## ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱՉԳԱՅԻՆ ԱԿԱԴԵՄԻԱ НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ АРМЕНИЯ

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## STEADY CONDITIONS OF AUTOCATALYTIC NONISOTHERMAL REACTIONS IN CSTR

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Abstract. The simulation CSTR has been carried out, in which the exothermal autocatalytic reaction proceeds. As distinct from a simple first order kinetics, in case of autocatalytic process in dimensionless coordinates "conversion – temperature" a rather diverse picture of possible types of thermal isoclinic line, including isola, is observed. It is established, that on the unstable branch of an isoclinic line only one steady state can exist. The analysis of oscillatory modes has shown that at change of governing parameter  $\gamma$  depending on other parameters, both smooth and rigid decay of limit cycle is possible. The adiabatic CSTR is steady always, and oscillatory modes in it are impossible.

The exothermal reactions in CSTR (continuously stirred tank reactor) are a significant object of macrokinetics [1]. In this field the bridge is thrown over the theory of thermal ignition and kinetics of chemical reactions in open systems.

For the first time, CSTR in which exothermal reaction proceeds has been analyzed by Zeldovich [2, 3]. In his papers, as well as in number subsequent publications, the simplest kinetic law, i.e. the first order reaction, was considered. It was found, that, depending on the values of parameters, the considered system can have one or three steady states.

Further development of the considered area has been realized in work of Salnikov and Volter [4]. These authors have confirmed the existence of one or three steady states in an exothermal first order reaction in CSTR and, besides, have considered a problem of stability of steady states.

Vaganov, Samoilenko and Abramov [5] have analyzed the stability of steady states. They have determined also the main types of phase portraits. It was shown that even in such simple process as first order reaction an extremely diverse picture arises: there are possible at least 35 different phase portraits.

Already in the first Zeldovich's works the fundamental analogy between exothermal processes in CSTR and phenomena of ignition and combustion was observed. Later Abramov and Merzhanov have analyzed in detail the conditions of thermal ignition in reactors of a similar kind [6].

In overwhelming number of the works dealing with exothermal reactions in CSTR, the simplest kinetic law, i.e. first order equation was used. At the same time a non-solved problem remains: how will be the behavior of such reactors in case of more complex kinetic law. Here we consider autocatalytic reactions. Note, that the conditions of thermal ignition in CSTR for a case of autocatalytic reactions have been reviewed earlier [7].

Further we follow the methodologies used in cited above papers (see, for example, [5]).

Let's accept following designations:  $\alpha$  (cal/cm<sup>2</sup>·s·deg) – heat-transfer coefficient; S (cm<sup>2</sup>) – surface area of reactor; V (cm<sup>3</sup>) – volume of reaction mixture in reactor; T (K) – temperature of reaction system in reactor;  $T_0$  (K) – ambient temperature;  $T_{input}$  (K) – temperature of reaction mixture entered into reactor;  $T_{initial}$  (K) – initial temperature in reactor; Q (cal/cm<sup>3</sup>) - heat effect of reaction; p (g/cm<sup>3</sup>) – density of reaction system (on input and output supposed identical);  $c_p$  (cal/g·deg) – thermal capacity of reaction system (supposed a constant); q (cm<sup>3</sup>/s) – volume rate of a mixture flow at input and at output);  $\eta$  – conversion (dimensionless);  $\eta_0$  – conversion in reaction system on input into reactor; t (s) – time; E (kcal/mol) – activation energy;  $k_0$  (s<sup>-1</sup>) – preexponential factor.

