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Critical autoignition conditions for arbitrary reaction order

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In this paper, the theoretical analysis of the critical autoignition conditions for exothermically reacting systems at any value of the reaction order was conducted. The calculated and approximate analytical dependencies for the relationship between the parameters at the ignition limit were obtained. On the basis of the obtained diagrams of critical parameters, the conditions of thermal explosion (TE) degeneration for reactions of arbitrary order were determined. It was established that the existing theory of TE gives the correct estimates of ignition temperatures for a given condition of exothermic reaction realization (heat transfer coefficient, specific surface area, initial concentration). However, the theory gives unsatisfactory predictions for the mentioned critical TE conditions at a given ambient temperature. Moreover, the classical theory cannot be applied in the intermediate case when the effect of reactant consumption is already significant but the reaction still proceeds with all the signs of a TE.

1. Introduction

One of the key problems of chemical kinetics is the problem of thermal stability of chemically reacting systems. For exothermically reacting systems, a transition from the slow chemical conversion mode to the self-acceleration regime is possible due to the strong dependence of chemical reaction rate on temperature (thermal explosion (TE)) [1,2]. This transition is accompanied by the fast increase in temperature and heat release rate. The theory of TE is a well-developed section of chemical kinetics. At the same time, there are a number of problems connected with the correct definition of critical TE conditions. Indeed, the necessary condition of TE realization is the smallness of Todes

parameter [3] which is the ratio of the characteristic time of heat release to the characteristic time of the chemical reaction. In terms of the classical TE theory [2,3], this parameter is equal to zero. Thus, this theory is based on the asymptotic approximation. In this case, the heating mode of reaction is determined by the ratio of heat release rate and the rate of heat removal. Thus, the heating regime does not depend on the rate of reaction product formation (the kind of kinetic function). In the classical work [2], the method which allows taking into account the reactant consumption in the first approximation was proposed. The more detailed calculation of such corrections is given by the method of integral manifolds [4–9]. This method is based on the general theory of nonlinear differential equations with a small parameter. Thus, this approach can be regarded as a quasi-classical method. However, this method has the following disadvantages: (i) the method unsatisfactorily predicts the critical conditions in states far from the classical theory (at a relatively high value of Todes parameter) [10–12]. The dependence obtained by the authors [9] should be considered as the most accurate. It should be noted that the authors of a recently published paper [13] propose a new criterion for determining the critical conditions which allowed to correct the results of [9] and to obtain a good agreement of experimental and calculated data. (ii) The use of this method does not make it possible to determine the TE degeneration conditions. In other words, there is an intermediate class of exothermic reactions which are characterized by the insignificant thermal effects and activation energies but at the same time the exothermic reactions proceed with all the signs of TE (heterogeneous reactions in the condensed phase, high-temperature synthesis [14,15], reactions in mechanically activated powder mixtures [16], etc.). Meanwhile, the problem of the ‘fast’ and ‘slow’ reactions separation is of great importance from the practical point of view. Sometimes, the slow synthesis is preferable (mild combustion [17], reaction control mode). In other cases, the fast combustion mode is preferred (high-temperature synthesis [14]). It should be borne in mind that the kinetic law of reaction product formation should be taken into account in the case of the relatively high rate of chemical reaction. Currently, the unambiguous criteria of autoignition and degeneration of a TE for any type of kinetic function are absent.

It is known that the effective reaction order can be fractional for complex and multi-stage reactions. Moreover, for the gas phase systems, the order of reaction can depend on pressure, conversion degree, temperature, etc. [18]. From this point of view, the problem of determining the critical conditions of TE for any reaction order is of great importance. In the above-mentioned models [4–9], the simplest relation between the critical values of parameters and reaction order was obtained as a small correction to the classical conditions of TE. However, the use of such corrections is limited (as will be clear from the further consideration).

In the works [10,19–21], an alternative method of calculating the critical conditions for any kind of kinetic function was proposed. The criteria obtained make it possible to establish the relationship between such parameters as heating of the system, conversion degree, parameters of Semenov, Todes, Arrhenius at the ignition threshold. In addition, the proposed method allows establishing the relationship between the parameters at the TE degeneration limit. Analysis of the critical conditions for the reactions of the first [10] and second [19] orders as well as for the kinetics of heterogeneous processes [20] showed a satisfactory agreement of the analytical calculation, numerical analysis and experimental results.

2. Statement of the problem

The classical set of equations of heat balance and chemical kinetics in the dimensionless form [2,4–9] can be represented as follows (table 1):

$$\text{and} \quad \left\{ \begin{aligned} \frac{d\theta}{d\tau} &= \varphi(y) \exp \left[\frac{\theta}{1 + \beta\theta} \right] - \delta\theta \\ \frac{dy}{d\tau} &= \gamma \varphi(y) \exp \left[\frac{\theta}{1 + \beta\theta} \right]. \end{aligned} \right. \quad (2.1)$$

Table 1. Nomenclature.

