QUASI-STATIONARY THERMAL REGIME OF EXPLOSIVE REACTIONS

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Abstract

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The nonstationary system of equations describing thermal explosion, in dimensionless variables*, has the form

$$\gamma \frac{d\theta}{d\tau} = e^{\theta}\varphi(\eta) - \frac{1}{\chi}\theta, \tag{1}$$

$$\frac{d\eta}{d\tau} = e^{\theta}\varphi(\eta). \tag{2}$$

Initial conditions: $\tau = 0$, $\eta = 0$, $\theta = 0$, $\eta = \frac{C_0 - C}{C_0}$—degree of conversion; $\theta = \frac{E}{RT_0^2}(T - T_0)$—heating; $\tau = k_0 e^{-E/RT_0} t$—time;

$$\chi = \frac{1}{4e\delta_{\text{cr}}} \frac{Q}{\lambda} \frac{E}{RT_0^2} d^2 k_0 e^{-E/RT_0}; \qquad \gamma = \frac{c\rho}{Q} \frac{RT_0^2}{E};$$

$\varphi(\eta)$ is a function expressing the law of the course of the reaction under isothermal conditions.

The criterion χ expresses the relation between the constants and the conditions under which the reaction proceeds. The criterion γ characterizes the explosive properties of the reaction. The smaller γ, the more sharply the explosive properties are expressed.

Notation: C—concentration of the initial products; C_0—initial value of the concentration of the initial products; T—temperature (deg.); T_0—initial value of the temperature (deg.); t—time (sec.); d—diameter of the reaction vessel (cm); E—activation energy (cal/mole); k_0—pre-exponential factor (sec^{-1}); Q—heat effect of the reaction (cal/cm^3); λ—thermal conductivity (cal/cm $\cdot$ sec $\cdot$ deg.); c—specific heat capacity (cal/g $\cdot$ deg.); ρ—density (g/cm^3); δ_{cr}—critical value of the Frank-Kamenetskii parameter ([1]) (for a plane-parallel vessel 0.88; cylindrical 2.00; spherical 3.32).

A general investigation of this type of system was carried out by Todes ([2–4]). He obtained expressions for the explosive limit, and also, by numerical integration

Fig. 1. Dependence of K on θ for $\gamma = 0.005,\ \eta_0 = 0.01,\ \varkappa = 1.55$

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methods, considered the kinetics of the reaction and of heating. Analyzing the results of Todes and our own experimental data, we came to the conclusion that under certain conditions there occurs a quasi-stationary regime of the course of the reaction, in which the amount of heat accumulation is small in comparison with the amount of heat input (almost all the heat released is removed from the reaction zone), and it may be neglected. The process of such a reaction consists, as it were, of a series of equilibrium, stationary states. The transition from one state to another occurs at the expense of an isothermal change in the reaction rate and, consequently, in the heat input. This means that, in the quasi-stationary regime, the principal role in the nonisothermal course of the reaction is played not by heat accumulation, but by isothermal–

* In transforming to dimensionless variables, the method of separation of the exponentials proposed by Frank-Kamenetskii ([1]) was used.

···change in rate.* Such a process is possible if the time required for thermal equilibrium to be established is much less than the reaction time, i.e., if during the time required for establishment the position of equilibrium shifts only slightly.

For self-accelerating reactions under isothermal conditions, consideration of the quasi-stationary regime makes it possible to obtain all the principal characteristics of the phenomenon of thermal explosion–the critical condition (explosion limit), the depth of the pre-explosion reaction, and the induction period.

Let us consider, without reducing the generality of the conclusions, the simplest type of self-accelerating reactions–first-order autocatalytic reactions:

$$\varphi(\eta) = (\eta + \eta_0)(1 - \eta),$$

where η_0 is the autocatalyticity criterion, a substantially small quantity (10^{-1}—10^{-3}). The criterion η_0, which, generally speaking, depends on T, may be regarded as constant in the integration [(4)].

Fig. 1. Dependence of K on θ for $\gamma = 0.005,\ \eta_0 = 0.01,\ \varkappa = 1.55$

The quasi-stationary system of equations has the form

$$e^{\theta}(\eta + \eta_0)(1 - \eta) - \frac{1}{\varkappa}\theta = 0, \tag{3}$$

$$\frac{d\eta}{d\tau} = e^{\theta}(\eta + \eta_0)(1 - \eta). \tag{4}$$

At $\tau = 0$, $\eta = 0$.

Equation (3) expresses the equilibrium relation between heating and the depth of conversion. Analysis of this relation shows that a quasi-stationary regime above the explosion limit can exist in the interval $\theta_0 < \theta < 1$ for values $\varkappa < 1/e\eta_0$. The smallest quasi-stationary heating θ_0 is found from the expression

$$\theta_0 e^{-\theta_0} = \varkappa\eta_0.$$

For $\theta < \theta_0$ the quasi-stationary regime has not yet been established; for $\theta > 1$ it has already broken down. For $\varkappa \gg 1/e\eta_0$ the specific character of the self-accelerating reaction plays no role (the explosion condition is satisfied by the initial rate), and quasi-stationary progress is in principle impossible.

