CONDITIONS FOR THE DEVELOPMENT OF A THERMAL EXPLOSION WITH BRANCHING-CHAIN REACTIONS

V. V. Azatyan, V. T. Gontkovskaya,
and A. G. Merzhanov

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In the theory of thermal explosions [1-4] the course of simple, single-stage autocatalytic reactions has been discussed in detail. Thermal explosions in systems with complex chemical processes have remained practically unstudied. In view of this, it is of the greatest interest to consider a widely encountered class of branching-chain processes. In such reacting systems, two mechanisms of the self-acceleration of the reaction are at work: thermal and chain; their combined appearance leads to specific regular laws, as follows from experimental data [5].

The present article uses one of the possible generalized schemes to consider the critical conditions for thermal explosion during branching-chain reactions with homogeneous breaking of the chains. It also discusses the effect of self-heating on a process without thermal explosion.

The mechanism of the reaction is represented by the following scheme:

$$\mathrm{A+B=x+y+p}, \tag{1}$$

$$\mathrm{x+A=y+p}, \tag{2}$$

$$\mathrm{y+B=y+2x}, \tag{3}$$

$$\mathrm{y+B+M=By+M}, \tag{4}$$

$$\mathrm{y+By=A+B}, \tag{5}$$

$$\mathrm{y+y=A}. \tag{6}$$

Here A and B are the starting substances; x and y are active intermediate products; By is an intermediate product (a slightly active radical, leading to breaking of the chains); p is the final product of the reaction; M is an arbitrary particle.

In accordance with this mechanism, the reaction is described by the following system of kinetic equations:

$$\begin{gathered}
\frac{d\,(\mathrm{x})}{dt} = k_1(\mathrm{A})(\mathrm{B}) - k_2(\mathrm{x})(\mathrm{A}) + 2k_3(\mathrm{y})(\mathrm{B}), \\
\frac{d\,(\mathrm{y})}{dt} = k_1(\mathrm{A})(\mathrm{B}) + k_2(\mathrm{x})(\mathrm{A}) - k_4(\mathrm{y})(\mathrm{B})(\mathrm{M}) - k_5(\mathrm{y})(\mathrm{By}) - 2k_6(\mathrm{y})^2, \\
\frac{d\,(\mathrm{By})}{dt} = k_4(\mathrm{y})(\mathrm{B})(\mathrm{M}) - k_5(\mathrm{y})(\mathrm{By}), \\
\frac{d\,(\mathrm{A})}{dt} = -k_1(\mathrm{A})(\mathrm{B}) - k_2(\mathrm{x})(\mathrm{A}) + k_5(\mathrm{y})(\mathrm{By}) + k_4(\mathrm{y})^2, \\
\frac{d\,(\mathrm{B})}{dt} = -k_1(\mathrm{A})(\mathrm{B}) - k_3(\mathrm{y})(\mathrm{B}) - k_4(\mathrm{y})(\mathrm{B})(\mathrm{M}) + k_5(\mathrm{y})(\mathrm{By}), \\
\frac{d\,(\mathrm{P})}{dt} = k_1(\mathrm{A})(\mathrm{B}) + k_2(\mathrm{x})(\mathrm{A}), \\
\frac{d\,(\mathrm{M})}{dt} = 0,
\end{gathered} \tag{I}$$

where k_i are the rate constants of the corresponding reactions.

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It is assumed that the reactions of the spontaneous generation and branching of the chains [stages (1) and (3), respectively] are endothermic, while the reactions of recombination [(4) and (6)] and reaction (5) are exothermic. It is also assumed that the reaction of the prolongation of the chains [Eq. (2)] is exothermic.

It is shown in [6] that in a consideration of thermal explosion the equation of the heat balance can be used instead of the partial differential equation of the thermal conductivity (i.e., the distribution of the temperature in the reaction vessel can be neglected). With such an approximation, the error in the value of the induction period does not exceed 25% for the case considered in [6].

The present article does not take account of the temperature gradients nor of the concentrations of the active centers of the chains in the reaction volume. The role of these gradients and the errors associated, in particular, with averaging of the temperature field, will be discussed separately.