The system behavior in reactor, in which autocatalytic reaction proceeds, is described by the following equations:

 $c_{\rm p} p(dT/dt) = k_0 Q \exp(-E/RT)(1-\eta)(\eta_0+\eta) - \alpha(S/V)(T-T_0) - c_{\rm p} \rho(q/V)(T-T_{\rm input})$ (1)  $d\eta/dt = k_0 \exp(-E/RT)(1-\eta)(\eta_0+\eta) - (q/V) \eta$ (2)

The equation (1) is an equation of heat balance. Its left-hand part is the rate of heat accumulation in a reaction system, first member of the right-hand part is the rate of heat accumulation due to exothermal autocatalytic reaction, second member is the rate of heat loss through reactor walls into environment, and third member is the rate of heat consumption for heating of an influent. The equation (2) is an equation of chemical kinetics. Its left-hand part represents the rate of change of reactant concentration in the reactor, first member of the right-hand part is the rate of concentration change as a result of a chemical reaction, and second member is a rate of reactant concentration change in the reactor due to output of a flow from reactor.

Initial conditions: t = 0,  $\eta = \eta_{input}$ ,  $T = T_{initial}$ .

Let's introduce some new designations. Let  $T^* = (\alpha ST_0 + c_p pq T_{input})/(\alpha S + c_p \rho q)$ . The value  $T^*$  has the sense of scale temperature, as at q = 0 we have  $T^* = T_0$ , and at  $q \rightarrow$  we have  $T^* = T_{input}$ . Let's accept the following notation for two last members in an equation (1):  $(\alpha S/V) + c_p \rho q/V$ 

 $= (\alpha S/V)^*.$ 

Then after simple transformations the equation (1) will take the form:

 $c_p \rho(dT/dt) = k_0 Q \exp(-E/RT) \cdot (1 - \eta)(\eta_0 + \eta) - (\alpha S/V)^*(T-T^*)$ , that is formally equivalent to Semenov equation for thermal explosion [8].

Let's proceed now to dimensionless variables. Let  $\tau = tk_0 \exp(-E/RT^*)$ ,  $\theta = E(T - T^*)/RT^{*2}$ ,  $\gamma = (RT^*/E)(pc_pT^*/Q)$ ,  $\beta = RT^*/E$ ,  $Da = (V/q)k_0 \exp(-E/RT^*)$ ,  $Se = (E/RT^{*2})[QV/(pc_pq + \alpha S)]k_0 \exp(-E/RT^*)$ . Here  $\tau$  is dimensionless time,  $\theta$  is dimensionless temperature. Da is Damköhler parameter,

describing a dimensionless mean time of the presence of a matter in reactor, Se is dimensionless parameter being analogue of Semenov parameter in theory of thermal explosion.

With introduced notations, the equations (1) and (2) can be written to a dimensionless kind:  $\begin{aligned} \gamma(d\theta/d\tau) &= (1 - \eta)(\eta_0 + \eta) \exp[\theta/(1 + \beta\theta)] - \theta/Se \equiv F(\eta, \theta) \end{aligned}$ (3)  $d\eta/d\tau &= (1 - \eta)(\eta_0 + \eta) \exp[\theta/(1 + \beta\theta)] - \eta/Da \equiv G(\eta, \theta) \end{aligned}$ (4)

Initial conditions:  $\tau = 0$ ,  $\eta = \eta_{input}$ ,  $\theta = E(T_{initial} - T^*)/RT^2$ .

Steady states of the system under consideration can be obtained by equating derivatives in the above-stated equations to zero. In outcome we have:

$(1 - \eta)(\eta_0 + \eta)\exp(\theta/(1 + \beta\theta) - \theta/Se = 0$	(5)
$(1 - \eta)(\eta_0 + \eta)\exp(\theta/(1+\beta\theta) - \eta/Da = 0$	(6)

Term by term subtraction of (5) from (6) results in:

$$\theta = \frac{Se}{Da}\eta\tag{7}$$

In the system of three equations (5) - (7) only two are linearly independent, and we can use any pair of these equations.

As the equations (5) and (6) correspond to constant (zero) values of derivatives, graphically they are described by the respective isoclinic lines. The kind of these isoclinic lines in co-ordinates  $\eta - \theta$  depends on parameters of the process, first of all, on the *Se* value. The isoclinic line depicted by the equation (5) corresponds to a steady state on temperature. Hereinafter we shall call it as thermal isoclinic line.

