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**HEAT AND MASS TRANSFER  
IN HETEROGENEOUS CATALYSIS. XXIV.\*****EFFECT OF HEAT  
AND MASS TRANSFER BETWEEN EXTERNAL SURFACE  
OF CATALYST PARTICLE AND BULK  
OF REACTION MIXTURE ON DYNAMIC BEHAVIOUR  
OF AN IDEALLY MIXED FLOW REACTOR**

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On a mathematical model is studied the dynamic behaviour of an ideally mixed flow reactor in which exothermic reaction of the first order takes place, whose rate is affected by heat and mass transfer between the external surface of the catalyst particle and the bulk of reaction mixture. For study of microstability of steady states of the reactor was used the first Ljapunov method. System of non-linear differential equations was transformed into a system of linear homogeneous differential equations of the first order with a singular point in the steady state of the reactor and the Poincaré classification of singular points was applied at the same time. The course of steadying of the reactor regime (macrostability) was studied on trajectories in a phase plane of temperature of the catalyst particle on concentration of the reactant in the reactor, obtained by numerical integration of the system of non-linear differential equations. It was found out that with exothermic reactions in steadying of concentration in the reactor can the temperature of the catalyst particle approach the steady state by damped oscillations. It was further found that stability of the steady state of the reactor regime depends on ratio of the reactor volume and the amount of catalyst. From the analysis of stability and from calculations follows that the steady state of the reactor regime can be stable even in the case that the steady state of the catalyst particle is not stable.

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In catalytic reactions with heat effect there builds up a temperature difference between the bulk of the reaction mixture and the external surface of the catalyst particle with a magnitude in steady state dependent on concentration of the reactant in the bulk of reaction mixture. Since the particle has a certain heat capacity, the temperature difference does not equalize at the concentration change of the reactant immediately to the steady state value but it is it continuously approaching. Therefore, at changes in composition of reaction mixture at steadying of the ideally mixed flow reactor the steadying of the particle surface temperature is slightly retarded to the concentration steadying in the reactor.

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This work aims at studying on a mathematic model the phenomena which results from this retardation in steadying of the reactor, *i.e.* to study the dynamic behaviour of the reactor.

Literature dealing with the problem of dynamic behaviour of systems in general is very comprehensive<sup>1-7</sup>. Mathematical models describing dynamic behaviour of the system have in majority a non-linear character and therefore the study of stability can be in some of the cases rather complex and difficult. Basical works on analysis of stability of systems are published by Ljapunov<sup>8</sup>, Poincarè<sup>9</sup> and Minorsky<sup>19</sup> who applied methods of non-linear mechanics to this problem. The mentioned authors approximated the original non-linear model of the system by the linear model. Ljapunov<sup>8,11</sup> has proved that linearization of the model in accordance with dependent variables in vicinity of the steady state and a following analysis of the linear model is well-founded and that the linearized model satisfactorily describes the given system in the closest vicinity of the steady state (the first Ljapunov method). For analysis of the given steady state can be then used for example the Poincarè classification of singular points<sup>9,12</sup>, the Routh-Hurwitz theorem<sup>13</sup> *etc.*

The linearized model, however, provides information on dynamic behaviour, resp. on stability of the system, only in the closest vicinity of the steady state (microstability). But we are very often interested in behaviour of the system farther from the steady state (macrostability). If the given system is solved either analytically or numerically, the technique of the phase plane can be used, *i.e.* mapping of the motion trajectories in the plane of dependently variable quantities (*e.g.* in the phase-plane temperature-concentration). Lately, a series of works uses the second (direct) Ljapunov method for analysis of stability of the system<sup>1,5-8,14</sup>.

A number of authors<sup>15-18</sup> studied the dynamic behaviour of the ideally mixed flow reactor. Summarily elaborated is the whole problem of stability of the ideally mixed flow reactor for example in monography by Aris<sup>19</sup>. The problem of heat and mass transfer effect between the external surface of the catalyst particle and the bulk of reaction mixture on dynamic behaviour of the ideally mixed flow reactor has not yet been made.

## THEORETICAL

### Mathematical Model

This work refers to the previous paper<sup>20</sup> and for derivation of the model are used the same assumptions. It is assumed that the reaction rate is a function of concentration and of temperature on the surface of the catalyst particle. Calculation is limited to reaction of the first order, for temperature dependence of the rate constant of the reaction is assumed validity of the Arrhenius equation. Then it holds

$$r_R = k_0 p_{As} \exp \left[ \frac{E}{R_g T T_s} (T_s - T) \right]. \quad (1)$$

For the transfer rate of matter *A* to the external surface of the particle was used the relation

$$r_D = k_g a_m (p_A - p_{As}). \quad (2)$$

For the rate of heat transfer from the particle surface to the bulk of reaction mixture

was used relation

$$r_h = k_h a_m (T_s - T). \quad (3)$$

It is assumed that the catalyst particle is non-porous and that it has infinite heat conductivity. The temperature inside the particle then equals to the temperature on the particle surface. Accumulation of the reactant on the particle surface is neglected. At the mentioned assumptions, the steadying of particle temperature is expressed by equation

$$r_R(-\Delta H) = k_h a_m (T_s - T) + c_{pk}(dT_s/dt) \quad (4)$$

with boundary conditions

$$t = 0, \quad T_s = T_{s,in}. \quad (4a)$$

For steady state

$$(dT_s/dt) = 0. \quad (4b)$$

If accumulation of reactant on the particle surface is neglected, the rate of chemical reaction equals to the rate of diffusion of substance *A* to the surface and then the equality holds

$$r_R = r_D. \quad (5)$$

The reactor is considered to be an ideally mixed flow reactor in which a reaction without the volume change takes place. The course of steadying of concentration in the reactor is then described by equation