On the basis of the scheme presented, the equation of the heat balance of the reaction system is written in the form

$$C_v\rho\frac{dT}{dt} = -Q_1k_1(\mathrm{A})(\mathrm{B}) + Q_2k_2(\mathrm{x})(\mathrm{A}) - Q_3k_3(\mathrm{y})(\mathrm{B}) + Q_4k_4(\mathrm{y})(\mathrm{B})(\mathrm{M}) +$$

$$+ Q_5k_5(\mathrm{By})(\mathrm{y}) + Q_6k_6(\mathrm{y})^2 - \alpha\frac{S}{V}(T-T_0), \qquad \text{(II)}$$

where Q_i are the absolute values of the heat effects of the corresponding stages; α is the heat-transfer coefficient; S and V are the surface and the volume of the reaction vessel; T_0 is the initial temperature, equal to the temperature of the walls of the vessel; ρ is the density of the reaction mixture; C_V is the heat capacity.

The system of kinetic equations (I) was solved simultaneously with heat-balance equation (II) using a computer, under the initial conditions: $t=0$; $T=T_0$; $(M)=(A)_0+(B)_0$; $(x)=(y)=(By)=p=0$; $(A)_0=(B)_0=\rho/2$. The concentrations and the density of the gas (ρ) are expressed in moles/cm^3. It is obvious that if ρ is expressed in g/cm^3, then

$$(\mathrm{A})_0 = (\mathrm{B})_0 = \frac{\rho}{2}\left(\frac{\alpha_A^0}{M_A} + \frac{1-\alpha_A^0}{M_B}\right),$$

where α_A^0 is the initial weight fraction of component A, and M_A and M_B are the molecular weights of A and B.

For a general consideration of processes taking place in accordance with the above scheme, it is expedient to write the equations using dimensionless quantities. The following simplifications were adopted:

1) $Q_1=Q_2=Q_3=Q_6=Q_0$; $Q_4=Q_5$; $Q_4+Q_0=Q_5+Q_0=Q$;

2) $E_1=E$; $E_3=\sigma\cdot E$; $E_2=E_4=E_5=E_6=0$;

In writing the relationships between the activation energies of the individual stages, we start from the fact that the rate constants of the recombinations and of reactions of type (4) depend only very weakly on the temperature and that the activation energy for prolongation of the chains is considerably less than the activation energy for generation and branching.

3) $k_1^0=k_2^0=k_3^0=k_5^0=k_6^0=k$,

where k_i^0 are the preexponential factors of the rate constants. This approximation is based on the fact that the values of the preexponential factors of the rate constants of bimolecular reactions of the active centers in branching-chain processes usually differ only very slightly between themselves. With respect to reactions of the spontaneous generation of chains (1), in the case of uncomplicated molecules, k_1^0 differs only insignificantly from the preexponential factors of the reactions of the active centers of the chains. In addition, after the induction period of chain ignition, the role of generation of chains is insignificant.

$$k_4^0 = k_4.$$

4) $Q_0/Q=\mu$; $\frac{Q_4}{Q}=\frac{Q_5}{Q}=1-\mu$.

The simplifications made do not violate the overall relationship between the rate constants and the heat effects of the individual stages of the process; therefore, a scheme with assumed values of the parameters reflects the picture of the phenomenon with quantitative correctness. At the same time, a decrease in the number of parameters permits considering the processes in general form and studying their most characteristic special features.

We introduce the dimensionless quantities:

$$n_1 = \theta = \frac{E}{RT_0^2}(T - T_0); \quad n_3 = \frac{(\mathrm{x})}{\rho}; \quad n_3 = \frac{(\mathrm{y})}{\rho}; \; n_4 = \frac{(\mathrm{A})}{\rho}; \quad n_5 = \frac{(\mathrm{B})}{\rho}; \quad n_6 = \frac{(\mathrm{P})}{\rho}; \quad n_7 = \frac{(\mathrm{Bx})}{\rho};$$

$$\tau = ke^{-\frac{E}{RT_0}}\rho t; \quad \varkappa = \frac{Q\rho^2 E}{\alpha \frac{S}{V} RT_0} ke^{-\frac{E}{RT_0}}; \; \gamma = \frac{c}{Q} \cdot \frac{RT_0^2}{E}; \quad m = e^{\frac{E}{RT_0}}; \quad n = e^{\frac{(1-\sigma)E}{RT_0}};$$

$$r = \frac{k_4\rho}{k} e^{\frac{E}{RT_0}}; \quad \beta = \frac{RT_0}{E}.$$

Using these quantities, we rewrite the above system of equations (I) and Eq. (II) in the form:

