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Thermal modes of bimolecular exothermic reactions: Concentration limits of ignition

Valeriy Yu. Filimonov *

Altay State Technical University, Barnaul, Lenina Str. 46, 656038, Russian Federation

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ABSTRACT

In the present work, the analytical investigation of the phase trajectories structures on the plane: heating rate-temperature for bimolecular exothermic reactions was carried out. This gave a possibility to divide the parametric plane Todes parameter–Semenov parameter into five characteristic regions with various modes of self-heating. It was established that all regions converge at a single point which determines the thermal explosion degeneration conditions. The correlation between Todes parameter, Semenov parameter and concentration ratio of initial reactants at the limit of the thermal explosion degeneration was found. The critical conditions for thermal explosion at any ratio of concentrations of initial reactants were determined. The approach proposed is a general one and allows analyzing both first and second order reactions.

1. Introduction

Determination of the self-ignition critical conditions for exothermically reacting systems is one of the key problems of the current combustion theory. According to the classical theory, a thermal explosion (TE) is possible when burn-up of the initial reactants is small during preheating [1,2]. In this case, the critical conditions of the TE are determined by the nonlinear algebraic equation of heat balance while the chemical kinetics equations are not taken into account. The latter is possible if the values of heat release and activation energy of reaction are relatively high and the characteristic time of reaction product formation greatly exceeds the characteristic time of self-heating [3,4]. This condition is determined by the small value of the Todes parameter [2] which is a basic assumption of the classical TE theory. At the same time, a lot of exothermically reacting systems are currently known including the systems with negligible heat release. Consequently, the analysis of the self-heating features at any value of the Todes parameter is the very important problem in terms of combustion theory. As shown by Shouman [5], the general analytical solution of this problem is associated with the serious mathematical difficulties. Despite the fact that it is a very old problem, the various aspects of Semenov theory are analyzed with the help of approximate analytical and numerical methods [6–12] up to now.

The detailed analysis of the thermal explosion critical conditions and conditions of the thermal explosion degeneration at any value of the Todes parameter was made in [13] for the first order exothermic reactions. Five characteristic regions which converge at the fixed point were defined on the parametric plane Todes parameter–Semenov parameter. This point can be considered as the point of the thermal explosion degeneration. It was established, that the critical conditions of ignition at the relatively high value of the Todes parameter may differ significantly from the conditions obtained in the classical theory. It should be noted that the practically significant first-order reactions occur at the exothermic pyrolysis of solid or liquid substances (ammonium dichromate, ammonium perchlorate, polymethylmethacrylate, etc.) [14]. In these cases, the self-inhibition of heating process by reaction product takes place because the kinetics of product formation depends on the content of the reactant. However, the situation changes when considering some binary mixtures in the gas or liquid phase. Indeed, the influence of the ratio of the initial concentrations of reactants on the chemical reaction rate and heating kinetics takes place in this case. Therefore, it is necessary to take into consideration the additional parameter (besides the Todes and Semenov parameters) which is connected with the ratio of the initial concentrations of reactants in general case of stoichiometric or non-stoichiometric mixtures. As a consequence, the problem of determination of concentration limits of ignition appears.

The obtaining of analytical dependences and parametric diagrams which allow predicting the development of heating process

* Address: St. Severo-Zapadnaya 173/31, 656052 Barnaul, Russia. Fax: +7 (3853)290930.

E-mail address: vyfilimonov@rambler.ru

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is a very important problem in terms of the challenges of explosion safety, pyrotechnics and energetics. In the present paper, the analytical investigation of the heating modes for bimolecular exothermic reactions was carried out.

2. Statement of the problem

2.1. Basic equations

In this paper, the bimolecular reactions which occur according to the scheme (1) are analyzed.

$$A_1 + A_2 \xrightarrow{k} \text{products} + Q \tag{1}$$

where A_1, A_2 are the components, Q is the heat of reaction, $k(T) = k_0\exp(-E/RT)$ is the reaction rate constant, k_0 is the pre-exponential factor, T is the absolute temperature, E is the activation energy. The set of the self-heating dynamics and the product formation kinetics equations can be written in the dimensionless form as follows [15]:

$$\begin{aligned} \tfrac{d\Theta}{d\tau} &= (1-y)(1-ay)\exp\Theta - \delta\Theta \\ \tfrac{dy}{d\tau} &= \gamma(1-y)(1-ay)\exp\Theta \end{aligned} \tag{2}$$

where $\tau = t/t_{ad}$ is the dimensionless time; $t_{ad} = cRT_0^2/QEk(T_0)[A_{02}][A_{01}]$ is the adiabatic reaction time; $\Theta = E(T - T_0)/RT_0^2$ is the dimensionless temperature; T_0 is the initial (ambient) temperature; $[A_{01}]$, $[A_{02}]$ are the initial molar concentrations of components; It is necessary to introduce the characteristic parameters: $t_- = \alpha S/c\rho V$ – the characteristic heat removal time; $t_r = [k(T_0)[A_{02}]]^{-1}$ – the characteristic reaction time, then: $\delta = t_{ad}/t_- = \alpha SRT_0^2/VQk(T_0)E[A_{01}][A_{02}]$ is the Semenov parameter, $\gamma = t_{ad}/t_r = c\rho RT_0^2/QE[A_{01}]$ is the Todes parameter; $y = ([A_{01}] - [A_1])/[A_{01}]$ is the conversion depth of component A_1; α is the heat transfer coefficient; $a = [A_{01}]/[A_{02}]$ is equivalence ratio of component A_1; V is the volume of the reacting system; S is the area of the reacting surface; c, ρ are the specific heat capacity and density of the mixture, respectively.