$$(F/R_g T)(p_{A0} - p_A) = r_R W + (dp_A/dt)(V/R_g T) \quad (6)$$

with boundary conditions

$$t = 0, \quad p_A = p_{A,in}. \quad (6a)$$

For steady state

$$(dp_A/dt) = 0. \quad (6b)$$

On combining and modifying the mentioned equations was obtained a system of non-linear differential equations of the first order whose solution describes the course of concentration steadying in the reactor. In the dimensionless form these equations can be written

$$\begin{aligned} d \Delta T / d\tau &= -\Delta T (B Da / \phi_m \Omega_m) + B Da R\beta = \\ &= -\Delta T (B Da / \phi_m \Omega_m) + B Da P_A \{ \phi_m + \exp [ -\Theta \Delta T / (1 + \Delta T) ] \}^{-1}, \end{aligned} \quad (7)$$

$$\begin{aligned} dP_A / d\tau &= P_{A0} - P_A - Da R\beta = \\ &= P_{A0} - P_A - Da P_A \{ \phi_m + \exp [ -\Theta \Delta T / (1 + \Delta T) ] \}^{-1}, \end{aligned} \quad (8)$$

with boundary conditions

$$\tau = 0, \quad \Delta T = \Delta T_{in}, \quad P_A = P_{A,in}; \quad (8a)$$

and for steady state

$$(d \Delta T / d\tau) = 0, \quad (dP_A / d\tau) = 0. \quad (8b)$$

In Eq. (7) and (8) are the quantities  $\Theta$ ,  $\phi_m$ ,  $\Omega_m$ ,  $Da$ , and  $B$  defined by relations

$$\Theta = E / R_g T, \quad \phi_m = r_{0m} / k_g a_m p_{Am}, \quad \Omega_m = (-\Delta H) k_g p_{Am} / k_h T, \quad (9, 9a, 9b)$$

$$Da = W r_{0m} R_g T / F p_{Am} = (P_{A0} - P_{Au}) / R\beta_u, \quad (9c)$$

$$B = V (-\Delta H) p_{Am} / W c_{pk} R_g T^2. \quad (9d)$$

The system of differential equations (7) and (8) was in this work solved numerically by the Runge-Kutta-method (Merson's modification) on the digital computer Elliott 4120. Initial values of quantities  $\Delta T$  and  $P_A$  were chosen and integrated as long as these quantities remained constant. Separatrix of this system of equations was determined by integration with negative time, with initial values of quantities  $\Delta T$  and  $P_A$  close to that in steady state.

#### *Analysis of Stability of Steady States of the Reactor*

For study of microstability of the regime of an ideally mixed flow reactor, *i.e.* stability of the regime in the closest vicinity of the steady state, can be used the first Ljapunov<sup>1-4,8,11,18</sup> method combined with the Poincaré classification of singular points (of steady states)<sup>1,3,9,12,18</sup>. The first Ljapunov method is based on the perturbation<sup>1</sup> method. Dependent variables  $\Delta T$  and  $P_A$  and the quantity  $R\beta$  is expressed as a function of small perturbations (deviations) from values of these quantities corresponding to the steady state:

$$P_A = P_{Au} + \Delta P'_A, \quad \Delta T = \Delta T_u + \Delta T', \quad R\beta = R\beta_u + \Delta R\beta \quad (10, 10a, 11)$$

where

$$R\beta = (P_A - \Phi_m R\beta) \exp [\Theta \Delta T / (1 + \Delta T)], \quad (11a)$$

$$R\beta_u = (P_{Au} - \Phi_m R\beta_u) \exp [\Theta \Delta T_u / (1 + \Delta T_u)], \quad (11b)$$

$$\Delta R\beta = (\partial R\beta / \partial P_A)|_{\Delta T, u} \Delta P'_A + (\partial R\beta / \partial \Delta T)|_{P_A, u} \Delta T'. \quad (11c)$$

In Eq. (11c) can be substituted for values of partial derivations the relations obtained by derivation of Eq. (11a). On combining relations (7), (8), (11), and (11c) a system of linear differential equations of the first order can be obtained

$$d \Delta T / d\tau = d \Delta T' / d\tau = X_1 \Delta T' + X_2 \Delta P'_A, \quad (12)$$

$$d P_A / d\tau = d \Delta P'_A / d\tau = X_3 \Delta T' + X_4 \Delta P'_A. \quad (13)$$

where  $X_1$  to  $X_4$  are constants defined by relations

$$X_1 = R\beta_u B D a \Theta (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2} - (B D a / \Phi_m \Omega_m), \quad (14)$$

$$X_2 = B D a R\beta_u / P_{Au}, \quad (14a)$$

$$X_3 = -R\beta_u D a \Theta (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2}, \quad (14b)$$

$$X_4 = -1 - D a R\beta_u / P_{Au}. \quad (14c)$$

The system of Eq. (12) and (13) can in general be solved<sup>3,4</sup> with a characteristic equation of the form

$$\alpha_{1,2} = 1/2 \{ X_1 + X_4 \pm [(X_1 - X_4)^2 + 4X_2 X_3]^{1/2} \} \quad (15)$$

where  $\alpha_{1,2}$  ( $\alpha_1 \neq \alpha_2$ ) are the roots of the characteristic equation. By using the Poincaré classification we can now decide about the stability of stationary solutions of the system of equations (12) and (13) and divide them in agreement with values  $\alpha_{1,2}$  into solutions of the type: node, focus, saddle and centre. As we deal with linear approximation of non-linear problem, we will no more consider the solution of the centre-type. Characteristics of particular types of stationary solutions are given in Table I.