T	temperature
T_0	initial temperature
E	activation energy
$\theta = (E/RT_0^2)(T - T_0)$	dimensionless temperature
y	conversion degree
θ_m	maximum temperature of exothermic reaction
y_m	corresponding conversion degree
$\varphi(y)$	kinetic function
$\gamma = cRT_0^2/QE$	Todes parameter
$\delta = \alpha SRT_0^2 \exp(E/RT_0)/QVEk_0[A_0]^n$	Semenov parameter
n	reaction order
$\beta = RT_0/E$	Arrhenius parameter
c	molar heat capacity
c_V	heat capacity per unit volume
Q	thermal effect of reaction
α	heat transfer coefficient
V	volume of reaction vessel
S	surface area of reaction vessel
k_0	pre-exponential factor
$[A]$	molar concentration of reactant

The initial conditions are: $\tau = 0, \theta = 0, y = y_0$. Here, γ is the Todes parameter (the ratio of the characteristic time of heat release $t_+ = cRT_0^2 \exp(E/RT_0)/QE k_0[A_0]^n$ to the characteristic time of chemical reaction $t_r = \exp(E/RT_0)/k_{0n}[A_0]^{n-1}$ for n -order reactions), δ is the Semenov parameter (the ratio of the characteristic time of heat release to the characteristic time of heat removal $t_- = c_V V/\alpha S$).

The numerical integration of the system (2.1) is elementary. However, despite the simplicity of the equations presented, the criteria for the transition of the system from the slow reacting mode to the TE regime are not clearly defined. As mentioned above, the system has an asymptotic solution: $\gamma \rightarrow 0, y \rightarrow 0, \varphi(y) \rightarrow \varphi(y_0)$. In this situation, the critical conditions $\theta_c = 1, \delta_c = e$ do not depend on the kinetic function, Todes and Arrhenius parameters and they are determined by the heat balance: rate of heat release – rate of heat removal [1,2] (hereinafter the index ‘ c ’ means a critical value). However, an increase in parameter γ leads to an increasing influence of reactant consumption (and structure of kinetic function) on critical conditions. Therefore, the problem is multidimensional (two variables θ, y and three parameters: δ, γ, β). Consequently, it becomes necessary to calculate a number of critical dependencies: $\theta_c(\delta, \beta), \theta_c(\gamma, \beta), y_c(\delta, \beta), y_c(\gamma, \beta), \gamma_c(\delta, \beta)$. In terms of the critical conditions analysis for this multiparametric problem, the numerical integration of system (2.1) is meaningless without clear and unambiguous mathematical criteria for TE realization. Numerical calculation of the system (2.1) must be performed only to verify these criteria. Thus, the numerical analysis should play only an auxiliary role.

In the papers [10,19–21], the method of maximum temperatures was proposed for calculating the critical TE conditions for system (2.1) (under conditions $\varphi(0) = 1, \varphi(1) = 0$). In this case, the

critical conditions have the form of an algebraic set of equations:

$$\varphi(y_m) = \delta \theta_m \exp \left[-\frac{\theta_m}{1 + \beta \theta_m} \right], \quad (2.2)$$

$$\frac{y_m - y_0}{\varphi(y_m)[F(y_m) - F(y_0)]} = \frac{\theta_m}{(1 + \beta \theta_m)^2} \quad (2.3)$$

and
$$y_0 + \gamma \theta_m = y_m(\theta_m) - [F(y_m) - F(y_0)]\varphi(y_m). \quad (2.4)$$

Here, θ_m is the maximum temperature which is defined by condition: $d\theta/d\tau = 0$ (equation (2.4)), y_m is the corresponding conversion degree, the functional $F(y) = \int dy/\varphi(y)$ can be considered as some kinetic potential. The set of equations (2.2)–(2.4) defines the abrupt transition from low-temperature modes (which are determined by condition $\gamma \theta_m \ll 1$) to high-temperature modes. In the classical TE theory, the following approximation is used: $\varphi(y) \approx \varphi(y_0)$ while in the works [19–21], the more general condition is proposed for characterizing the low-temperature regime at $\gamma \theta \ll 1$:

$$F(y) \approx F(y_0). \quad (2.5)$$

A transition to high-temperature regime is considered as an impossibility of the condition (2.5) realization. Equation (2.2) defines the connection between variables when the maximum temperature is reached, equation (2.4) defines the maximum temperatures, equation (2.3) defines the critical conditions. The partial cases of the system ((2.2)–(2.4)) for the first [10] and second [19] order reactions were analysed. In this paper, the method of critical conditions calculation for the kinetic function of the form $\varphi(y) = (1 - y)^n$ is proposed. It is well known that the reaction order n is an integer for elementary one-stage reactions. However, the system (2.1) is also valid for many chain or multi-stage reactions when the reaction order n is fractional. In this case, the kinetics of reaction product formation is determined by the effective activation energy and effective pre-exponential factor.