$$\gamma \frac{dn_1}{d\tau} = \gamma \frac{d\theta}{d\tau} = -\mu e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 + \mu m n_2 n_4 - \mu n e^{\frac{\sigma\theta}{1+\beta\theta}} n_3 n_5 + (1-\mu) r n_3 n_5 n_8 + (1-\mu) m n_3 n_7 + \mu m n_3^2 - \theta/\varkappa;$$

$$\frac{dn_2}{d\tau} = e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 - m n_2 n_4 + 2ne^{\frac{\sigma\theta}{1+\beta\theta}} n_3 n_5;$$

$$\frac{dn_3}{d\tau} = e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 + m n_2 n_4 - r n_3 n_5 n_8 - m n_3 n_7 - 2mn_3^2;$$

$$\frac{dn_4}{d\tau} = -e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 - m n_2 n_4 + m n_3 n_7 + mn_3^2;$$

$$\frac{dn_5}{d\tau} = -e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 - ne^{\frac{\sigma\theta}{1+\beta\theta}} n_3 n_5 - r n_3 n_5 n_7 + m n_3 n_7;$$

$$\frac{dn_6}{d\tau} = e^{\frac{\theta}{1+\beta\theta}} n_4 n_5 + m n_2 n_4;$$

$$\frac{dn_7}{d\tau} = r n_3 n_5 n_8 - m n_3 n_7;$$

$$\frac{dn_8}{d\tau} = 0.$$

This system of equations was integrated numerically using an implicit difference scheme, described in [7, 8]. The calculations were made with the following values of the dimensionless parameters:

$$\gamma = 2 \cdot 10^{-3}; \; \beta = 3 \cdot 10^{-2}; \; r = 3.805 \cdot 10^4; \; n = 4.47 \cdot 10^6; \; m = 3.164 \cdot 10^9.$$

The value of $\varkappa$ was varied from 0 to 0.200×10^{-2}. These values of the dimensionless parameters correspond to the following values of the starting quantities: $k = 0.6 \times 10^{14}$ cm^3/(mole · sec); $k_4 = 0.36 \times 10^{15}$ cm^6/(mole^2 · sec); $T_0 = 800$°K; $\rho = 2 \times 10^{-6}$ mole/cm^3; E = 35.0 kcal/mole; $E_3 = 15.0$ kcal/mole; $Q_0 = 20.0$ kcal/mole; $Q_4 = Q_5 = 50.0$ kcal/mole. It was assumed that the energy evolved by the recombination of the active centers y is radiated to a considerable degree. The above values are close to the real values of the corresponding parameters for the usual reactions of active centers of chains.* In the calculations only the parameter $\varkappa$ was varied. This means that the parameters of the chain reaction, as well as the initial temperatures and concentrations, remained unchanged in the different variants of the calculation. Only the heat-transfer conditions changed. An isothermal course of the reaction corresponds to the subcritical region; i.e., there is chain autoignition. Actually, the initial conditions adopted correspond to positive values of the branching factor of the chains

$$\varphi = 2k_3(\mathrm{B}) - 2k_4(\mathrm{B})(\mathrm{M}) > 0.$$

Figures 1-4 give the dependences of the dimensionless concentration of the active centers of the chains (x)/ρ and of the temperature Q on τ, showing the time evolution of the process. An examination of these curves leads to the following conclusions.

1. Depending on the parameter $\varkappa$, the process may consist of one or two flashes, or more accurately, of one or two stages of progressive autoacceleration. During the development of the first stage, the temperature does not change and the kinetics of the process do not depend on the parameter $\varkappa$. This constitutes chain autoignition.

The second stage, also taking place with autoignition, occurs only with relatively large values of $\varkappa$. Under these circumstances, very large values both of (x), (y), and θ, and of the rates of their increase, are attained. The reaction goes to completion in a very short time. This constitutes thermal explosion (Fig. 4 and curves 8-14 on Figs. 1-3).

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*It is obvious that the heat effect of the endothermic reaction (3) must be less than its activation energy. Since, however, in the present article a study is not being made of the elementary reaction (3), but of the complex process as a whole and of the heat balance of the reaction system, with the simplifications adopted which make it possible to reduce the number of parameters, such an excess of Q_3 over E_3 is not basic.