On substituting of relations (14) to (14c) into definition relations for quantities  $S$ ,  $D$ , and  $Q$  we obtain

TABLE I

Characteristics of Stationary Solutions of the System of Equations (12) and (13) by Use of Poincaré Classification

Type of solution	$S$	$D$	$Q$	Stability
Saddle	$>0$	$-$	$-$	unstable
Node	$<0$	$\geq 0$	$<0$	stable
	$-$	$-$	$>0$	unstable
Focus	$-$	$<0$	$<0$	stable
	$-$	$<0$	$>0$	unstable

$$S = R\beta_u \Theta B D a (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2} - (B D a / \Phi_m \Omega_m) (1 + D a R\beta_u / P_{Au}), \quad (16)$$

$$D = [R\beta_u \Theta B D a (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2} - (B D a / \Phi_m \Omega_m) + 1 + D a R\beta_u / P_{Au}]^2 - 4 B D a^2 R\beta_u^2 \Theta (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2} / P_{Au}, \quad (16a)$$

$$Q = R\beta_u \Phi B D a (1 - R\beta_u \Phi_m / P_{Au}) (1 + R\beta_u \Phi_m \Omega_m)^{-2} - (B D a / \Phi_m \Omega_m) - 1 - D a R\beta_u / P_{Au}. \quad (16b)$$

## RESULTS AND DISCUSSION

### *Analysis of Dependence of Curves Describing the Steady States of the Catalyst Particle and Steady States of the Ideally Mixed Flow Reactor*

If the catalyst particle is in a steady state, the dependence of relative reaction rate on relative partial pressure of the reactant in bulk of the reaction mixture is described by curve which is further denoted as curve  $R\beta_u$  (Eq. (11b))<sup>20</sup>. If the mass and heat transfer effect between the external surface of the catalyst particle and the bulk of the reaction mixture (effect of the external mass and heat transfer) is eliminated for the first order reaction the curve  $R\beta_u$  is a straight line with the slope equal to one passing through the origin. Due to imperfect external mass and heat transfer there form, between the particle surface and bulk of the reaction mixture, concentration and temperature differences which are altering the dependence of relative reaction

rate on relative partial pressure of the reactant. The effect of external mass and heat transfer and of temperature on the relative reaction rate is dependent on values of parameters  $\Phi_m$ ,  $\Omega_m$ , and of constant  $\Theta$ . Physical meaning of these parameters was discussed in previous papers<sup>20</sup>. Constant  $\Theta$  is a dimensionless activation energy and it characterizes the sensibility of the rate constant to temperature changes. Parameter  $\Omega_m$  is the highest temperature difference which can build up between the particle surface and bulk of the reaction mixture divided by temperature of bulk of the reaction mixture. Parameter  $\Phi_m$  determines the position of the system between the kinetic and diffusion regions.

In exothermic reactions is the reaction rate increasing due to imperfect heat transfer as compared to the rate in kinetic region. According to values of the discussed parameters, is the curve  $R\beta_u$  a smooth one with an inflex point, or in a certain region of the discussed parameters in strongly exothermic reactions a curve on which in a certain region of partial pressures of reactant there correspond to a single value of partial pressure three values of a dimensionless reaction rate (Fig. 1 and 2). In the second case there correspond to a single value of partial pressure three states of the particle. As it was indicated in previous papers, the states with the highest and lowest reaction rates are stable, as concerns the particle catalyst, with the state at the mean value of the reaction rate unstable. For definition of conditions of existence of three steady states it is more advantageous to work with an inversion function  $P_A = P_A(R\beta)$  because this function is a smooth one. From the graphical plot follows that the steady state of the particle is, as concerns the particle, unstable, when

$$\left(\frac{\partial P_A}{\partial R\beta}\right)_u < 0. \quad (17)$$

In the region of partial pressures in which this condition can be fulfilled, exist three steady states of the catalyst particle at a single value of partial pressure.

To keep the ideally mixed flow reactor in a steady state, the following condition (Eq. (6)) must be fulfilled

$$R\beta Da = P_{A0} - P_A. \quad (18)$$

In the coordinate axes  $R\beta$  and  $P_A$  is this condition fulfilled in points situated on the straight line passing through the point  $(P_A = P_{A0}, R\beta = 0)$  with the slope  $Da^{-1}$  (this line will be hereinafter called the operating line of the reactor). If a catalytic reaction takes place in the ideally mixed flow reactor which is affected by the external mass and heat transfer, then in the steady state must be fulfilled the condition of a steady state both as concerns the catalyst particle as well as the reactor. The steady states of the system are therefore in the coordinates  $R\beta$  and  $P_A$  determined by the point of intersection of the operating line of the reactor with the curve  $R\beta_u$ . When we assume

that the particle is in a steady state and that consequently the particle state moves along the curve  $R\beta_u$ , the criterion of stability of the steady state can be formally applied as concerns the reactor (concentration stability of the reactor). The steady state is as concerns the reactor stable in the case for which the condition is fulfilled

$$(\partial P_A / \partial R\beta)|_u > (P_{Au} - P_{A0}) / R\beta_u = -Da. \quad (19)$$

The so defined stability will be further on called the stability as concerns the reactor and will be distinguished from the stability as concerns the whole system. The stability as concerns the system includes both effects of reactor properties and of the catalyst particle.

According to the shape and position of curve  $R\beta_u$  with regard to initial partial pressure  $P_{A0}$  and according to the value  $Da$  can be the condition of steady state of the system fulfilled either in one or in three points. In three points it is fulfilled when the inequality holds

$$(\partial P_A / \partial R\beta)|_u < (P_{Au} - P_{A0}) / R\beta_u = -Da. \quad (20)$$

The steady states may be of three types, *i.e.* the stable state as concerns the reactor as well as the catalyst particle (A), the unstable state as concerns the particle and unstable as concerns the reactor (B), and the unstable state as concerns the particle and stable as concerns the reactor (C). In all five different cases can occur and they are given in Table II. For simplification the both cases and the steady state are represented by numbers and letters which are further used in the discussion.