The basic assumption of the classical theory is $y \ll 1$ (or $ay \ll 1$) during preheating. Thus, the reactants consumption does not influence the critical conditions of TE in this case. These conditions are determined by the impossibility of the stationary solution of the heat balance equation [1]. This gives:

$$d\Theta/d\tau = 0,\ \Theta = 1,\ \delta_{cr} = e \tag{3}$$

In the general case (2), the dependence of parameter δ_{cr} on parameter γ should take place. The conditions (3) must be the limiting case of dependence $\delta_{cr}(\gamma)$ at $\gamma \to 0$ [5]. In order to analyze the set (2) taking into account the reactants consumption, the authors [16] proposed to consider the phase trajectories in the plane: $\Theta - y$. From this point of view, the appearance of the inflection point on this trajectory defines the critical conditions of TE. However, this leads to incorrect results. The authors [17] showed that the critical conditions are determined by the appearance of inflection points on thermogram $\Theta - \tau$. Following this idea, the author [13] proposed to consider the phase trajectories in the plane $d\Theta/d\tau - \Theta$ that led to a completely new understanding of the problem. With the use of this approach, the characteristic regions of self-heating on the plane $\gamma - \delta$ were found and the critical conditions of TE for the first-order reactions were obtained. In the present study, the method proposed in [13] is applied to the set (2) at any value of parameter a.

Let us find y from the first equation of the set (2). As a result, we obtain:

$$y_{1,2} = \frac{a+1}{2a} \pm \sqrt{\frac{1}{4}\left(\frac{a-1}{a}\right)^2 + \frac{1}{a}\left(\frac{d\Theta}{d\tau} + \delta\Theta\right)\exp(-\Theta)} \tag{4}$$

After substitution this expression into the second equation (2), we obtain the first order differential equation:

$$\xi\frac{d\xi}{d\Theta} = \xi^2 + \xi(\Theta - 1) \pm \eta(\xi + \Theta)\exp\Theta\sqrt{B^2 + (\xi + \Theta)\exp(-\Theta)} \tag{5}$$

with the initial condition $\Theta = 0;\ \xi = 1/\delta$

where:

$$\xi = \frac{1}{\delta}\frac{d\Theta}{d\tau} \tag{6}$$

is the dimensionless heating rate [13],

$$\eta = 2\gamma\sqrt{\frac{a}{\delta}} \tag{7}$$

$$B = \frac{a-1}{2\sqrt{a\delta}} \tag{8}$$

The parameter B determines the deviation of the mixture composition from the stoichiometric composition ($a = 1$). Thus, Eq. (5) determines the dependence of the heating rate on temperature or the phase trajectories in the plane $\xi - \Theta$. Following the procedure proposed in [13], let us consider a family of inflection isoclines $d\xi/d\Theta = 0$ on thermograms (dependence $\Theta(\tau)$), or extrema of the phase trajectory $\xi(\Theta, \eta, B)$:

$$\xi_e^2 + \xi_e(\Theta - 1) = \pm\eta(\xi_e + \Theta)\exp\Theta\sqrt{B^2 + (\xi_e + \Theta)\exp(-\Theta)} \tag{9}$$

The family of isoclines (9) is presented in Fig. 1. Obviously, the point a is the point of saddle-node bifurcation in the plane $\xi_e - \Theta$ at $\eta = 0$ (Semenov theory, $\gamma = 0$). This point determines the critical conditions of ignition in the classical TE theory: $\xi = 0,\ \Theta = 1$ (the conditions (3)). Under this condition, the inflection point appears on the thermogram and we can observe the unlimited growth of temperature. From this point of view, the parameter $\eta > 0$ is the parameter which destroys the bifurcation. The branches 1′, 2′ have no physical meaning. Indeed, the unlimited growth of temperature is possible in this case. In real case, the reactant consumption takes place and unlimited growth of temperature is impossible.

In other words, the Semenov theory is a partial case of intersection of the surface (8) and the plane $\eta = 0$.

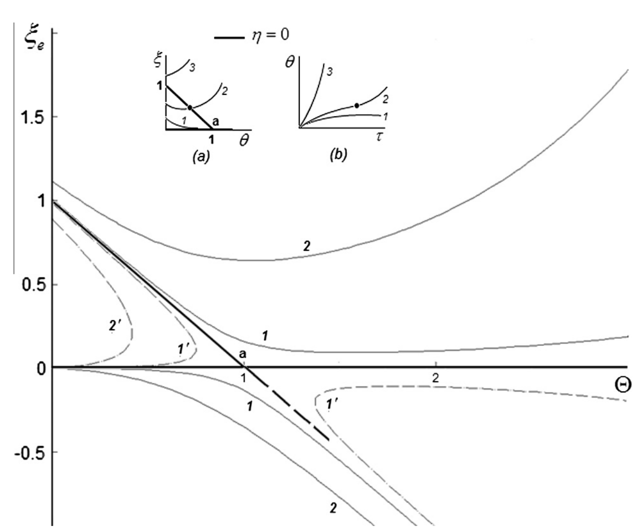

Fig. 1. The family of extrema isoclines (9) at B = 0, 5.1, 2 – "+" branches in Eq. (9), 1′, 2′ – "−" branches (lower branch 2′ is to the right and below the curve 1′ and is not represented in the figure). (1) 1′ – η = 0, 01; (2) 2′ – η = 0, 1. (a) – The phase trajectories on the plane $\xi - \Theta$ at η = 0 (Semenov theory), (b) – the corresponding thermograms.