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Abstract

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ON THE QUASI-STATIONARY THEORY OF THERMAL EXPLOSION

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According to the quasi-stationary theory of thermal explosion, developed for self-accelerating reactions ([1–3]), explosion* arises as a result of a displacement of the position of equilibrium between heat generation and heat removal, which occurs owing to an isothermal increase in the reaction rate. The quasi-stationary course of the pre-explosion process in the regimes considered is predetermined by the properties of explosive reactions and by the presence of isothermal self-acceleration. However, quasi-stationary regimes of another type are possible, independent of self-acceleration of the reaction. These are forced, self-unregulated regimes, caused by a displacement of the position of equilibrium between heat generation and heat removal due to a slow change of some system parameter with time according to a definite law not connected with the course of the reaction.

In the present work, within the framework of the quasi-stationary theory, the characteristics of thermal explosion under dynamic conditions of a linear increase with time of the temperature of the surrounding medium (heating at a constant rate) are considered.

The initial system of equations has the form

$$c\rho\frac{dT}{dt} = Qk_0e^{-E/RT}\varphi(\eta) - \alpha\frac{S}{V}(T - T_0), \qquad \frac{d\eta}{dt} = k_0e^{-E/RT}\varphi(\eta), \qquad T_0 = wt. \tag{1}$$

Initial conditions: $t = 0,\ T = T_0,\ \eta = 0$.

Notation: T is the temperature in the reaction zone (°K); T_0 is the temperature of the surrounding medium (°K); η is the degree of conversion; t is time (sec); α is the heat-transfer coefficient (cal/cm^2 · sec · deg); V is the reaction volume (cm^3); S is the surface giving off heat (cm^2); Q is the heat of reaction (cal/cm^3); E is the activation energy (cal/mol); k_0 is the pre-exponential factor; c is the specific heat (cal/g · deg); ρ is the density (g/cm^3); w is the rate of change of T_0 (deg/sec); $\varphi(\eta)$ is a function expressing the law of the reaction course under isothermal conditions.

In the case when there is no temperature distribution in the reaction zone, α is the coefficient of heat transfer from the surface of the charge (or from the inner surface of the reaction vessel—for liquids) to the surrounding medium. In the presence of distributions of temperature, T and η have the meaning of volume-averaged quantities, while α is an effective heat-transfer coefficient ([2]).

A specific feature of forced regimes is the possibility of a quasi-stationary course of the pre-explosion process for any types of reactions, irrespective of their kinetic regularities.

The forced quasi-stationary regime is easily represented on the Semenov diagram (Fig. 1), using the model of a zero-order reaction. Under dynamic conditions (variable T_0) the heat generation is expressed by a family of straight lines corresponding to different values of T_0 (or t). In the course of the reaction, the position of equilibrium (the points of intersection of heat generation and heat removal) is displaced along the heat-generation curve. One may consider heat generation and heat removal as connected with different systems

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* In this work, as is usual in the theory of thermal explosion, we do not distinguish explosion from ignition and by explosion understand a rapid, essentially nonstationary course of the reaction.

coordinates, coincident along the abscissa axis and moving relative to one another with velocity w. The explosion occurs at the moment of contact. With a linear increase of T_0, the course of a zero-order reaction always ends in explosion for any w. If the heating rate w is less than the rate at which thermal equilibrium is established, then the pre-explosion process develops quasi-stationarily. Otherwise, thermal equilibrium does not have time to be established, and the reaction proceeds nonstationarily.

For real systems, owing to burnout (a decrease in the reaction rate due to consumption of the initial substance), there exists a critical value of the heating rate w_{cr}. Under slow heating ($w < w_{\text{cr}}$), the substance has time to react without explosion; under rapid heating ($w > w_{\text{cr}}$), the quiet course of the reaction ends in explosion.

Fig. 1. Semenov diagram

The mathematical meaning of the forced quasi-stationary regime consists in the smallness of the intrinsic rate of heat accumulation in comparison with the imposed one:

$$d(T - T_0)/dt \ll dT_0/dt \quad \text{or} \quad d(T - T_0)/dT_0 \ll 1 \quad \text{or} \quad dT/dT_0 \simeq 1, \qquad (2)$$

i.e., in the forced quasi-stationary regime the rate of change of the temperature in the reaction zone is close to the heating rate. The quasi-stationary character of the course of the reaction is illustrated in Fig. 2.