To obtain a full picture of the types of thermal isoclinic line, we shall address to the equation (5). It is quadratic equation relative to  $\eta$ . Its solution is:

$$\eta_{1,2} = \frac{1 - \eta_0}{2} \pm \sqrt{\frac{(1 + \eta_0)^2}{4} - \frac{\theta}{Se}} e^{\frac{-\theta}{1 + \beta\theta}}$$
(8)

Let's introduce following notations:

$$f(\boldsymbol{\theta}) = \boldsymbol{\theta} e^{-\frac{\boldsymbol{\theta}}{1+\boldsymbol{\beta}\boldsymbol{\theta}}}$$

$$g(\eta) = Se \frac{(1+\eta_0)^2}{4}$$

It is evident that the sign of the subduplicate in (8) (and, therefore, the number of solutions of this equation) depends on the ratio between  $f(\theta)$  and  $g(\eta)$ . It is suitable to observe the indicated ratio graphically showing the functions  $f(\theta)$  and  $g(\eta)$  with  $\theta$  as abscissa. Then  $f(\theta)$  will be described by curve 1 on Fig. 1 and  $g(\eta)$ , as it does not depend from  $\theta$ , will be represented by horizontal lines 2 – 6. On Fig. 1 such relations for the case  $\beta = 0.2$  are shown, and the values  $g(\eta)$  for horizontal lines (bottom-up) are equal accordingly 0.3; 0.35; 0.4; 0.48 and 0.5.



**Figure 1.** Functions  $f(\theta)$  (1) and  $g(\theta)$  (2 – 6) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ . For 2 – 6 *Se* values are equal 1.176; 1.377; 1.568; 1.880 and 1.961 consequently.

We see, that, depending on the ratio between  $f(\theta)$  and  $g(\eta)$ , five different situations are possible (for horizontal lines bottom-up): one interception with the left-hand branch, one interception and one contact, three interceptions, one contact and one interception with a right-hand branch, one interception with a right-hand branch.

Let's look now, as these different situations will be exhibited on a phase plane in co-ordinates  $\eta - \theta$ . For this purpose, supposing  $\eta_0 = 0.01$ , we select values *Se* so that the function  $g(\eta)$  being equal to mentioned above values 0.3, 0.35, 0.4, 0.48 and 0.5. The corresponding *Se* values are equal 1.176; 1.377; 1.568; 1.880 and 1.961 respectively.

For the solution of this problem we shall use the equation (5).

The case Se = 1.176. The thermal isoclinic line for this case is shown on Fig. 2. It represents a curve with maximum.

The case Se = 1.377. The thermal isoclinic line is shown on Fig. 3. It represents a curve and a point arranged from above.

The case Se = 1.568. The thermal isoclinic line presented on Fig. 4 consists of two parts, lower branch and isolated upper branch, which is isola. Between them a "forbidden region" exists. This region covers the temperature range, which is inaccessible in steady conditions at selected values of parameters irrespective of the initial conditions. Such nature of isoclinic line has merely kinetic nature and is a consequence of non-linear kinetics. "Forbidden region" exists because we decided a quadratic equation (5), not having the solutions at negative value of the subduplicate in (8). Nothing similar is observed in simple first order kinetics [5].

The case Se = 1.88. The thermal isoclinic line is shown on Fig. 5. Here there is a coalescence of the lower branch of isoclinic line with isola. The coalescence occurs, when the contact of a curve 1 and straight line 5 in Fig. 1 takes place. For this case we have [7]:

$$Se = \frac{4\theta_s}{(1+\eta_0)^2} \cdot e^{-\frac{\theta_s}{1+\beta\theta_s}}, \text{ where } \theta_s = \frac{1-2\beta + \sqrt{1-4\beta}}{2\beta^2}$$

The case Se = 1.961. The thermal isoclinic line is shown on Fig. 6.