The aim of this analysis was to determine how a system behaves in particular cases at a dynamic process, *i.e.* to determine which of the steady states are stable as concerns the whole system and also what determines one of several possible steady states into which the systems comes. As a dynamic process is considered such process which takes place at a constant temperature in the reactor, constant partial pressure of the reactant at the reactor inlet and constant value of  $Da$ , when a certain initial temperature of the catalyst particle ( $\Delta T_{in}$ ) and a certain initial partial pressure ( $P_{A,in}$ ) in the reactor are set.

#### *Analysis of Limiting Cases of Dynamic Behaviour of the System*

The course of dynamic processes can be followed by temperature changes of the catalyst particle, partial pressure of the reactant in the reactor, and the reaction rate. For recording the course of changes of the mentioned quantities it is advisable to use trajectories in the phase-plane  $R\beta$  on  $P_A$ , as well as of  $\Delta T / \Phi_m \Omega_m$  on  $P_A$ . The



coordinate  $\Delta T/\Phi_m\Omega_m$  has been used instead of coordinate  $\Delta T$  because in the steady state is valid the relation

$$R\beta_u = \Delta T_u/\Phi_m\Omega_m. \quad (21)$$

In the used coordinates is therefore the curve  $R\beta_u$  identical with the curve  $\Delta T_u/\Phi_m\Omega_m$ . This means that also the position of steady states is in both coordinate systems identical.

The course of dynamic changes of the reactor state and of the catalyst particle is in the dynamic process dependent on ratio of rate of temperature change of the catalyst particle to the rate of concentration change in the reactor. This ratio is affected by ratio of the particle heat capacity to the mass capacity of the reactor. Quantities which affect the ratio of these capacities are included in the parameter  $B$  (Eq. (9d)), which can be interpreted as the ratio of heat which would have been evolved by conversion of the reactant present in the reactor at its standard partial pressure to the heat accumulated in the catalyst at temperature of the bulk phase. The value of parameter  $B$  can be in practice varied by changing the ratio of the reactor volume to the amount of catalyst. To the limiting value of parameter  $B$  correspond two limiting cases of dynamic behaviour of the reactor. For  $B = \infty$  the reactor capacity is by far higher than the capacity of the catalyst particle. Therefore, at any dynamic process, the particle passes at first immediately into the steady state without a composition change of the reaction mixture in the reactor, *i.e.* into the steady state which corresponds to the initial partial pressure in the reactor. Changes of partial pressure in the reactor then take place at the steady state of the particle. The course of changes at the dynamic process is in both coordinate systems expressed by identical trajectory (Fig. 1 and 2). The particle state passes first into the steady state along the curve  $P_A = \text{const.} = P_{A,\text{in}}$  to the curve  $RB_u$ , which is identical with the curve  $\Delta T/\Phi_m\Omega_m$ . Along this curve then moves the state of the system into its steady state. Direction of the motion along the curve  $RB_u$  is determined by mutual position of the point in respect to the operating line of the reactor. If the point is situated below the operating line of the reactor, the state of the system moves toward higher values of partial pressure in the reactor, if it is situated above it then the state of the system moves toward lower values of partial pressure. In case that exist two steady states which are stable both as concerns the reactor and the particle (case III) than the state into which the system comes is determined by the initial particle temperature and by the initial partial pressure of the reactant in the reactor. The separatrix (line in the phase-plane which separates the "correspondence of trajectories" to particular steady states) separating the regions of two stable steady states is formed by part of the curve  $R\beta_u$ , respectively by  $\Delta T_u/\Phi_m\Omega_m$  on which are situated steady states unstable as concerns the particle (Fig. 2). In cases II and V when exists only a single steady state of the system which is unstable as concerns the particle, and stable as concerns

the reactor, or when exist three steady states of the system, all unstable as concerns the particle, the reactor works in the limiting cycle whose trajectory is in both coordinate systems identical and independent on the value of Damköhler number  $Da$  (Fig. 1 and 2). In case IV when three steady states exist from which only one is stable as concerns the particle, the system always steadies in this state (Fig. 1).

In the second limiting case ( $B = 0$ ), the capacity of the reactor is far smaller than the capacity of the catalyst particle. At the dynamic process therefore first changes the partial pressure in the reactor to the value corresponding to the steady state as concerns the reactor without a change in temperature of the particle. This rapid

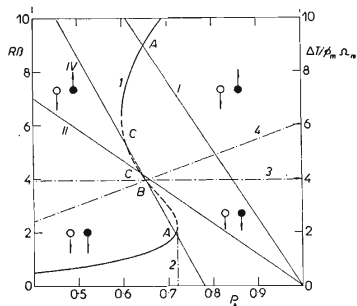


FIG. 1

Effect of External Heat and Mass Transfer on First Order Reaction in a Flow, Perfectly Mixed Reactor

$\theta = 20.42$ ,  $\Phi_m = 0.061$ ,  $\Omega_m = 0.5165$ ,  $P_{A0} = 1$  (case I and II),  $P_{A0} = 0.78$  (case IV).

Dashed line denotes steady states stable as concerns the catalyst particle, dash and dot the separatrix, black points with arrow denote the steady state in which the system steadies in the given region limited by the separatrix for  $B = 0$ , empty points with arrow for  $B = \infty$ , other symbols used are the same as that in Table II. 1 dependence  $R\beta_u$ , resp.  $\Delta T_u/\Phi_m\Omega_m$  on  $P_A$ ; 2  $B = \infty$ ; 3  $B = 0$  in coordinates  $\Delta T/\Phi_m\Omega_m$  on  $P_A$ ; 4  $B = 0$  in coordinates  $R\beta$  on  $P_A$ .

