-y}dy}{\left(\frac{\delta - y}{\delta}\right)\left(\lambda + \alpha \int_y^{y_0} \frac{se^{-s}ds}{f\left(\frac{\delta - s}{\delta}\right)}\right)}. \quad (12)$$

Figure 2 shows the curves of function $\varphi(y_0)$ (curves 2 and 3) for $\delta = 5.0$ and various values of α and λ. In Fig. 3b, the critical curves for α and λ are plotted in the parameter plane from results of numerical calculation. They are determined from the conditions

$$\varphi_{\max}(\lambda_{cr}^{(1)}) = 1; \quad \varphi_{\min}(\lambda_{cr}^{(2)}) = 1.$$

The point $(\alpha_{cr}, \lambda_{cr})$ is determined from the condition

$$\begin{aligned} \varphi(y_{cr}) &= 1, \\ \varphi'(y_{cr}) &= 0, \\ \varphi''(y_{cr}) &= 0. \end{aligned} \quad (13)$$

In other words, at the point of inflection of function $\varphi(y_0)$, its value must be unity, while its derivative must be zero. For $\lambda > \lambda_{cr}^{(1)}$ and $\lambda < \lambda_{cr}^{(2)}$ Eq. (12) has one solution, while for $\lambda_{cr}^{(2)} < \lambda < \lambda_{cr}^{(1)}$, it has three solutions.

II. REACTION VESSELS WITH EXTERNAL HEAT EXCHANGER

An adiabatic reaction vessel with a countercurrent heat exchanger, both of ideal displacement, is examined (Fig. 1b). In dimensionless form, the system of equations for the steady-state process has the form:

$$\frac{dx}{d\xi} = -\mu e^{\theta} f(x), \quad (14)$$

$$\frac{d\theta}{d\xi} = \delta\mu e^{\theta} f(x), \quad (15)$$

$$\frac{d\tau_2}{d\xi_1} = \alpha_1(\tau_3 - \tau_2), \quad (16)$$

$$\frac{d\tau_3}{d\xi_1} = \alpha_1(\tau_3 - \tau_2). \quad (17)$$

*It is obvious, however, that for $y_0 > \delta$ (i.e., $x < 0$), the initial system of equations becomes physically unacceptable, which makes it purposeless to examine $\varphi(y_0)$ at $y_0 > \delta$.

**The absence of a solution to Eq. (9) does not mean that an actual physical process cannot be steady. It indicates primarily that the kinetic function in its adopted form does not hold for small values of x.

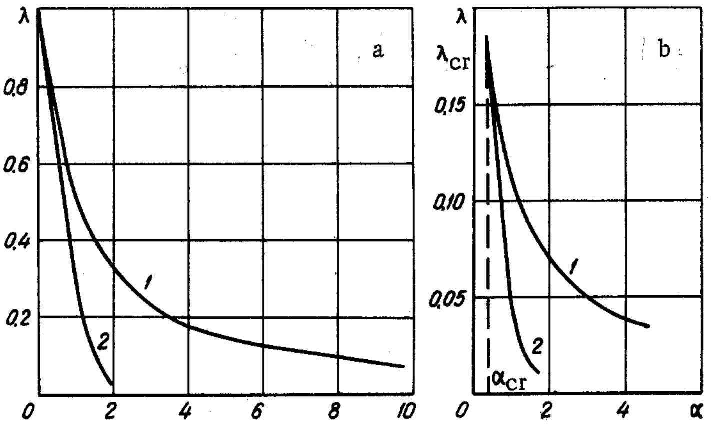

Fig. 3. Curves of the critical parameter values for a reaction vessel with internal heat exchanger: a) for a zero-order reaction, b) for a first-order reaction, $\delta = 5$; 1) λ_{1cr}, 2) λ_{2cr}.

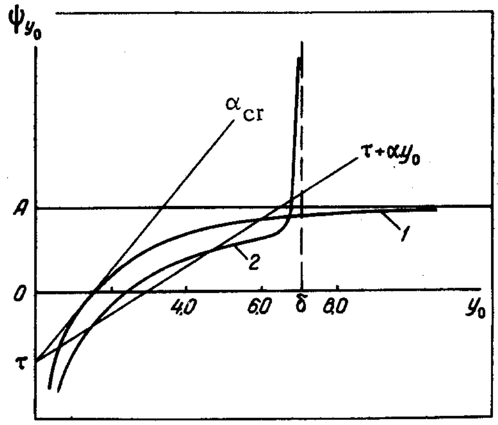

Fig. 4. Curves for determining the steady modes of operation of a reactor vessel with an external heat exchanger. 1) For a zero-order reaction; 2) for a reaction of positive order, $r \geq 1$.