As a result of solving the system of equations (3)–(4), the following expressions were obtained: the critical condition

$$\varkappa = \frac{4}{e(1+\eta_0)^2};$$

the depth of the preliminary reaction

$$\eta_{\text{expl}} = \frac{1-\eta_0}{2} - \sqrt{\left(\frac{1+\eta_0}{2}\right)^2 - \frac{1}{e\varkappa}};$$

the induction period

$$\tau_{\text{ind}} = \frac{1}{2}\int_{\theta_0}^{1} \frac{(1-\theta)e^{-\theta}\,d\theta}{\theta\sqrt{\left(\frac{1+\eta_0}{2}\right)^2 - \frac{1}{\varkappa}\theta e^{-\theta}}}.$$

* In the adiabatic regime, for example, on the contrary, heat accumulation plays the main role.

The induction period (dimensional) at the explosive limit is equal to

$$t_{\text{cr}} = \frac{1}{k_0(1+\eta_0)}\, e^{E/RT_0} \int_{\theta_0(\eta_0)}^{1} \frac{(1-\theta)e^{-\theta}\,d\theta}{\theta\sqrt{1-\theta e^{(1-\theta)}}}.$$

As is seen from this expression, t_{cr} is determined only by the constants of the rate of the isothermal reaction and does not depend on quantities essential for thermal explosion, such as Q, λ, etc., which affect only the position of the explosive limit. This property can be used to determine rate constants from experimental data on thermal explosion.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. Curves of the dependence of θ on τ, obtained as a result of solving the nonstationary system (solid line) and the quasistationary system (dotted line). The parameter values are the same as for Fig. 1.

It is convenient to calculate the time course of the reaction by the formula

$$\tau = \chi \int_0^{\eta} \frac{d\eta}{\theta(\eta, \chi, \eta_0)}.$$

Here $\theta(\eta, \chi, \eta_0)$ is found from equation (3).

To solve the question of the conditions for existence of a quasistationary regime, let us introduce the quantity

$$K = \gamma \frac{d\theta}{d\eta}.$$

This quantity is the ratio of the rate of heat accumulation to the rate of heat input and characterizes the regime of the reaction course. For an adiabatic regime $K = 1$, for a stationary regime $K = 0$, and for a quasistationary regime $K \ll 1$.

In Fig. 1 the dependence of K on θ, obtained by numerical integration, is presented. As a criterion of quasistationarity one may choose the value of K at the point θ_0. An approximate calculation (valid for small K) gives

$$K_0 \simeq \frac{\chi\gamma}{(1-\theta_0)e^{-\theta_0}}. \tag{5}$$

Fig. 3. Graphical interpretation of the equation of heat balance. 1 and 2—curves of heat input corresponding to the initial and maximum rates; 3—straight line of heat removal; 4—integral curve of heat input. The parameter values are the same as for Fig. 1.

The quasistationary regime may be regarded as a limiting form of nonisothermal reaction course as $K_0 \to 0$. The quantity K_0 may be small either because χ is small (conditions close to isothermal), or because γ is small. For reactions leading the process to thermal explosion, γ is of the order of 10^{-2}–10^{-3}. Therefore a quasistationary regime of self-accelerating reactions always exists also above the explosive limit (when χ is not small). The width of the region (in χ) of quasistationary course of the pre-explosion reaction depends on the degree of self-acceleration. For reactions

with normal kinetics, the quasi-stationary regime exists only below the explosion limit beyond the maximum heating and is, naturally, of no interest.

The process of establishment of the quasi-stationary regime can be investigated by solving the system of equations (1), (2) for $0 < \theta < \theta_0$ and $0 < \eta < \eta_{\text{st}}$. The condition of quasi-stationarity corresponds to $\eta_{\text{st}} \ll \eta_0$. As a result of an approximate solution for small values of θ_0 (satisfying the representation $e^{\theta_0} \approx 1 + \theta_0$), expressions were obtained for η_{st} and τ_{st}:

$$\ln\left(\frac{1}{1 - x\eta_0}\frac{\eta_{\text{st}}}{\eta_0}\right) + x\eta_0 = -\frac{(1 - x\eta_0)^2\eta_{\text{st}}}{x\gamma\,\eta_0},$$

$$\tau_{\text{st}} = -\frac{x\gamma}{1 - x\eta_0}\ln\left(\frac{1}{1 - x\eta_0}\cdot\frac{\eta_{\text{st}}}{\eta_0}\right).$$

Figure 2 shows the curves $\theta(\tau)$, obtained by numerical integration of the system (1)–(2) and from the solution of the system (3)–(4) with a correction for establishment.

If the reaction proceeds non-quasi-stationarily because γ is insufficiently small, then the following estimate can be given for τ_{ind}:

$$x\int_0^{\eta_{\text{expl}}}\frac{d\eta}{\theta(x,\eta)} < \tau_{\text{ind}} < \int_0^{\eta_{\text{expl}}}\frac{d\eta}{\varphi(\eta)}.$$

The lower estimate is obtained under the assumption that η_{expl} is reached quasi-stationarily; the upper one, isothermally.

The quasi-stationary regime is conveniently observed on a diagram (Fig. 3) as the closeness of the integral heat-release curve to the straight line of heat removal.

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Note: Figure translations are in progress. See original paper for figures.