3. Critical conditions

(a) Critical temperatures

We will analyse the undiluted mixtures when $y_0 = 0$. In this case, the set of equations (2.2)–(2.4) can be represented in the form:

$$(1 - y_m)^n = \delta \theta_m \exp \left[-\frac{\theta_m}{1 + \beta \theta_m} \right], \quad (3.1)$$

$$\frac{y_m(n - 1)}{1 - y_m - (1 - y_m)^n} = \frac{\theta_m}{(1 + \beta \theta_m)^2} \quad (3.2)$$

and
$$\gamma = \frac{1}{\theta_m} - \frac{\delta}{n - 1} \exp \left(-\frac{\theta_m}{1 + \beta \theta_m} \right) \left\{ n \left[\delta \theta_m \exp \left(-\frac{\theta_m}{1 + \beta \theta_m} \right) \right]^{1/n-1} - 1 \right\}. \quad (3.3)$$

We will assume that the value of n is positive.

Let us consider the dependence (3.3) for different values of the parameters (figure 1). As follows from the figure, the diagrams are determined by the curves of bistability. An increase in the value of reaction order leads to a decrease in the critical value of parameter γ because the growth of the reaction order is a factor inhibiting the rate of heat release.

In order to compensate for the kinetic inhibition, it is necessary to decrease the rate of product formation by decreasing the value of parameter γ (because of $dy/d\tau \sim \gamma$). The decrease in the parameter γ_c is bounded by its zero value from below (classical TE conditions at $\theta_m = 1$, figure 1a). However, there is a limitation from above. A decrease in the value of reaction order leads to an increase in the value of parameter γ_c that leads to the accumulation of reaction product during preheating. This inevitably leads to degeneration of TE (mode 1, figure 1b). Thus, it makes sense to talk about the reaction order of degeneration.

Figure 1. Diagrams of maximum temperatures for various values of parameters at $\beta = 0$ (equation (3.3)). The points indicate the critical states of the reacting system: (a) $\delta = 2$; (b) $\delta = 1$.

Figure 2. Diagrams of critical parameters for various values of reaction order at $\beta = 0$. Solid lines—the critical values of parameter δ , dashed lines—critical values of temperature.

In order to analyse the connection between the critical values: δ_c , θ_c , y_c , let us consider equations (3.1) and (3.2). In this case, these dependences can be determined analytically (figure 2). Reducing the parameter δ_c determines the decrease in the rate of heat removal that promotes the ignition. In order to remain at the limit of ignition, parameter γ must increase. This leads to an increase in the reactant consumption, accumulation of reaction product y_c and TE degeneration (minimum points on the solid lines, figure 2). The process is accompanied by an increase in critical heating.

An increase in the reaction order leads to reduce the critical value of the parameter δ for the reasons indicated above. Substituting y_m from equations (3.1) into equation (3.2) we arrive to the dependence:

$$\theta_c = (n-1)(1+\beta\theta_c)^2 \left\{ \left[\frac{\exp(\theta_c/(1+\beta\theta_c))}{\delta\theta_c} \right]^{1/n} - 1 \right\} \left\{ 1 - \left[\frac{\exp(\theta_c/(1+\beta\theta_c))}{\delta\theta_c} \right]^{1/n-1} \right\}^{-1}. \quad (3.4)$$

Figure 3 shows the dependences of critical temperature on parameter δ for two values of reaction order as a result of solving the transcendental equation (3.4).

Figure 3. Dependence of critical temperature on parameter δ at various values of reaction order in accordance with the results of numerical calculation of equations ((3.1) and (3.2)) at $\beta = 0$. D_1, D_2 are the points of degeneration $1', 2'$ are the results of the analytical dependence (3.7) calculation.

Following [19–21], we assume conditionally: $\theta_c = 1 + \theta'$ where θ' is a value of the first order of smallness and $\beta\theta'$ is a value of the second order of smallness. Thus, we obtain:

$$\exp\left[\frac{\theta_c}{1 + \beta\theta_c}\right] \approx \exp(1 + \theta') \exp(-\beta), \quad (3.5)$$

The substitution of equations (3.5) in equation (3.4) gives:

$$\theta_c \approx (n-1)(1+2\beta) \frac{(e/\delta)^{1/n} \exp(-\beta/n) - 1}{1 - (e/\delta)^{1/n-1} \exp[-\beta(1/n-1)]}. \quad (3.6)$$

For the limiting case of Frank–Kamenetsky problem ($\beta = 0$, high activation energies and low critical temperatures [1,2]) we obtain:

$$\theta_c \approx (n-1) \frac{(e/\delta)^{1/n} - 1}{1 - (e/\delta)^{1/n-1}}. \quad (3.7)$$

The dependences (3.7) are shown in figure 3 by dashed lines. As follows from the figure, the dependence (3.7) satisfactorily corresponds to the results of the numerical calculation up to degeneration conditions (which will be considered below). Using equation (3.7), it is easy to obtain the classical condition: $\delta = e$, $\theta_c = 1$. However, the condition $n \rightarrow 0$ at $\delta < e$ leads to the condition $\theta_c \rightarrow 1$ again that really should be valid in terms of the classical theory [1,2] for the zero-order reactions. At $n = 2$, the critical temperature is: $\theta_c \approx \sqrt{e/\delta}$ that corresponds to the results of the investigation [21].