The boundary conditions are

$$\tau_2|_{\xi_1=0} = \tau_0; \quad \tau_3|_{\xi_1=l} = \theta|_{\xi=l} = \theta_f;$$
$$x|_{\xi=0} = 1; \quad \theta|_{\xi=0} = \tau_2|_{\xi_1=l} = \theta_{in}. \quad (18)$$

The system (14)–(18) has two first integrals which express the law of conservation of energy in the adiabatic layer and the heat exchanger:

$$\delta x + \theta = \delta + \theta_{in}, \quad (19)$$
$$\tau_3 - \tau_2 = \theta_f - \theta_{in}. \quad (20)$$

By expressing x in (19) through $(\theta - \theta_{in})$ and denoting $\theta - \theta_{in} = y$, $\theta_f - \theta_{in} = y_0$, it may be seen that obtaining a steady-state solution from (14) and (15) with allowance for (20) reduces to the solution of the transcendental equation

$$\psi(y_0) = \ln \int_0^{y_0} \frac{e^{-y}\,dy}{\delta\mu f\left(\frac{\delta - y}{\delta}\right)} = \tau_0 + \alpha_1 y_0. \quad (21)$$

The shape of the function $\psi(y_0)$ will be examined. As in the preceding problem, two different cases are possible.

1. The function $f((\delta - y)/\delta)$ has no zeros on the right semiaxis, and so forth (see the preceding problem). In this case, function $\psi(y_0)$ grows monotonically, while as $y_0 \to \infty$, $\psi(y_0) \to A_1$, where $A_1 = \ln \int_0^{\infty} \frac{e^{-y}dy}{\delta\mu f\left(\frac{\delta - y}{\delta}\right)}$. If, in addition, $\psi''(y_0) > 0$,* i.e., $\psi(y_0)$ is a convex function, then it has the shape shown in Fig. 4 (curve 1).

In this case, for $\alpha_1 < \alpha_{cr}$, Eq. (21) has two solutions, while for $\alpha_1 > \alpha_{cr}$, it has no solutions.

2. The function $f((\delta - y)/\delta)$ has a zero of the p-th order at $y = \delta$, and has no zeros at $y < \delta$. In this case, function $\psi(y_0)$ grows monotonically, has a logarithmic singularity at point $y_0 = \delta$ for $p \geq 1$, and has no singularities for $p < 1$. If, in addition, the function $\psi''(y_0)$ has a single zero on the segment $[0, \delta]$,** then the function $\psi(y_0)$ has the shape shown in Fig. 4 (curve 2). It can be seen from Fig. 4 that for almost all values of the parameters α_1, λ, and δ, except certain critical ones, Eq. (21) has one or three solutions. As in the case of an internal heat exchanger, it can be shown that the steady mode that corresponds to the condition $\psi'(y_0) - \alpha_1 < 0$ is unstable from physical considerations, while the stability of the steady modes that correspond to the condition $\psi'(y_0) - \alpha_1 > 0$ is physically acceptable.

The following practical examples will be examined:

a) A zero-order reaction. In this case, $f(x) = 1$ and

$$\psi(y_0) = \ln(1 - e^{-y_0})/\lambda, \quad (22)$$

where $\lambda = \delta\mu$. Function $\psi(y_0)$ has the shape shown in Fig. 4 (curve 1); here $A_1 = -\ln\lambda$. The relation $\lambda_{cr}(\alpha_1)$ can be obtained in explicit form from the condition that the straight line $\tau_0 + \alpha_1 y_0$ is a tangent to the curve $\psi(y_0)$. From here, we get

$$\lambda_{cr} = \lambda e^{\tau_0} = \frac{\alpha_1^{\alpha_1}}{(1 + \alpha_1)^{1+\alpha_1}}. \quad (23)$$

The curve of this function is analogous to curve 1 in Fig. 3. For $\lambda < \lambda_{cr}$, there exist two steady-state solutions, while for $\lambda > \lambda_{cr}$, steady-state solutions do not exist.

b) A reaction of any positive order of r. In this case, function $f(x) = x^r$, and

$$\psi(y_0) = \ln \int_0^{y_0} \frac{e^{-y}dy}{\lambda(\delta - y)^r}, \quad (24)$$

where $\lambda = \mu\delta^{1-r}$ has the shape shown in Fig. 4 (curve 2), the curve $\psi(y_0)$ having one point of inflection. The relation $\lambda_{cr}(\alpha_1)$ has the same form as in the case of an internal heat exchanger (Fig. 3b). The point $(\alpha_{cr}, \lambda_{cr})$ is determined from the conditions:

$$\alpha_{cr} = \psi'(y_{cr}), \quad \psi''(y_{cr}) = 0. \quad (25)$$

This means that α_{cr} is the derivative of the function $\psi''(y_0)$ at its point of inflection. For $\lambda > \lambda_{cr}^{(1)}$ and $\lambda < \lambda_{cr}^{(2)}$ there exists a unique solution. For $\lambda_{cr}^{(2)} < \lambda < \lambda_{cr}^{(1)}$ there exist three solutions.