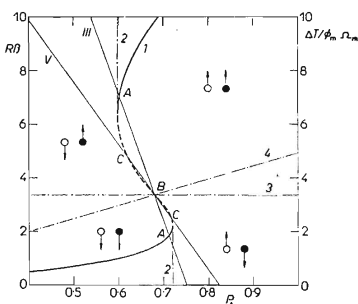


FIG. 2

Effect of External Heat and Mass Transfer on First Order Reaction in a Flow, Perfectly Mixed Reactor

$P_{A0} = 0.75$  (case III), resp.  $P_{A0} = 0.825$  (case V); other symbols used are the same as that in Fig. 1.

change can be expressed in coordinates  $R\beta$  on  $P_A$  as a quick motion from the initial point along the isothermal line to the operating line of the reactor. The isotherms describe the dependence of reaction rate on partial pressure of the reactant in the reactor at constant temperature of the catalyst particle. For the first order reaction the isotherms form a family of lines passing through the origin and are defined by Eq. (11a) for the case  $T_s = \text{const}$ . After reaching the operating line of the reactor, the state of the system moves slowly along the operating line toward the steady state. The motion direction is determined by position of the point in respect to the curve  $R\beta_u$ . If the point lies on the operating line of the reactor below the branch of curve  $R\beta_u$  denoting the stable states as concerns the particle or below the branch denoting stable states of the particle and, simultaneously, above the branch denoting unstable states of the particle, then it moves toward the lower partial pressure. If it lies below the branch denoting stable states of the particle or, simultaneously, above the branch denoting unstable states of the particle, it moves in direction of the higher partial pressure.

It follows from the results that in the discussed limiting case the state of the system cannot in any way move along the limiting cycle. States which are unstable as concerns the particle and stable as concerns the reactor, behave in the system as stable. Therefore, there can occur only two cases, *i.e.* either there exists only a single stable

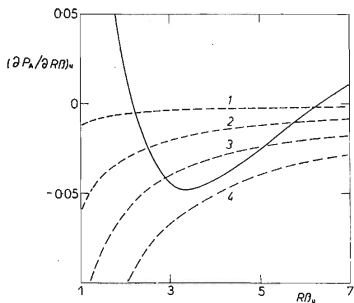


FIG. 3

Boundaries of Values of Parameter  $B$  Separating the Stability and Instability Regions [Eq. (22)]

$Da = 0.0432$ ,  $P_{A0} = 0.825$ ; Solid line denotes the dependence defined by Eq. (23), dashed line the one defined by Eq. (22).  
1  $B = 50$ , 2  $B = 10$ , 3  $B = 5$ , 4  $B = 3$ .

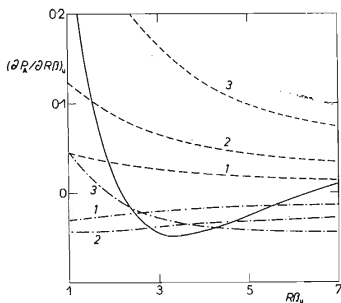


FIG. 4

Effect of Value of Parameter  $B$  on the Character of Steady State

$Da = 0.0432$ ,  $P_{A0} = 0.825$ ; Dashed and dash and dot lines denote the upper and lower limits of dependences defined by Eq. (24), other symbols used are the same as that in Fig. 3.  
1  $B = 50$ , 2  $B = 10$ , 3  $B = 2$ .

steady state or there exist two stable steady states. In the case of two steady states, the separatrix separating their regions in coordinates  $R\beta$  on  $P_A$  is an isotherm passing through the middle state which is unstable both as concerns the reactor as well as the particle. In coordinates  $\Delta T/\Phi_m \Omega_m$  is the separatrix determined by the isothermal line passing through this middle unstable state. It is obvious that only the initial particle temperature determines into which of the two possible stable steady states the regime of the system moves in the dynamic process. If the particle temperature is at the beginning of the dynamic process higher than corresponds to the separatrix, the system moves to the upper steady state, if it is lower, the system moves to the lower steady state.

From comparisons of both limiting cases follows that the parameter  $B$  characterizing the ratio of the reactor capacity to the particle capacity can significantly affect the behaviour of the system. First, some of steady states can behave, according to value of this parameter, as stable or as unstable, and further, in certain regions of initial particle temperature and of initial partial pressure the course of separatrix separating the regions of two stable steady states can be dependent on parameter  $B$ . Diagram of regions pertaining to individual steady states is given in Fig. 1 and 2.

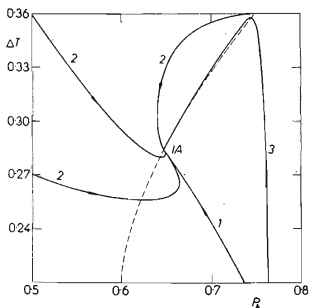


FIG. 5

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of the Reactant in Reactor for Case 1 (diffusion branch)

$Da = 0.0391$ ,  $P_{A0} = 1$ . Dashed line denotes the dependence of  $\Delta T_u$  on  $P_A$ .  $1 B = 0.8$ ,  $2 B = 1$ ,  $3 B = 50$ .

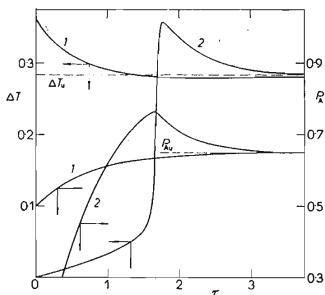


FIG. 6

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for the Case Given in Fig. 5

$1 B = 1$ ,  $2 B = 50$ .