Let us represent the dependence (3.7) in the form:

$$\theta_c \approx (n-1) \left(\frac{e}{\delta}\right)^{1/n} \frac{1 - (1+x)^{-1/n}}{1 - (1+x)^{1/n-1}}. \quad (3.8)$$

The value $x = e/\delta - 1$ can be considered as a small parameter. Taking into account that the third factor in equation (3.8) weakly depends on x , one can obtain the simpler dependence:

$$\theta_c \approx \left(\frac{e}{\delta}\right)^{1/n}. \quad (3.9)$$

Figure 4. Diagrams of critical parameters for the first-order reactions at $\beta = 0$: (a) the authors of [9]; (b) the authors of [13]; (c) the authors of presented work. The points indicate the critical state of the system.

(b) Diagrams of critical parameters. verification of the model

(i) Thermal explosion modes

To verify the method, it is necessary to compare the results of the calculation based on criteria (3.1)–(3.3) with the data obtained by other authors and the results of the numerical calculation.

Figure 4 presents the results of calculations obtained by the authors of this work, the authors of [9,13], and the results of a numerical analysis of the system (3.1).

The dependences (a) and (b) were obtained using the formulae:

$$\delta_c = e \left[1 - 2.946\gamma^{2/3} + 4/9\gamma \ln \left(\frac{1}{\gamma} \right) \right], \quad (3.10)$$

and

$$\delta_c = e[1 - 2.25(\gamma)^{2/3}]. \quad (3.11)$$

As follows from the figure, the calculation based on the results of [9] corresponds to the numerical calculation very accurately at $\gamma < 0.037$. For higher values, there are discrepancies with both numerical calculations and the results of other authors. Thus, the curves *b,c* more accurately predict critical conditions for large values of the parameter γ . In order to obtain the satisfactory results for small values of parameter γ , from the point of view of the first approximation, we can substitute $\theta_c = 1$ in equation (3.3):

$$\gamma_c \approx 1 - \frac{1}{n-1} \left[n \left(\frac{\delta}{e} \right)^{1/n} - \frac{\delta}{e} \right]. \quad (3.12)$$

Figure 5 shows the critical parameters diagrams $\gamma_c(\delta)$ for various calculation options. The solid lines correspond to numerical calculation of the set of equations (3.1)–(3.3) at $\beta = 0$. As follows from the figure, the analytical calculation (with the use of equations (3.7), (3.8)) exactly corresponds to results of numerical calculation of the system (3.1)–(3.2) up to the points of degeneration. The simplified formula (3.12) well corresponds to results of numerical calculation at $\gamma < 0.05$. Therefore, the demarcation line divides the parametric plane into three regions as in previous studies [10,19–21]. With an increase in reaction order, the region of TE shrinks and the region of degeneration expands.

Figure 5. Critical parameters diagrams for various calculation options at $\beta = 0$. D_1, D_2, D_3 are the points of TE degeneration. I, II, III are the characteristic regions of reactions modes for $n = 0.5$. I—the post critical region, II—the subcritical region, III—the region of degenerate modes.

Figure 6. Transition modes. The dependence of parameter δ on maximum temperatures at various values of parameter γ obtained by numerical integration of the system (2.1) at $\beta = 0$. (a) $n = 0.5$; (b) $n = 2.5$. The points indicate the critical states of the system.

(ii) Transition modes

As indicated above, the TE is not clearly pronounced at high values of parameter γ . Therefore, an additional stage of the method verification is the analysis of the change in the maximum temperatures with the change in the parameter γ . The dependences of parameter δ on maximum temperatures (which characterize the transition from TE to degeneration) are presented in figure 6.

As expected, with an increase of parameter γ , the sensitivity of the system to the change of parameter δ decreases. It can be argued that the TE is clearly pronounced in the interval $\gamma < 0.1$ at $n = 0.5$ (figure 6a). In this case, the dependence is characterized by a kink at the critical point. At the larger values of parameter γ , the smooth transition to a high-temperature regime takes place. In this situation, the critical conditions determine the effective (danger) value of parameter δ beginning from which the uncontrolled heating of the system occurs. The quasi-classical method of integral manifolds is not applicable here. TE is degenerated at $\gamma = 0.25$. With the change of parameter δ , the maximum temperatures change smoothly up to the adiabatic temperatures at $\delta = 0$. At $n = 2.5$ (figure 6b), the system is more sensitive to the change in parameter δ .

Figure 7. Diagrams of critical parameters and phase trajectories of the system at $\beta = 0, z = 10^{-8}$. $a-c$ are the demarcation lines at various values of reaction order; 1–4 are the phase trajectories (4.2) at various values of parameter b . The arrows indicate the direction of the initial temperature T_0 increase. The points of the lines intersection define the critical conditions.