Fig. 2. Temperature regime of the course of the reaction under dynamic conditions.
1—$w > w_{\text{cr}}$, 2—$w < w_{\text{cr}}$.
$T_0^* < T_0 < T_{0\,\text{expl}}$—quasi-stationary regime (q. s. r.);
$T_0 \ll T_0^*$—establishment of q. s. r.;
$T_0 > T_{0\,\text{expl}}$—breakdown of q. s. r.

Before proceeding to the solution of the equations, it is expedient to expand the exponential by the Frank-Kamenetskii method ([2]). In view of the very sharp temperature dependence of the Arrhenius term, the expansion is always carried out near the temperature at which the most intense reaction occurs. In the present problem this temperature is T_{0m}^* (Fig. 2).

$$e^{-\frac{E}{RT}} \simeq e^{-\frac{E}{RT_{0m}^2}}\, e^{\frac{E}{RT_{0m}^2}(T-T_{0m})}.$$

This expansion is valid at temperatures close to T_{0m}. At temperatures far from T_{0m},

* Above the ignition limit, $T_{0\,\text{expl}}$ is taken instead of T_{0m} (Fig. 2).

the expansion is invalid, but there the entire term with the exponential becomes negligible. Owing to this circumstance, use of the Frank-Kamenetskii transformation leads to a small error and is widely applied in the thermal theory of combustion and explosion processes.

Using the quasistationarity condition (2) and introducing the dimensionless quantities

$$\theta = \frac{E}{kT_{0m}^2}(T - T_{0m}), \quad \varkappa = \frac{Q}{\alpha S/V}\frac{E}{RT_{0m}^2}k_0 e^{-E/RT_{0m}}, \quad \theta_0 = \frac{E}{RT_{0m}^2}(T_0 - T_{0m}),$$

$$\gamma = \frac{c\rho}{Q}\frac{RT_{0m}^2}{E}, \quad \omega = \frac{w}{k_0 e^{-E/RT_{0m}}}\frac{E}{RT_{0m}^2}, \quad \beta = \frac{E}{RT_{0m}},$$

we reduce (1) to the form

$$(\theta_0 = -\beta; \quad \theta = -\beta; \quad \eta = 0)$$

$$e^{\theta}\varphi(\eta) - \frac{1}{\varkappa}(\theta - \theta_0) - \omega\gamma = 0, \tag{3}$$

$$\omega\frac{d\eta}{d\theta} = e^{\theta}\varphi(\eta). \tag{4}$$

The dimensionless system of equations (3), (4) describes the quasistationary course of the reaction under conditions of linear heating. The scheme for its solution is evident. Integrating (4), we obtain the dependence $\eta(\theta)$, which we substitute into (3). Analysis of the relation $f(\theta, \theta_0) = 0$ makes it possible to calculate all the principal characteristics of thermal explosion.

Let us carry out a specific calculation of the characteristics for the example of a monomolecular reaction. The object of the calculation is to determine the critical heating rate ω_{cr}, the temperature of explosion onset $T_{0\text{expl}}$, the depth of pre-explosion reaction η_{expl}, and other characteristics. For a monomolecular reaction $\varphi(\eta) = 1 - \eta$;

$$\eta = 1 - e^{-\frac{1}{\omega}(e^{\theta} - e^{-\beta})}.$$

The term $e^{-\beta}$ is significant only at large negative values of θ, i.e., when the reaction practically does not proceed. Therefore we shall consider the limiting case $\beta \to \infty$. Then

$$\eta = 1 - e^{-\frac{1}{\omega}e^{\theta}}, \tag{5}$$

$$\varphi[\eta(\theta)] = e^{-\frac{1}{\omega}e^{\theta}}. \tag{6}$$

Substituting (6) into (3), we obtain

$$e^{\theta - \frac{1}{\omega}e^{\theta}} - \frac{1}{\varkappa}(\theta - \theta_0) - \gamma\omega = 0. \tag{7}$$

Expressions (7) and (5) lead to the dependences $\theta = \theta(\theta_0, \omega, \varkappa, \gamma)$ and $\eta = \eta(\theta_0, \omega, \varkappa, \gamma)$, which constitute the solution of the quasistationary system (3), (4). Since at the ignition limit for $\theta_0 = 0$ the maximum self-heating is attained, then

$$\left.\frac{d(\theta - \theta_0)}{d\theta_0}\right|_{\theta_0 = 0} = 0. \tag{8}$$

Differentiating (7) with respect to θ_0 and taking (8) into account, we obtain

$$\theta_m = \ln\omega; \tag{9}$$

θ_m is the maximum self-heating of the system, attained during the course of the reaction at the ignition limit. Substituting (9) into (5), we find the depth of conversion corresponding to the maximum self-heating: $\eta_m = 1 - 1/e \simeq 0.632$,