*Analysis of Microstability of Steady States as Concerns the System*

For analysis of the system behaviour was used the Poincaré classification of singular points. The list of criterions used for the classification is given in Table I. From the analysis were made the following conclusions: The steady state to be stable, the inequality  $Q < 0$  must hold, which can be transformed into relation

$$(\partial P_A / \partial R\beta)|_u > P_{A0} \Phi_m \Omega_m / B (P_{Au} - P_{A0}) = -P_{A0} \Phi_m \Omega_m / R\beta_u B Da, \quad (22)$$

where the value of derivation on the left side of equation is determined by relation

$$(\partial P_A / \partial R\beta)|_u = \Phi_m + (P_{Au} - R\beta_u \Phi_m) / R\beta_u - R\beta_u \Phi_m \Omega_m \Theta (1 + R\beta_u \Phi_m \Omega_m)^{-2} \cdot (P_{Au} - R\beta_u \Phi_m) / R\beta_u. \quad (23)$$

The right-hand term of inequality (22) is always negative. From its comparison with the condition of stability of the catalyst particle (Eq. (17)) follows that the stability condition is always fulfilled when the steady state is stable as concerns the particle (state A (Fig. 3)). The steady states stable as concerns the particle are consequently stable for reactions of first order also as concerns the system. These stable steady

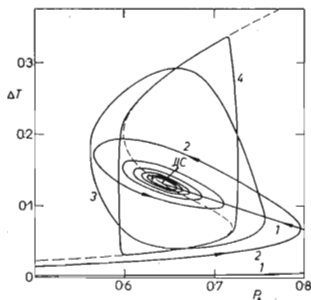


FIG. 7

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case II

Da = 0.0852,  $P_{A0} = 1$ . 1 B = 0.1, 2 B = 2, 3 B = 10, 4 B = 500; other symbols used are the same as that in Fig. 5.

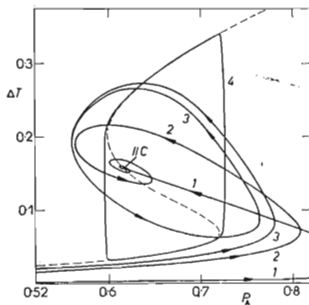


FIG. 8

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case II

Da = 0.0769,  $P_{A0} = 1$ . 1 B = 0.1, 2 B = 2, 3 B = 5, 4 B = 500; other symbols used are the same as that in Fig. 5.

states (A) can either be stable points of junction or stable foci according to value of quantity  $D$  (Table I). Steady state is the point of junction when holds the relation

TABLE II

Summary of Possible Stability Cases in a Flow, Perfectly Mixed Reactor with Significant Effect of External Heat and Mass Transfer

Case symbol	Number of states	State (No)	Stability		Fig.
			particle	reactor	
<i>I</i>	1	<i>I</i> A (1)	stable	stable	1
<i>II</i>	1	<i>II</i> C (1)	unstable	stable	1
<i>III</i>	3	<i>III</i> A (2)	stable	stable	2
		<i>III</i> B (1)	unstable	unstable	2
<i>IV</i>	3	<i>IV</i> A (1)	stable	stable	1
		<i>IV</i> B (1)	unstable	unstable	1
		<i>IV</i> C (1)	unstable	stable	1
<i>V</i>	3	<i>V</i> B (1)	unstable	unstable	2
		<i>V</i> C (2)	unstable	stable	2

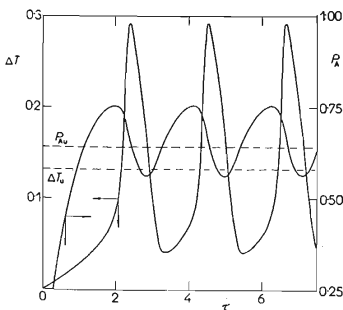


FIG. 9

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case of the Limiting Cycle (Fig. 7) for  $B = 10$

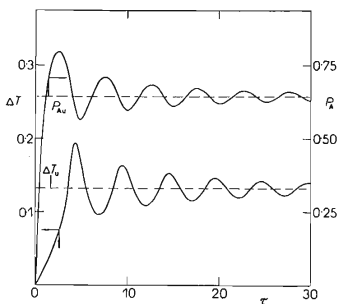


FIG. 10

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for the Case of Stable Focus (Fig. 7) for  $B = 2$

$$\{1 - c + 2[c(b - 1)]^{1/2}\}/ab \leq (\partial P_A/\partial R\beta)|_u \leq \{1 - c - 2[c(b - 1)]^{1/2}\}/ab, \quad (24)$$

where

$$a = R\beta_u/P_{Au} = (P_{A0} - P_{Au})/DaP_{Au}, \quad (25)$$

$$b = BDa/\Phi_m\Omega_m, \quad (25a)$$

$$c = R\beta_u Da/P_{Au} = (P_{A0} - P_{Au})/P_{Au}. \quad (25b)$$

The dynamic characteristics in parameter  $B$  are determining whether the steady state is the point of node or the focus. In limiting cases  $B = 0$  and  $B = \infty$  is the state always the point of junction; it can be the focus in case the steadying rate of the reactor is commensurable with the steadying rate of the catalyst particle. Examples of the effect of value of parameter  $B$  on character of the steady state are given in Fig. 4. Steady states (A), i.e. stable states as concerns the particle will not be considered in the following discussion, it concerns only states unstable as concerns the particle.

If the steady state is a saddle, it is always unstable as concerns the system and it is situated on the separatrix. Condition of existence of a saddle  $S > 0$  can be transformed into relation

$$(\partial P_A/\partial R\beta)|_u < (P_{Au} - P_{A0})/R\beta_u = -Da. \quad (26)$$

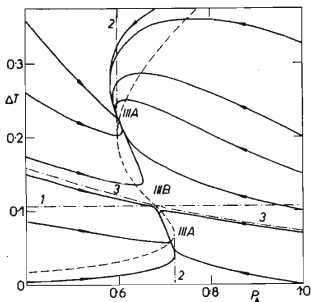


FIG. 11

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case III

$Da = 0.0209$ ,  $P_{A0} = 0.75$ ; Dashed line denotes the dependence of  $\Delta T_u$  on  $P_A$ , dash and dot line the separatrix. 1  $B = 0$ , 2  $B = \infty$ , 3  $B = 1.55$ .