4. Influence of reaction order

In order to calculate the critical values, the dependence $\gamma_c(\delta)$ (figure 5) must be supplemented by the equation of the relationship between the parameters. For n -order reactions, the Semenov parameter and Todes parameter have the form [1,2]:

$$\delta = \frac{\alpha S R T_0^2}{Q V k_0(n) A_0^n E} \exp\left(\frac{E}{R T_0}\right), \quad \gamma = \frac{c R T_0^2}{Q E}, \quad (4.1)$$

where α is the heat transfer coefficient, V is the volume of reaction vessel, S is the surface area of heat removal, $k_0(n)$ is the pre-exponential factor, A_0 is the initial concentration of component A, Q is the thermal effect of reaction, c is the heat capacity of the system per mole of component A.

As follows from equation (4.1), the equation of connection can be represented in the form:

$$\delta = \gamma z \exp\left(\frac{b}{\sqrt{\gamma}}\right), \quad (4.2)$$

where:

$$z = \frac{\alpha S}{V c k_0 A_0^n}, \quad b = \sqrt{\frac{c E}{Q R}}. \quad (4.3)$$

Equation (4.2) determines the trajectory of the imaging point movement in the plane $\gamma-\delta$. In accordance with equations (4.1), the increase in parameter γ determines the increase in the ambient temperature. It is easy to estimate that the real range of the parameter b change is: $b = 2 \div 6$ for the reaction in the gas phase. The estimation of the parameter z is difficult because the range of possible values of pre-exponential factor k_0 is very significant.

Figure 7 shows the phase trajectories of the system with respect to demarcation lines. As follows from the figure, a transition in the TE region along an arbitrary trajectory is impossible. The possibility of a transition is determined by two independent ways: (i) the increase in initial temperature (the movement along the trajectories 1–4 in the direction indicated by the arrows); (2) the movement along the horizontal trajectory 4' at a given initial temperature by increasing the concentration A_0 or by reducing the effective heat removal factor $\alpha S/V$.

An increase in parameter b (a decrease in the thermal effect Q) leads to an increase in the critical value of parameter γ . This inevitably leads to degeneration of TE. Thus, the movement of the imaging point from the right to the left (into the post critical region) is impossible with

Figure 8. Dependences of the critical parameters on reaction order at the limit of degeneration at $\beta = 0$.

a decrease in parameter γ . For trajectories 1–3, the critical value of parameter γ almost does not depend on the path of transition into the post critical region. An increase in reaction order leads to an insignificant increase in parameter γ_c and a significant decrease in parameter δ_c (at the constant value of parameter b). As a consequence, in states far from degeneration, the ignition temperature weekly depends on the reaction order. When approaching the degeneration limit, the sensitivity of the parameter γ_c to a change in the order of the reaction substantially increases. The calculation shows that all the listed models [4–9,13] including the presented one are in quite satisfactory agreement with the classical theory [2] in the interval $\gamma < 0.01$. The discrepancy with the results of the numerical analysis depends on the order of the reaction and does not exceed 10% at $n \leq 3$.

5. Degeneration conditions

Owing to the fact that the order of reaction is arbitrary, it is impossible to obtain an analytic expression for degeneration conditions because it is connected with the solution of an algebraic equation of arbitrary order (including fractional). The degeneration conditions should be regarded as the conditions of the absence of equations (3.1) and (3.2) solutions which can be represented in the form: $d\delta_c/dy = 0$ that leads to condition:

$$(1 - y) \left(1 - \frac{1}{\theta_c} \right) \frac{d\theta_c}{dy} = n. \quad (5.1)$$

Taking into account equations (3.1)–(3.3), it is possible to obtain the dependence of the parameters on the reaction order at the limit of degeneration. Figure 8 shows the dependences of parameters on reaction order at the limit of degeneration. The value of y_d determines the maximum possible content of the reaction product at which TE still takes place. As follows from the figures, the increase in reaction order leads to decrease in parameters γ_d , δ_d at the limit of degeneration because the growth of the reaction order is a factor inhibiting the rate of heat release. As a consequence, the decrease in the limit content of reaction product and an increase in the value of preheating occur.

Using the diagrams presented, one can estimate the values of parameters at which the ignition of the system is impossible at any environment temperature. For example, TE is possible when $n = 0.7$, $\gamma = 0.15$ at the certain value of the parameter δ_c . However, it is impossible at any value of parameter δ_c when $n = 2.5$ at the same value of parameter γ . Thus, the generalized criterion for a slow exothermic reaction realization has the form:

$$\gamma = \frac{cRT_0^2}{QE} > \gamma_d(n). \quad (5.2)$$

For the gas phase systems, the controlling parameter is: $\alpha S/VA_0^n$ (formula (4.1)) the value of which can be varied in a wide range (parameter z). It should be noted that the determination

Figure 9. Dependence of parameter z (formula (4.3)) on reaction order at various values of parameter b (logarithmic scale) and $\beta = 0$. The regions of degenerate modes are above the curves.

Figure 10. Diagrams of critical parameters: (a) dependence of critical value of parameter γ on the value of parameter β for the first-order reactions 1 — $\delta = 1$; 2 — $\delta = 1.25$; 3 — $\delta = 1.5$; 4 — $\delta = 1.75$, (b) dependence between the parameters at the limit of degeneracy for various orders of reaction. The regions of TE existence are under the curves.

of the limiting concentrations A_0 (when the reaction occurs without any signs of TE) is a very important problem from point of view of explosion safety and chemical kinetics.