The reviewed examples cover all diversity of kinds of a thermal isoclinic line, which can arise in the studied autocatalytic reaction. The Figs. 2 - 6 demonstrate, as the evolution of isoclinic line proceeds at *Se* value increasing. At small *Se* values the isoclinic line represents a curve with a maximum (Fig. 2). At subsequent *Se* value increasing some value is reached, when isola arises (Fig. 3). It exists in some range of *Se* values (Fig. 4), and then disappears at some *Se* values, joining with the lower branch of isoclinic line (Fig. 5). In the course of further increasing *Se* values, the branches of isoclinic line diverge to the right and to the left, and isoclinic line takes the form shown on Fig. 6. It is interesting to note, that the right-hand branch of isoclinic line presented on Fig. 6 rather resembles an isoclinic line for the case of a simple first order reaction [5]. In other words, the transition from a simple kinetics to an autocatalytic reaction as though "adds" the left-hand branch of isoclinic line on Fig. 6. As a whole it is possible to draw a conclusion that the transition from a simple kinetics to complex one (on an example of autocatalysis) results in a large diversification of kinds of thermal isoclinic line.



Figure 2. Dependences (7) and (8) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 1.176.

The steady states of investigated system can be found by solution of a system of equations (5) and (7). The thermal isoclinic lines corresponding to equation (5) are shown in Fig. 2 - 6, and equation (7) is presented with straight lines coming from the point of origin. As an example such straight lines are

shown on Fig. 2 and 6. Comparing the indicated straight lines with thermal isoclinic lines on Fig. 2 - 6, it is easy to see that the considered system can have ether one, or three steady states.



**Figure 3.** Dependences (7) and (8) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 1.377.



**Figure 4.** Dependences (7) and (8) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 1.568.



**Figure 5.** Dependences (7) and (8) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 1.880.



Figure 6. Dependences (7) and (8) at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 1.961.

The main problem in research of processes proceeding in open systems is the problem of stability of steady states. The approaches to the stability analysis of dynamic systems are well-known [1, 9]. In frame of these approaches, it is possible to determine the types of stability of steady states at different values of parameters. On Fig. 7, on the basis of the analysis of equations (5) and (7) in co-ordinates Se - Da, the areas of existence of one (top of a figure) and three (bottom) steady states are divided. On Fig. 8 the result of analysis resulting in determination of the type of steady state stability is shown. As it was just marked, the bottom of a figure corresponds to the area of three steady states; the stability region only of one of them (high temperature) is here presented. The similar analysis has shown, that the low temperature steady state is stable (stability of the "stable node" type), and the steady state corresponding to medium temperatures, is absolutely unstable (instability such as "saddle").

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**Figure 7. The** regions of steady state stability at  $\beta = 0.02$ ,  $\gamma = 0.02$ ,  $\eta_0 = 0.01$ .

At the research of stability of steady states, one of main problems is that of the mechanism of stability change. From equations (3) and (5) it follows, that parameter  $\gamma$  does not influence on the position of steady state. On the other hand, it affects on the type of its stability undoubtedly. Let's consider a part of right-hand branch of a thermal isoclinic line of Fig. 6 between points 1 and 2. These points correspond to extremes on the dependence of  $\eta$  on  $\theta$  for a right-hand branch. The given part is selected because at very small value of  $\gamma$  (a limit at  $\gamma \rightarrow 0$ ), i.e. at very large heat effects of reaction, a limit cycle takes place, i.e. the system is in unstable oscillatory state (for reaction of first order this problem is reviewed in [5]). Therefore hereinafter we shall call the branch between points 1 and 2 as unstable branch.



**Figure 8.** The regions of steady state stability at  $\beta = 0.02$ ,  $\gamma = 0.02$ ,  $\eta_0 = 0.01$ .

1 -stable node, 2 -stable focus, 3 -unstable focus, 4 -stable node, 5 -stable focus, 6 -unstable focus, 7 -unstable node.

On Fig. 6 straight line coming from point of origin, intercepts a thermal isoclinic line in three points, i.e. for a system three steady states are possible. At that two interceptions take place on the left-hand branch and only one – on right hand one. There is a problem: whether always it so? Whether there is a situation, when all three interceptions take place on right-hand branch? Let's show, that it is impossible.

