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Thermal modes of monomolecular exothermic reactions: Two-dimensional model

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ABSTRACT

A new method for theoretical analysis of the self-heating kinetics for monomolecular exothermic reactions has been proposed. It has been shown, that consideration of the phase trajectories of reaction in the phase plane: the heating rate – temperature enables detection of the qualitative changes of the phase portrait under the changes of the Todes or Semenov criteria. This gives a possibility to analyze the diversity of various reaction modes for any reaction order. From this point of view, the classical Semenov theory of thermal explosion developed for zero-order reactions is a particular case. As an illustration of this method, the detailed phase trajectories analysis has been performed for the case of first-order reactions. The regions of the thermal explosion degeneration, fastest reaction mode region and transition regions have been established. The necessary and sufficient conditions for the thermal explosion have been formulated.

Examples of the application of the method for calculation of specific reactions are presented; the comparison with the classical theory is performed.

1. Introduction

Determination of the conditions of an exothermic reaction realization in the progressive self-heating mode (thermal explosion mode, TE) is one of the most important problems of the current combustion theory. In accordance with the classical theory developed by Semenov [1–3], the condition of TE means impossibility of thermal equilibrium between the exothermically reacting system and its environment. During TE, the burn-up of reactants leads to the decrease in the heating rate due to the kinetic inhibition by the reaction products. Nevertheless, in terms of the classical theory, realization of TE is possible in the case of sufficiently small burn-up of the initial reactants during preheating. This is the reason why the specific features of the products formation kinetics (the kinetic function structure) do not matter during preheating. This is determined by the small value of the Todes criterion [4]. Smallness of the Todes criterion is a basic assumption of the classical TE theory. In this case, the critical conditions for TE can be found from the condition of balance between the rate of heat release and rate of heat removal without taking into account a burn-up. This approximation allows obtaining the analytic expressions for the TE critical conditions, calculation of the critical value of the ambient temperature and corresponding critical heating of the reacting system [1–4]. However, we must bear in mind that the steady-state heat balance mentioned above is impossible with consideration process of the burn-up. Indeed, the rate of a homogeneous chemical reaction is determined by the law of mass action. Therefore, it is necessary to take into consideration both the heat balance equation and the equation of chemical kinetics in general case. Thus, the critical value of Semenov criterion must depend on the value of Todes criterion. However, the analytical solution of this problem is connected with some mathematical difficulties. For this reason, the thermal explosion theory was developed with the help of approximate analytical [5–8] and numerical methods [9–12]. At the same time, a qualitative analysis of these critical phenomenon is possible in terms of the dynamic system theory with considering the phase trajectories of self-heating process on the corresponding phase planes (the phase portrait reconstruction) [13]. In this paper, we suggest a method for analysis of self-heating modes of exothermically reacting systems in terms of the non-stationary thermal explosion theory by the studying of the structures of the phase trajectories.

2. Basic equations and parameters

The classic system of the self-heating dynamics and the product formation kinetics equations for homogeneous n-th order reactions can be written in the dimensionless form as follows [13]:

$$\begin{aligned} &\frac{d\Theta}{d\tau} = (1-y)^n \exp\Theta - \delta\Theta \\ &\frac{dy}{d\tau} = \gamma(1-y)^n \exp\Theta \\ &\tau = 0; \quad \Theta = y = 0 \end{aligned} \tag{1}$$

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where $\tau = t/t_{ad}$ is the dimensionless time; $t_{ad} = cRT_0^2 \exp(E/RT_0)/QEk_0\rho^{n-1}$ is the adiabatic reaction time; $\Theta = E(T - T_0)/RT_0^2$ is the dimensionless temperature; T_0 is the initial (ambient) temperature; y is the conversion depth (or fraction reacted); $\delta = t_{ad}/t_-, t_- = c\rho V/\alpha S$ is the characteristic heat removal time; V is the volume of the reacting system; S is the area of the sample surface; c, ρ are the specific heat capacity and density of the reactant, respectively, α is the heat transfer coefficient; $\gamma \equiv Td = cRT_0^2/QE$ is the Todes criterion [4]; E is the activation energy; Q is the heat of reaction; k_0 is the pre-exponential factor. It was assumed that the condition $RT_0/E \ll 1$ was holds.

It is well known, that the classical theory gives exact values of the critical parameters for the zero-order reactions at $n = 0$ [1–4]:

$$\Theta = 1, \quad \delta = e \tag{2}$$

However, results Eq. (2) are approximately valid under condition $\gamma \ll 1$, (because the burn-up of a reagent has no significant effect on the heat balance on this condition) and hence $y \ll 1$ during preheating. This condition, however, is not clearly defined. Therefore, it is necessary to investigate the kinetics of self -heating process at any value of γ and to establish the relationship between critical value of Todes criterion and Semenov criterion. This problem was not considered in Semenov theory and is analyzed below.

Let us find y from the first equation of the system (1) and substitute into the second equation; simultaneously, let a new variable $u = d\Theta/d\tau$ (heating rate) be introduced. As a result, we obtain:

$$u\frac{du}{d\Theta} = u^2 + \delta u(\Theta - 1) - \gamma n(u + \delta\Theta)^{2-1/n}\exp(\Theta/n) \tag{3}$$

For the further analysis, it is convenient to transform Eq. (3) to a reduced one-parameter form. After the introduction of new variables $\xi = u/\delta$, and $\eta = \gamma n\delta^{-1/n}$, we obtain the equation:

$$\xi\frac{d\xi}{d\Theta} = \xi^2 + \xi(\Theta - 1) - \eta(\xi + \Theta)^{2-1/n}\exp(\Theta/n), \tag{4}$$

with the initial condition: $\Theta = 0, \quad \xi = 1/\delta$.