Figure 9 shows the dependences of the logarithm of the parameter z_d on reaction order on the limit of degeneration at various values of parameter b . At $n > 0.5$, the dependencies are almost linear. This indicates an exponential dependence $z_d(n)$. As follows from the figure, the value of parameter z strongly depends on parameter b . Thus, the size of the region of TE realization depends significantly on the relationship cE/Q (formula (4.3)). An increase in parameter b leads to the compression of TE parametric area. As follows from formula (4.3), an increase in parameter b can be associated with a reduction in the thermal effect and/or an increase in the value of activation energy.

On the other hand, an increase in the order of the reaction requires a decrease in the parameter z_d which can be determined by reduction in the rate of heat removal $\alpha S/V$ or by an increase in the initial concentration A_0 (in accordance with formula (4.3)).

A previous analysis was performed for the case when $\beta = 0$. However, it is quite clear that the value of this parameter could significantly influence on both critical conditions and degeneration conditions at its relatively high values. Figure 10 shows the dependence of the critical value of parameter γ on parameter β .

Figure 11. Dependence of ignition temperature on parameter z at $\beta = 0$ for the reactions (R1)–(R3) (logarithmic scale) (a); Dependence of ignition temperature on parameter z for the reaction (R3) in the region (b). 1—presented model; 2—classical theory [2]. The thermograms were calculated with the use of numerical calculation of the system (2.1).

As follows from figure 10a, for the large values of the parameter γ , the influence of the parameter β on the degeneration conditions is manifested especially significantly. When $\delta \approx 1$, a TE is impossible already at $\gamma \approx 0.025$. With an increase of the parameter δ , the interval of the existence of critical conditions expands. At the limit of degeneration, the large values of parameter γ are determined by the regions where parameter β is small. The region of TE existence shrinks with increasing the value of the reaction order large values of the parameter corresponding to small regions, but the region of existence of TV shrinks with increasing values of the reaction order (figure 10b).

6. Critical conditions for exothermic reactions of various orders

Let us consider the dependence of ignition temperature on external conditions for three exothermic reactions of various orders:

and

The reaction (R1)—azomethane decomposition [22]. This is the first-order reaction with activation energy $E = 214.4 \text{ kJ mol}^{-1}$ and thermal effect $Q = 180.17 \text{ kJ mol}^{-1}$ (the molar heat capacity $c = 107.7 \text{ J mol}^{-1} \text{ K}^{-1}$). The reaction (R2) (hydrogen chloride synthesis) is a classic example of a multi-stage reaction of fractional order [18,23] because it proceeds through a series of intermediate stages. In this case, the reaction order is $n = 3/2$, the effective activation energy $E = 144.136 \text{ kJ mol}^{-1}$, the thermal effect— $Q = 185.2 \text{ kJ mol}^{-1}$ (the molar heat capacity— $c = 63.54 \text{ J mol}^{-1} \text{ K}^{-1}$). The reaction (R3) (nitrous oxide decomposition) is a second-order reaction [24] with activation energy $E = 240 \text{ kJ mol}^{-1}$ and thermal effect $Q = 163 \text{ kJ mol}^{-1}$. The dependences of ignition temperatures on parameter z for these reactions are presented in figure 11. The calculation of the ignition temperature was made using the formula:

$$T_{\text{ig}} = E\sqrt{\gamma(z)}/bR. \quad (6.1)$$

The critical conditions were determined using the numerical solution of the set of equations (3.1)–(3.3), (4.2) (intersection of the phase trajectories and demarcation lines figure 8). In view of the fact that the pre-exponential factor k_0 can vary within the very significant limits, the value of z (formula (4.3)) is represented on a logarithmic scale.

Table 2. Reaction R3: critical conditions.

$T_{\text{ig}} (^{\circ}\text{C})$	γ_c	δ_c	θ_c	ΔT_c	y_c	$\beta\theta_c$
1000	0.0266	1.866	1.2	67	0.16	0.048