In point of intersections of thermal isoclinic line with straight line coming from point of origin, the equations (7) and (8) are simultaneously valid. As we are interested with the right-hand branch of thermal isoclinic line only, we shall take from the equation (8) only a solution signed plus. Placing (7) into (8) and having entered notation  $\sigma = Se/Da$ , after simple transformations we receive

$$e^{-\frac{\partial\eta}{1+\beta\sigma\eta}} = \frac{Da}{\eta}(\eta+\eta_0)(1-\eta)$$
<sup>(9)</sup>

The right member of this equation as function of  $\eta$  is described by monotonically decreasing curve without inflection points. The left-hand part of equation at positive values of parameters is also described by monotonically decreasing curve without inflection points. Therefore, for these curves three and more interception is impossible. Two interceptions are also impossible, because in this case reactor would have an even number of steady states that is invalid. This implies that at positive values of parameters the equation (9) can have not more than one solution, quod erat demonstrandum. Thus, at the given values of parameters on unstable branch of thermal isoclinic line the only unstable steady state and the only oscillatory regime are possible.

We already noted that at very small values of  $\gamma a$  limit cycle takes place. If  $\gamma$  is increased, the limit cycle step-by-step changes, and at some value  $\gamma = \gamma_0$  it depletes. The value of  $\gamma_0$  can be found from the relationship [5]  $\partial F/\partial \theta + \chi \cdot \partial G/\partial \eta = 0$ .

Two mechanisms of limit cycle decay, smooth and rigid, are possible [10]. In the first case increasing the value of  $\gamma$  is accompanied by monotonic decreasing the oscillation amplitude. Finally, at  $\gamma = \gamma_0$  the amplitude becomes equal to zero, i.e. the oscillations cease and limit cycle contracts into the point. In the second case at  $\gamma = \gamma_0$  steady state becomes stable, generating an unstable limit cycle. At further growth of  $\gamma$  this cycle joins with a stable limit cycle, forming semi-stable limit cycle, which then depletes.

It is possible to judge on character of stability variation by value of the third focal factor [9, 10]. If it is negative, there is a smooth decay of limit cycle, and if it is positive, rigid decay takes place.

We calculated the third focal factor using a methodology described in [11] (we don't show the expression for the third focal factor in view of its inconvenience). The results presented in Fig. 9 show that both types of stability change are possible. At smaller values of  $\theta$  the mechanism of smooth decay of a limit cycle will be realized, and at the larger values of  $\theta$  rigid decay takes place. Note, that the kind of dependence presented in Fig. 9, in many respects is determined by  $\beta$ value. Therefore at other  $\beta$  the character of this dependence can be different.

In conclusion it is useful to consider a special case of adiabatic reactor, when the heat loss from reactor is absent. In this case  $\tau = 0$ , and using given above expressions for *Se*, *Da* and  $\gamma$  in dimensional quantities, we obtain

$$Da/Se = \gamma(10)$$
Subtracting term by term (3) and (4), we shall receive
$$\gamma \frac{d\theta}{d\tau} = \frac{d\eta}{d\tau} + \frac{\eta}{Da} - \frac{\theta}{Se}$$
or in other kind
$$\frac{d(\gamma\theta - \eta)}{d\tau} = -\frac{1}{Da}(\gamma\theta - \eta)$$

Integration to an arbitrary constant gives

$$\gamma \theta - \eta = e^{-\frac{\tau}{Da}}$$

This means that at tendency of  $\tau$  to infinity the following relation takes place:

$$\theta \rightarrow \frac{1}{\gamma} \eta$$



**Figure 9.** Dependence of third focal factor from  $\theta$  at  $\eta_0 = 0.01$ ,  $\beta = 0.2$ , Se = 2.

Thus, the phase trajectory approaches at a straight line depicted by equation (7), not intercepting it (we remind, that the case is considered, when the equation (10) is fulfilled). It is evident, that at such behavior of phase trajectory the oscillation regime is impossible, and, therefore, adiabatic reactor is always steady. Let's remark, that this conclusion is obtained without use of a kind of the reaction kinetic law, so that it is correct for any process following to mass action low. It, in turn, means that origin of instability in CSTR is largely connected with the process of a heat loss.

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