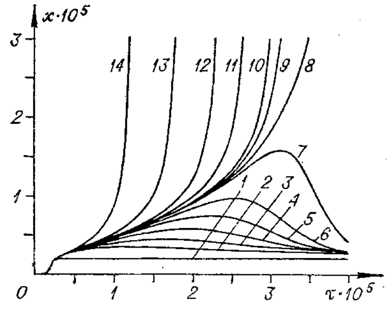

Fig. 1

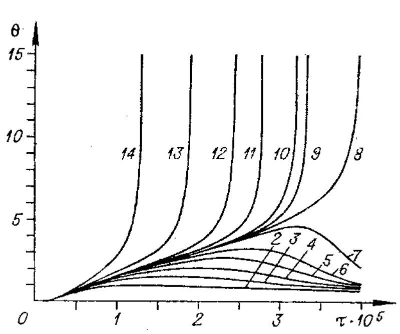

Fig. 2

Fig. 1. Dependence of relative concentration of active centers (x) on τ with the following values of $\varkappa$: 1) 0; 2) $0.1 \cdot 10^{-2}$; 3) $0.120 \cdot 10^{-2}$; 4) $0.130 \cdot 10^{-2}$; 5) $0.135 \cdot 10^{-2}$; 6) $0.137 \cdot 10^{-2}$; 7) $0.1380 \cdot 10^{-2}$; 8) $0.1381 \cdot 10^{-2}$; 9) $0.1382 \cdot 10^{-2}$; 10) $0.1383 \cdot 10^{-2}$; 11) $0.1390 \cdot 10^{-2}$; 12) $0.141 \cdot 10^{-2}$; 13) $0.150 \cdot 10^{-2}$; 14) $0.200 \cdot 10^{-2}$.

Fig. 2. Dependence of dimensionless temperature on τ. (Numbers of curves correspond to the values of $\varkappa$ given in Fig. 1.)

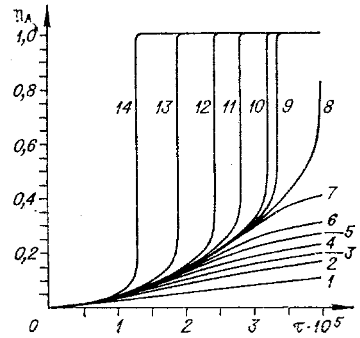

Fig. 3. Dependence of relative burn-up (η) on τ. (Numbers of curves correspond to the values of $\varkappa$ given in Fig. 1.)

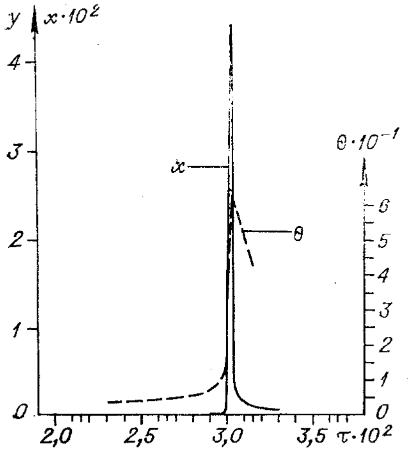

Fig. 4. Dependence of x and θ on τ with $\varkappa = 0.141 \cdot 10^{-2}$.

With small values of $\varkappa$, after chain autoignition, in definite stages of the starting combustion, there is a relatively small rise in the value of θ followed by a decrease. With these values of $\varkappa$, the rise in the value of the rate constant for branching of the chains (k_3) due to self-heating, is not able to compensate the decrease in the branching factor of the chains due to the small consumption of the starting substances. It follows from a comparison of Fig. 2 and 3 that up to the moment of a decrease in the value of θ the concentrations of the starting substances can actually decrease only very slightly. This is a case of chain autoignition with self-heating, which, however, does not lead to thermal explosion.

We note that the small rate of fall of the concentration of active centers of the chains (on the scale shown on Fig. 1), after attaining a maximum in the isothermal case, and with very small values of $\varkappa$, requires for its explanation the very rare branching of the chains.

2. The development of a thermal explosion during the course of a branching reaction is rather clearly expressed and, in particular, takes place in a very narrow interval of values of $\varkappa$, i.e., there exist critical conditions for thermal explosion which, in the present case, we shall characterize by the value of the parameter $\varkappa$ that is decisive for the conditions described above ($\varkappa_{cr}$). Thermal explosion sets in with $\varkappa \geq \varkappa_{cr}$. The value of $\varkappa_{cr}$ can be found from the curve of the dependence of the maximal values of θ, x, and y attained during the course of the process on the value of $\varkappa$ (Fig. 5).