Thus, knowing the parameter z it is easy to determine the ignition temperature. For the given reactions, the range of change in the parameter $z = 10^{-14} \div 10^{-2}$ defines the range of change in the ignition temperature 200–2000°C. However, it should be borne in mind that the reaction order and the values of kinetic constants correspond to a certain interval of temperatures, pressures and concentrations which are defined empirically. For this reason, it is necessary to consider the certain region of the change in parameter z and temperature. For example, the reaction R3 is the second-order reaction and its kinetics is well studied in the temperature interval 727–1077°C [23]. The ignition modes were investigated in the range of pressure 0.2–0.8 atm. [2]. It is easy to calculate that the critical value of parameter γ at $T = 1000^{\circ}$ is $\gamma_c \approx 0.026$. Taking into account figure 9, we obtain: $\gamma_c \ll \gamma_d \approx 0.15$ for the second-order reactions. Thus, the system is far from the state of degeneration. In this case, the ignition temperature $T_{\text{ig}} = 1000^{\circ}$ corresponds to the value $z = 10^{-8}$. Using the formula (4.3) and the values of parameters $k_0 = 5 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $\alpha S/V \approx 10^3 \text{ W m}^{-3} \text{ K}$, [24] we obtain $A_0 \approx 2 \text{ mol m}^{-3}$ that corresponds to the value of pressure $p \approx 0.2 \text{ atm}$. This is in good agreement with the experimental results [2]. In addition, at the corresponding value of $\delta_c = 1.866$, the approximate formula (3.10) gives a value of the critical parameter $\gamma_c = 0.029$ which is in satisfactory agreement with the calculated value $\gamma_c \approx 0.026$. As follows from figure 11*b*, the classical theory predicts the ignition temperature relatively well. The absolute difference between the classical theory and the presented model is about 20°C the relative difference is about 2%. Thus, the classical theory satisfactorily predicts the ignition temperatures for a given value of the parameter z in states far from degeneration. However, this theory gives the unsatisfactory predictions when considering the inverse problem of determining the critical value of parameter z at a given environment temperature (figure 11*b*). The relative difference between the values of z is 50% at $T_{\text{ig}} = 1000^{\circ}\text{C}$ and 200% at $T_{\text{ig}} = 1100^{\circ}\text{C}$. The results of calculating the critical conditions using the formulae: (3.2) and (3.9) are presented in table 2. At a given ignition temperature, the conversion degree is 16%. It cannot be regarded as an insignificant correction to the classical conditions. This causes a significant error in calculating the critical value of the parameter z on the basis of classical conditions. The condition for applying the model (2.2)–(2.4): $\gamma_c\theta_c \ll 1$ for the low-temperature regime [19–21] is performed with good accuracy.

In conclusion, it should be noted that the ignition temperatures for the reactions (R1) and (R3) are close due to the fact that the activation energies and thermal effects are close although the orders of the reactions differ by a factor of two. This confirms the fact that the ignition temperature depends weakly on the reaction order in the states far from degeneration.

7. Results and discussion

On the basis of investigations [10,19–21], the analysis of the critical autoignition conditions for arbitrary order of exothermic reactions was carried out. The kinetics of one-stage and multi-stage reactions which are determined by the kinetic function of the form $\varphi(y) = (1 - y)^n$ was considered. The analysis conducted allows extending the basic provisions of the classical theory [1,2,23] within the framework of which it is impossible to predict the degeneration conditions of TE. It was established that an increase in the value of reaction order leads to a decrease in the critical value of Todes parameter γ_c to compensate for the corresponding increase in the influence of kinetic inhibition (figure 4). Therefore, an increase in the order of reaction leads to compression of the post critical region on the parametric diagram (figures 4 and 7) while the degeneration region expands. The calculation of TE degeneration conditions for any reaction order was made (figures 8–10). The corresponding demarcation lines allow determine the parametric regions of TE existence. The calculation of ignition temperatures for nitrous oxide decomposition showed that

the classical theory gives a completely satisfactory prediction for the value of ignition temperature at the given reaction conditions (parameter z). However, this theory gives a significant error in the determination of the critical value of parameter z at a given environment temperature T_0 (inverse problem). With an increase in parameter γ , the classical theory gives more and more incorrect results.

It was shown that we can use the analytical dependences (3.9) and (3.12) in the states far from degeneration ($\gamma \ll \gamma_d$) with good accuracy.

8. Conclusion

In this study, an analysis of the critical ignition conditions for arbitrary reaction order was carried out using the maximum temperature method. The dependences of the critical heating on conversion degree, Semenov and Todes parameters were obtained at the limit of ignition. It was established that the ignition temperature weakly depends on reaction order for highly exothermic reactions. However, this dependence becomes strong for weakly exothermic reactions. The critical parametric diagrams presented allow calculating the ignition temperatures with good accuracy under given conditions and solving the inverse problem of determining the critical conditions for its realization under given environment temperature. The conditions of TE degeneration were analysed and the dependence of the Todes parameter on the Arrhenius parameter at the limit of degeneracy for reactions of any order is established. This is of great importance for reactions in the gas phase because these conditions allow establishing the concentration limits for the ignition of gas mixtures. The results obtained may be of interest from the point of view of chemical kinetics, explosion safety and energetics.

Ethics. This work did not involve any active collection of human data, but only computer simulations of human behaviour.

Data accessibility. This work contains the experimental data for reactions R1–R3. The corresponding references [22–24] are available for these papers: <https://aip.scitation.org/doi/10.1063/1.1727048> <https://www.osti.gov/biblio/6082197-mathematical-theory-combustion-explosions> <https://www.sciencedirect.com/science/article/pii/S0082078406801098>.

Authors' contributions. V.Y.F. carried out the analytical investigations, developed the mathematical model, participated in the design of the study and drafted the manuscript. K.B.K. carried out the numerical calculation of the basic equations of the mathematical model and helped draft the manuscript. Both authors gave the final approval for publication.