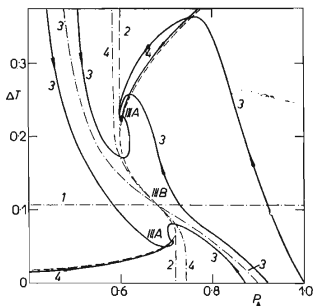


FIG. 12

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case III

1  $B = 0$ , 2  $B = \infty$ , 3  $B = 9$ , 4  $B = 50$ ; other symbols used are the same as that in Fig. 11.

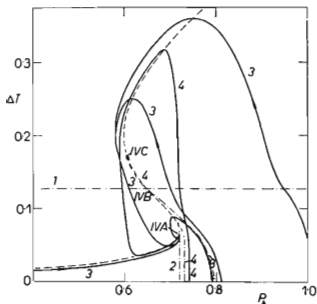


FIG. 13

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case IV

$Da = 0.03227$ ,  $P_{A0} = 0.78$ . 1  $B = 0$ , 2  $B = \infty$ , 3  $B = 10$ , 4  $B = 50$ ; other symbols used are the same as that in Fig. 11.

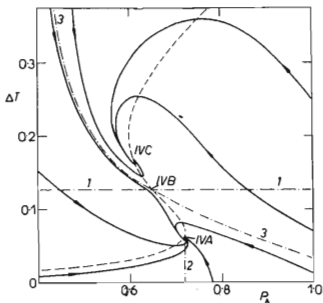


FIG. 14

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case IV

1  $B = 0$ , 2  $B = \infty$ , 3  $B = 3$ ; other symbols used are the same as that in Fig. 11.

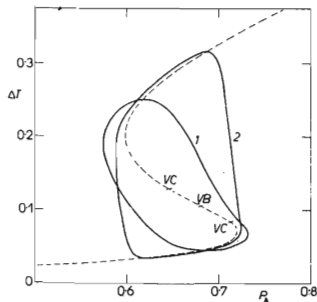


FIG. 15

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case V

$Da = 0.0432$ ,  $P_{A0} = 0.825$ ; 1  $B = 10$ , 2  $B = \infty$ ; other symbols used are the same as that in Fig. 5.

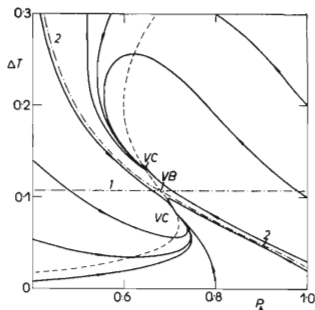


FIG. 16

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case V

1  $B = 0$ , 2  $B = 2$ ; other symbols used are the same as that in Fig. 11.



From comparison of this relation with the condition of existence of three steady states (Eq. (20)) follows that the steady state is the saddle always and only when it is situated on the part of curve  $R\beta_u$  determining unstable states as concerns the particle and when it is simultaneously the middle one of the three steady states. These middle steady states which are unstable as concerns the particle as well as the reactor (points  $B$ ) are therefore always unstable also as concerns the system. Points ( $B$ ) are not considered in the further discussion.

The most interesting behaviour of the system can be anticipated in steady states which are unstable as concerns the particle and stable as concerns the reactor (points  $C$ ). These steady states can be either the stable point of node or stable focus according to the magnitude of parameter  $B$ . Behaviour of the system in these states is dependent on the ratio of heat capacity of the catalyst particle to the mass capacity of the reactor and it can be considerably affected for inst. by the change in ratio of the catalyst amount to the reactor volume. Stability of the system in these states is affected by two opposite dynamic processes, i.e. by unstable dynamic behaviour of the particle and, by stable dynamic behaviour of the reactor. From results of evaluation the conclusion is made that dynamic properties of that process which is faster have the prevailing effect on stability of the system. It means that the reduction of the reactor volume or increase of the amount of catalyst which relatively speeds up the steadying of concentration in the reactor, leads to stabilization of the steady state and, *vice versa*, increase of the reactor volume or reduction of the catalyst amount which relatively speeds up the steadying of the particle temperature, leads to instability of the steady state. Boundary of values of parameter  $B$  which separates the regions of stability from instability, is dependent on values of parameters  $\Theta$ ,  $\Phi_m$ ,  $\Omega_m$ , i.e. on properties of the reaction and hydrodynamic conditions and on the position of the steady state

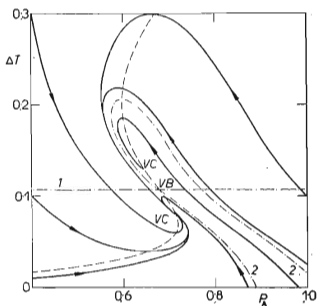


FIG. 17

Course of Temperature Steadying of Catalyst Particle and of Partial Pressure of Reactant in Reactor for Case  $V$

1  $B = 0$ , 2  $B = 3$ ; other symbols used are the same as that in Fig. 11.

on the curve  $R\beta_u$ . For the steady state it is the more difficult to reach stability the farther it is on the curve  $R\beta_u$  from the branch denoting steady stable states as concerns the catalyst particle. On value of parameter  $B$  depends also whether the steady state is the point of node or the focus. The conclusion of an analysis is in agreement with conclusion for points stable as concerns the particle. For the steady state to behave as a focus the capacities of the reactor and of the particle must be comparable. It means that the rate of changes of the particle temperature must be commensurable with the rate of concentration changes in the reactor. Therefore for small values of parameter  $B$  is the steady state an unstable point of node and with increasing value of parameter  $B$  it passes successively into unstable focus, stable focus and stable point of junction.