3. Phase trajectories analysis

3.1. Overall analysis

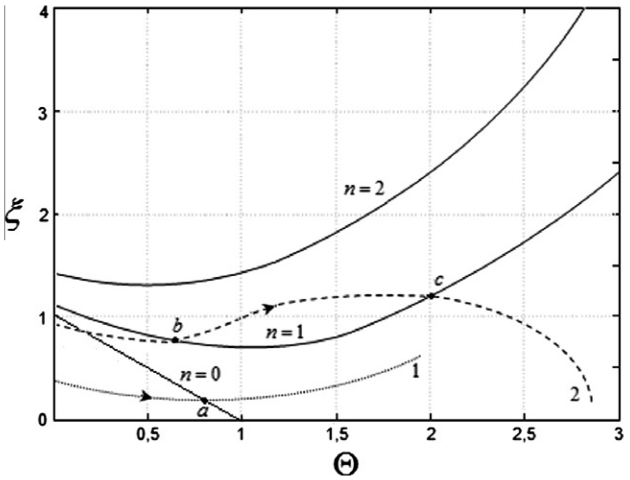

Fig. 1. Inflection isoclines of phase trajectory (4) for monomolecular reactions of various order (solid lines) at $\eta = 0$, 1. 1, 2 – Schematic representation of corresponding phase trajectories. (a–c) The extremum points of the phase trajectory (inflection points on the thermogram).

Eq. (4) determines the dependence of the heating rate on temperature, or the phase trajectories in the plane ξ–Θ, and describes all monomolecular reactions of any order (including fractional orders). This is the Abel equation of the second kind, which cannot be integrated by quadratures. However, the equality to zero of the right hand side of Eq. (4) determines a family of inflection isoclines on thermograms (dependence $\Theta(\tau)$), or extrema of the phase trajectory $\xi(\eta, \Theta)$:

$$\xi^2 + \xi(\Theta - 1) - \eta(\xi + \Theta)^{2-1/n}\exp(\Theta/n) = 0 \tag{5}$$

The solution of algebraic Eq. (5) gives an expression for these isoclines $\xi_i(\Theta, \eta, n)$, as illustrated by Fig. 1. Obviously, qualitative features of the heating process are determined by the intersection of the phase trajectory $\xi(\Theta)$ and inflection isocline $\xi_i(\Theta)$.

Let us consider some particular cases:

1. $n = 0$ (Semenov theory). The proposed method of analysis allows us to consider the problem in the plane ξ–Θ. If $n = 0$ and $\eta = 0$, the solution of Eq. (5) takes the simplest form

$$\xi_i = 1 - \Theta \tag{6}$$

As it is seen in Fig. 1, the phase trajectory has the minimum point (point a). This point appears due to the influence of the heat removal. Obviously, the minimum point appears under conditions: $\xi = 0, \ \Theta = 1$ and with the use of the first equation of the set (1) at $y = 0$ the well-known critical conditions (2) can be obtained.

2. $n > 0$, The extreme points can be observed on the phase trajectory, Fig. 1a. The appearance of the high temperature maximum point c is associated with the influence of the kinetic inhibition which prevents the unlimited growth of the temperature. The appearance of the minimum point b is associated with the influence of the heat removal. However, the point b does not always exist on the phase trajectory. Therefore, it is necessary to investigate the Eq. (5) for the presence of a minimum. By differentiating the expression (2) with respect to temperature Θ under condition $d\xi_i/d\tau = 0$ we can obtain:

$$\xi_i = \eta(\xi_i + \Theta)^{1-1/n}[2 - 1/n + (\xi_i + \Theta)/n]\exp(\Theta/n) \tag{7}$$

Eqs. (5) and (7) determine the conditions for the existence of a minimum on the inflection isoclines. Combined consideration of Eqs. (5) and (7) gives:

$$\xi_{\min} = f(n) - \Theta, \tag{8}$$

where $\xi_{\min}$ is the ordinate of the minimum point on the isoclines (Fig. 1), $f(n)$ is the function which depends only on the order of the reaction:

$$f(n) = 1 + \left(\sqrt{n^2 + 4n} - n\right)/2 \tag{9}$$

The substitution Eq. (8) into Eq. (5) gives:

$$f - \Theta = \eta f^{2-1/n}\exp(\Theta/n)/(f - 1) \tag{10}$$

The graphical solution of this transcendental equation is presented in Fig. 2, where:

$$\varphi(\eta, n) = \eta f^{2-1/n}/(f - 1) \tag{11}$$

As it is seen in Fig. 2, only one minimum point is present on the isocline when $f_1 > \phi$. The minimum point disappears when $\Theta = 0$ and $f = \phi$. Returning to the variables γ, δ, the condition for the existence of a minimum ($f_1 > \phi$) can be written as follows:

$$\gamma < \delta^{1/n}f^{1/n-1}(f - 1)/n = \delta^{1/n}\lambda(n) \tag{12}$$

where:

$$\lambda(n) = f^{1/n-1}(f - 1)/n \tag{13}$$

From Eq. (13), we have $\lambda = 0,62$ for the first order reactions and $\lambda = 0,24$ for the second order reactions.