Figure 3. Dependence of the main characteristics of thermal explosion on the heating rate. $\omega_{\text{cr}} \simeq 2 \cdot 10^3$ deg/sec

Figure 1: Figure 3. Dependence of the main characteristics of thermal explosion on the heating rate. $\omega_{\text{cr}} \simeq 2 \cdot 10^3$ deg/sec

and substituting (9) into (7) and taking into account that $\theta_{0m} = 0$, we obtain the relation between the quantities ω, $\varkappa$, and γ at the ignition limit

$$\omega/e - \ln \omega/\varkappa - \gamma\omega = 0. \tag{10}$$

Fig. 3. Dependence of the main characteristics of thermal explosion on the heating rate. $\omega_{\text{cr}} \simeq 2 \cdot 10^3$ deg/sec.

Analyzing this relation, we arrive at the conclusion that at the ignition limit

$$\chi_{\text{cr}}(1/e - \gamma) = 1/e, \qquad \omega_{\text{cr}} = e, \tag{11}$$

and also

$$\theta_{\text{cr}} = 1; \qquad \eta_{\text{cr}} = 1 - 1/e. \tag{12}$$

Above the ignition limit, expression (10) is invalid. The relation between the parameters ω, χ, and γ is found from (7) by substituting $\theta_0 = 0$ and $\theta = \theta_{\text{cr}} = 1$ *:

$$e^{(1-e/\omega)} - (1/\chi + \omega\gamma) = 0. \tag{14}$$

The depth of the pre-explosive reaction, according to (6), is

$$\eta_{\text{expl}} = 1 - e^{-e/\omega}. \tag{15}$$

By substituting into (10)–(15) the expressions for the dimensionless quantities (3), all the principal characteristics of the thermal explosion are calculated. In particular, T_{0m} is found from (11), $T_{0\,\text{expl}}$ from (14), and ω_{cr} from (12).

Figure 3 shows the results of a numerical calculation carried out for the following parameter values: $k_0 = 10^{18}$ sec^{-1}; $E = 45000$ cal/mole; $Q = 1000$ cal/cm^3; $\alpha = 10^{-3}$ cal/cm$^2 \cdot$ sec $\cdot$ deg; $S/V = 4/d$; $d = 0.44$ cm; $c = 0.3$ cal/g $\cdot$ deg; $\rho = 1.5$ g/cm^3.

Without entering into a detailed analysis of the dependences obtained, we note the following:

1. The critical heating rate ω_{cr} depends on the diameter of the reaction vessel (or charge); the smaller this diameter, the larger ω_{cr}.
2. The pre-explosive heating, according to (13) and (3), is equal to $\Delta T_{cr} = RT_{0cr}^2/E$, i.e., it is related to the critical temperature in the same way as under static conditions (for $T_0 = \text{const}$).
3. The depth of the pre-explosive reaction under critical conditions is large ($\eta_{cr} \approx 63\%$). The large value of η_{cr} is a specific feature of the quasistationary course of the reaction (under static conditions the explosion develops essentially nonstationarily and η_{cr} is equal to several percent). With increasing ω/ω_{cr}, the depth of the pre-explosive reaction decreases.
4. The dynamic temperature $(T_{0cr})_d$ exceeds the static temperature $(T_{0cr})_{st}$ by the amount of the pre-explosive heating ΔT_{cr}. With increasing ω/ω_{cr}, the temperature of explosion onset T_{0expl} decreases, approaching the value $(T_{0cr})_{st}$.
5. The quasistationarity criterion in dimensionless quantities is equal to $K_0 \approx \omega\chi\gamma$. Since γ is always small for reactions capable of thermal explosion (10^{-2}–10^{-3}), at the ignition limit $K_0 = e\gamma \ll 1$, i.e., near critical conditions the quasistationary regime always holds. The interval of rates at which quasistationary maturation of the explosion occurs depends on γ and may be considerable. In real cases $1 < \omega/\omega_{cr} < 2 \div 20$.

In the present work, the characteristics of thermal explosion have been calculated for a monomolecular reaction. According to the scheme considered, calculations can easily be carried out for bimolecular, autocatalytic, and other reactions.

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* In the theory of thermal explosion it is customary to distinguish the pre-explosive process from the explosion by the magnitude of the heating. Development of the explosion corresponds to $\theta - \theta_0 > \theta_{cr}$.