#### Examples of Courses of Temperature Steadying of Catalyst Particle and of Reactant Concentration in the Reactor

Examples of the course of steadying were obtained by integration of the system of equations (7) and (8) at the assumption that at steadying the temperature of the flowing reaction mixture and the value of Damköhler number  $Da$  do not change. Results of calculation are given by the course of trajectories in the phase plane  $\Delta T$  on  $P_A$ , and by dependences of the catalyst particle temperature and of partial pressure of the reactant in the reactor on the dimensionless time. The numbering of examples is identical with the one used in Table II.

*Case I.* A single steady state exists which is always stable. Dependence of the particle temperature and partial pressure in the reactor is, usually, a smooth curve or a curve with only one extreme. Only exceptionally, the state approaches the steady state by damped oscillations whose amplitude is small and which are strongly damped (Fig. 5 and 6).

*Case II.* There exists a single steady state stable as concerns the reactor and unstable as concerns the particle. If the particle state steadies more quickly (large value of parameter  $B$ ), the state of the system moves along the limiting cycle whose shape and magnitude are dependent on the value of parameter  $B$ . The limiting cycle always passes in vicinity of points in which  $(\partial P_A / \partial \Delta T_u) = 0$ , because in vicinity of these points the particle state changes very slowly<sup>20</sup>. With the decrease of value of parameter  $B$  this state becomes the stable focus. The system approaches this focus by damped oscillations. Damping of oscillations is dependent on the position of steady state on the curve  $R\beta_u$  and is the bigger the closer is the point to the parts of the curve characterizing states stable as concerns the particle. At low values of parameter  $B$  the steady state behaves like stable point of junction (Fig. 7 to 10).

*Case III.* There exist two always stable states and one state always unstable. Stable states are, with regard to the value of parameter  $B$ , either the point of node (Fig. 11) or the focus (Fig. 12). Their behaviour is similar to that of case I. On the value of parameter  $B$  is dependent also the separatrix separating regions of individual states.

*Case IV.* There exists one state always stable (lower state), one state always unstable (middle state) and one state with the stability dependent on magnitude of parameter  $B$ . If the particle state steadies rapidly (value of  $B$  is large) it is unstable as concerns the system and the separatrix starts from this state. The state of the system always passes to the lower state (Fig. 13). If the partial pressure in the reactor steadies rapidly (value of  $B$  is small) this state is stable as concerns the system (Fig. 14).

*Case V.* There exists one steady state always unstable and two states (lower and upper) with the stability dependent on value of parameter  $B$ . If the particle state steadies more rapidly than the partial pressure in the reactor (value of parameter  $B$  is large) the states are unstable as concerns the system and the state of the system moves along the limiting cycle encircling all three steady states. Form of the cycle depends on value of the parameter  $B$  (Fig. 15). By reducing value of parameter  $B$  the lower and upper steady states become stable as concerns the system (Fig. 16). The separatrix can, however, sometimes have such a form that it is possible to reach the upper steady state only from a narrow region of initial conditions (Fig. 17). This region widens with the decrease of value of parameter  $B$ .

## LIST OF SYMBOLS

$a$	quantity defined by Eq. (25)
$a_m$	external surface of catalyst particle in unit of mass
$b$	quantity defined by Eq. (25a)
$B$	parameter defined by Eq. (9d)
$c$	quantity defined by Eq. (25b)
$c_{pk}$	specific heat of catalyst
$D = (X_1 - X_4)^2 + 4X_2X_3$	dimensionless quantity
$Da$	Damköhler number Eq. (9c)
$E$	activation energy of reaction
$F$	volumetric flow rate of feed into reactor
$k$	rate constant of reaction
$k_0$	rate constant of reaction at temperature $T$
$k_g$	mass transfer coefficient
$k_h$	heat transfer coefficient
$p_A$	partial pressure of reactant in bulk of reaction mixture
$p_{Am}$	standard partial pressure of reactant in bulk of reaction mixture
$p_{A0}$	partial pressure of reactant in feed into reactor
$p_{As}$	partial pressure of reactant on surface of catalyst particle
$P_A = p_A/p_{Am}$	relative partial pressure of reactant
$P_{A0} = p_{A0}/p_{Am}$	relative partial pressure of reactant in feed into reactor
$Q = X_1 + X_4$	dimensionless quantity
$r_0$	reaction rate at temperature $T$ at conditions when is eliminated effect of external heat and mass transfer
$r_{0m}$	reaction rate $r_0$ related to partial pressure $p_{Am}$
$r_D$	rate of mass transfer [Eq. (2)]
$r_h$	rate of heat transfer [Eq. (3)]
$r_R$	reaction rate [Eq. (1)]
$R = r_R/r_0$	effectiveness factor of external heat and mass transfer
$R_g$	gas constant
$S = X_2X_3 - X_1X_4$	dimensionless quantity
$t$	time
$T$	temperature of bulk of reaction mixture
$T_s$	temperature of catalyst particle surface
$V$	volume of reactor
$W$	weight of catalyst
$X_1, X_2, X_3, X_4$	constants defined by Eq. (14) to (14c)
$\alpha$	root of characteristic equation (15)

$\beta = r_0/r_{0m}$	dimensionless quantity
$\Delta H$	enthalpy of reaction
$\Delta P'_A$	quantity defined by Eq. (10)
$\Delta T = (T_s - T)/T$	temperature difference
$\Delta T'$	quantity defined by Eq. (10a)
$\Delta R\beta$	quantity defined by Eq. (11)
$\theta = E/R_g T$	constant
$\tau = tF/V$	dimensionless time
$\Phi_m$	parameter defined by Eq. (9a)
$\Omega_m$	parameter defined by Eq. (9b)

## Subscripts

- in initial value of quantity at the beginning of dynamic operation  
 u value of quantity in steady state

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