It is not difficult to determine $\varkappa_{cr}$ with sufficient accuracy as the abscissa of the sharp rise in the values of θ, x, and y. In accordance with Fig. 5, in the given case, $\varkappa_{cr} = (1.3805 \pm 0.0005) \cdot 10^{-3}$. In a more rigorous statement, the value of $\varkappa_{cr}$ can be defined as the abscissa of the point of inflection on the curve of the dependence of the value of θ (as well as on the curves of the dependence of x and y) on the value of $\varkappa$.

3. As can be seen from Figs. 3 and 5, the value of the pre-explosion heating, i.e., the maximal degree of heating with $\varkappa < \varkappa_{cr}$, is approximately equal to 4.6 (in units of θ). From this, taking account of the values of E and T_0, we obtain $\Delta T \approx 390°C$.

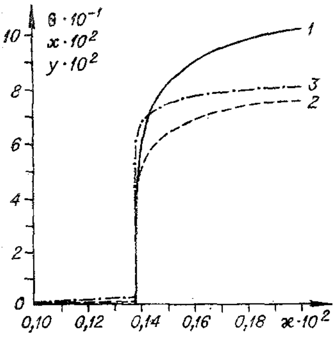

Fig. 5. Change in the maximal values of (x) (1), (y) (2), and θ (3) as a function of $\varkappa$.

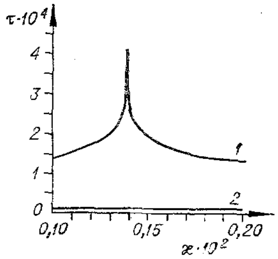

Fig. 6. Dependence of time required for the attainment of the maximal temperature and of the induction period of a thermal explosion on $\varkappa$ (1). (The value of the induction period for a chain-type ignition is shown by the straight line 2.)

It must be noted that in the reactions considered previously in the theory of thermal explosion[1] the pre-explosion heating is equal to zero. Thus, in branching-chain reactions, there are considerably higher degrees of pre-explosion heating. This can be explained by the fact that after the induction period of chain ignition the role of the generation of chains, with its high activation energy, becomes insignificant. The laws governing the process are determined by the remaining stages, whose activation energies are not great, since they take place with the participation of free atoms and radicals. Due to this, a reaction with a considerable rate takes place (and the reaction mixture is heated up appreciably) also in the absence of a thermal explosion. In spite of the fact that under these conditions a thermal explosion does not take place, the rate of the reaction as well as the depth of the conversion can be substantially greater than in the case of an isothermal course of the reaction.

The presence of a considerable effect of self-heating on the process, in spite of the small activation energy of its limiting stage, must be explained by an increase in the branching ability of the chains with a rise in temperature. As a result of self-heating, with $\varkappa < \varkappa_{cr}$ there is an increase in the concentrations of the active centers and a shortening of the reaction time, as can be seen from Figs. 1-3.

Since $E_1 = 0$, $E_2 = 15$ kcal/mole, and $k_2^0 = k_3^0$, with small degrees of self-heating (x) < (y). With the concentrations of the starting substances under consideration, the consumption of (y) in accordance with reactions (4) and (5) cannot change this relationship. Therefore, in the reaction scheme describing a process with $\varkappa \leq \varkappa_{cr}$, the quadratic recombination of the active centers (x) is not taken into account. Under conditions of thermal explosion, as a result of the strong rise in temperature, the difference between k_2 and k_3 becomes so slight that it cannot compensate for the consumption of (y) in accordance with reactions (4)-(6). Therefore, with $\varkappa \geq \varkappa_{cr}$, the maximal concentration of (y) is found to be somewhat less than $(x)_{max}$ (see Fig. 5).

It is obvious that as a result of the considerable change in the ratio of the rate constants of the individual stages, brought about by the large change in the temperature with thermal explosion, the set of main stages describing the process may change. Since, however, the present article considers the conditions for the development of thermal explosion, as well as the course of the reaction when there is no thermal explosion, the above mechanism remains unchanged over the whole interval

$$0 \leqslant \varkappa \leqslant \varkappa_{cr}.$$

As can be seen from Figs. 1-4 and 6, the induction period for chain ignition is considerably less than the induction period for thermal explosion and the time required for the attainment of a maximal temperature over the whole investigated range of values of $\varkappa$. With $\varkappa = \varkappa_{cr}$, up to the moment when thermal explosion sets in, the depth of the conversion $\eta_{(cr)} \simeq 0.4$-0.6 [the curve on Fig. 2], which is close to the corresponding value of this parameter in the case of simple autocatalysis.

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