III. REACTION VESSEL WITH A COMBINED HEAT EXCHANGER

In this case, the system of steady-state equations has the form (see Fig. 1b):

$$\frac{dx}{d\xi} = -\mu e^{\theta} f(x), \quad (26)$$

$$\frac{d\theta}{d\xi} = \mu\delta e^{\theta} f(x) - \alpha(\theta - \tau_1), \quad (27)$$

$$\frac{d\tau_1}{d\xi} = \alpha(\theta - \tau_1), \quad (28)$$

$$\frac{d\tau_2}{d\xi_1} = \alpha_1(\tau_3 - \tau_2), \quad (29)$$

$$\frac{d\tau_3}{d\xi_1} = \alpha_1(\tau_3 - \tau_2). \quad (30)$$

The boundary conditions are

$$x|_{\xi=0} = 1; \quad \tau_1|_{\xi=0} = \theta|_{\xi=0}; \quad \tau_1|_{\xi=l} = \tau_2|_{\xi_1=l} = \theta_{in};$$
$$\tau_2|_{\xi_1=0} = \tau_0; \quad \tau_3|_{\xi_1=l} = \theta|_{\xi=l} = \theta_f. \quad (31)$$

With the aid of the results obtained for the cases I and II, it can be readily shown that the problem of solving the system (26)–(30) reduces to the solution of the transcendental equation

$$\varphi_1(y_0) = \int_0^{y_0} \frac{e^{-y}dy}{f\left(\frac{\delta - y}{\delta}\right)\left(\lambda e^{\tau_0 + \alpha_1 y_0} + \alpha \int_y^{y_0} \frac{se^{-s}ds}{f\left(\frac{\delta - s}{\delta}\right)}\right)} = 1, \quad (32)$$

*The condition $f'(x) \leq 0$, for example, is sufficient for this to occur.

**The condition $f'(x) < 0$, $f''(x) \geq 0$ is sufficient for this to occur.

where $\lambda = \delta\mu$. As in the problems I and II, two different cases are possible:

$$1)\ f\left(\frac{\delta - y}{\delta}\right) \neq 0 \text{ and } 2)\ f\left(\frac{\delta - y}{\delta}\right) = 0 \quad \text{for} \quad y = \delta.$$

In case 1), the function $\varphi_1(y_0)$ with a single maximum has the shape shown in Fig. 2 (curve 4). Hence, for almost all parameter values except certain critical ones, the problem has either two or no solutions.

In case 2) the function $\varphi_1(y_0)$ has the shape shown in Fig. 2 (curve 5). Hence, as a rule, the problem has one or three solutions.

NOTATION

c is the concentration of one of the reagents (taken as the key reagent); c_0 is the initial concentration; $x = c/c_0$ is the dimensionless concentration; r is the reaction rate; E is the activation energy; T is the reaction zone temperature; R is the gas constant; T_0 is the temperature read-off starting point; T_1 is the temperature of the initial mixture in the heating zone in an external heat exchanger; T_2 is the temperature of the initial mixture in the heating zone of an external heat exchanger; T_3 is the temperature of the hot reacted mixture in an external heat exchanger; L is the length of the reaction vessel; V is the volume of the reaction vessel; k(T) is the reaction rate constant; v is the volumetric flow rate; h is the thermal effect of reaction; γ is the volumetric heat capacity of the reactive mixture; k_T is the heat transfer coefficient; d is the diameter of heat-exchanger tubes; $\xi = l/L$ is the dimensionless coordinate in the reaction vessel, read from the point of penetration of the mixture into the reaction zone; $\xi_1 = l_1/L_1$ is the dimensionless coordinate in the external heat exchanger, read from the point of initial-mixture entrance; $\theta = E(T - T_0)/RT_0^2$; $\tau_i = E(T_i - T_0)/RT_0^2$ ($i = 1, 2, 3$) are the corresponding dimensionless temperatures; α and α_1 are the dimensionless heat transfer coefficients in an internal and external heat exchanger, respectively.

REFERENCES

1. V. G. Levich and A. M. Brodskii, DAN SSSR, **165**, no. 2, 1965.

2. I. I. Ioffe and L. M. Pis'men, Engineering Chemistry of Heterogeneous Catalysis [in Russian], Moscow, Izd. Khimiya, 1965.

3. Van Heerden, Ind. Eng. Chem., **45**, 1242, 1953.

4. M. G. Slin'ko and A. L. Muller, Kinetika i kataliz, **2**, 467, 1961.

5. M. G. Slin'ko, V. S. Beskov, and V. B. Skomorokhov, Khimicheskaya promyshlennost, no. 9, 641, 1963.

6. R. F. Baddour, P. L. Brian, B. A. Logeais, and J. P. Eymery, Chem. Eng. Sci., **20**, no. 4, 281, 1965.

7. T. I. Zelenyak, Differentsial'nye Uravneniya [Differential Equations], **2**, 205, 1966.

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