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References

1. Williams FA. 1989 *Combustion theory*, p. 708. Boca Raton, FL: CRC Press.
2. Frank-Kamenetsky DA. 1969 *Diffusion and heat transfer in chemical kinetics*, p. 574. New York, NY: Plenum Press.
3. Todes OM, Melent'ev PV. 1939 The theory of thermal explosion. *J. Phys. Chem.* **13**, 52–58.
4. Adler J, Enig JW. 1964 The critical conditions in thermal explosion theory with reactant consumption. *Combust. Flame* **8**, 97–103. (doi:10.1016/0010-2180(64)90035-5)
5. Gray P, Lee PR. 1965 Thermal explosion and the effect of reactant consumption on critical conditions. *Combust. Flame* **9**, 201–203. (doi:10.1016/0010-2180(65)90068-4)
6. Gray BF. 1973 Critical behaviour in chemical reacting systems: An exactly soluble model. *Combust. Flame* **21**, 317–325. (doi:10.1016/0010-2180(73)90023-0)
7. Kassoy DR, Linan A. 1978 The influence of reactant consumption on the critical conditions for homogeneous thermal explosion. *J. Mech. Appl. Math.* **31**, 99–112. (doi:10.1093/gjmath/31.1.99)
8. Lacey AA. 1983 Critical behaviour of homogeneous reacting systems with large activation energy. *Int. J. Eng. Sci.* **21**, 501–515. (doi:10.1016/0020-7225(83)90098-8)

9. Babushok VI, Goldhstein VM, Sobolev VA. 1990 Critical conditions for thermal explosion with reactant consumption. *Combust. Sci. Technol.* **70**, 81–89. (doi:10.1080/00102209008951613)
10. Filimonov VY. 2017 Critical ignition conditions in exothermically reacting systems: first-order reactions. *Proc. R. Soc. A* **473**, 1–12. (doi:10.1098/rspa.2017.0145)
11. Shouman A, El-Saed SA. 1997 Accounting for reactant consumption in the thermal explosion problem. Part II. A direct solution with application to the Frank-Kamenetskii problem. *Combust. Flame* **108**, 361–386. (doi:10.1016/S0010-2180(96)00121-6)
12. Shouman A, El-Saed SA. 1998 Accounting for reactant consumption in the thermal explosion problem III. Criticality conditions for the Arrhenius problem. *Combust. Flame* **113**, 212–223. (doi:10.1016/S0010-2180(97)00168-5)
13. Sánchez-Rodríguez D, Farjas J, Roura P. 2017 The critical condition for thermal explosion in an isoperibolic system. *AIChE J.* **63**, 3979–3993. (doi:10.1002/aic.15727)
14. Merzhanov AG. 1994 Solid flames: discoveries, concepts, and horizons of cognition. *Combust. Sci. Technol.* **98**, 307–336. (doi:10.1080/00102209408935417)
15. Prokof'ev VG, Smolyakov VK. 2002 Unsteady combustion regimes of gasless systems with a low-melting inert component. *Combust. Explos. Shock Waves* **38**, 143–147. (doi:10.1023/A:1014990529587)
16. Mukasyan AS, Khina BB, Reeves RV, Son SF. 2011 Mechanical activation and gasless explosion: nanostructural aspects. *Chem. Eng. J.* **174**, 677–686. (doi:10.1016/j.cej.2011.09.028)
17. Minamoto Y, Swaminathan N, Cant RS, Leung T. 2014 Reaction zones and their structure in mild combustion. *Combust. Sci. Technol.* **186**, 1075–1096. (doi:10.1080/00102202.2014.902814)
18. Upadhyay SK. 2008 *Chemical kinetics and reaction dynamics*, p. 256. New York, NY: Springer.
19. Filimonov VY, Koshelev KB. 2017 Criteria of thermal stability of exothermically reacting systems. Second order reactions. *Proc. Comb. Inst.* **36**, 423–432. (doi:10.1016/j.proci.2016.09.003)
20. Filimonov VY, Koshelev KB, Sytnikov AA. 2017 Thermal modes of heterogeneous exothermic reactions. Solid-phase interaction. *Combust. Flame* **185**, 93–104. (doi:10.1016/j.combustflame.2017.06.020)
21. Filimonov VY, Koshelev KB. 2017 Generalized criteria of volume ignition for one-stage exothermic reactions. *Propell. Explosives Pyrotech.* **42**, 175–183. (doi:10.1002/prep.201600064)
22. Page M, Pritchard HO, Trotman-Dickenson AF. 1953 The thermal decomposition of azomethane. *J. Chem. Soc. Paper* **792**, 3878–3881. (doi:10.1039/jr9530003878)
23. Zeldovich YaB, Barenblatt GI, Librovich VB, Makhviladze GM. 1985 *The mathematical theory of combustion and explosions*, p. 597. New York, NY: Consultants Bureau.
24. Johnsson JE, Glarborg P, Dam-Johansen K. 1992 Thermal dissociation of nitrous oxide at medium temperatures. *Symp. Proc. Comb. Inst.* **24**, 917–923. (doi:10.1016/S0082-0784(06)80109-8)