A. G. MERZHANOV, V. G. ABRAMOV, V. T. GONTKOVSKAYA

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A. G. MERZHANOV, V. G. ABRAMOV, V. T. GONTKOVSKAYA

ON THE REGULARITIES OF THE TRANSITION FROM SELF-IGNITION TO IGNITION

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It is known that in an explosive system two limiting regimes of thermal inflammation can be realized: self-ignition (thermal explosion) and ignition. The regularities of the transition from self-ignition to ignition as a function of various factors (the dimensions and initial temperature of the system, the ambient temperature, etc.) have been almost entirely unstudied. One can only mention the article by Zinn and Mader ([1]), in which the results of certain numerical calculations of the temperature dependence of ignition delay times are given.

In the present work, the nonstationary temperature field inside a reacting system during the process of inflammation is investigated theoretically, with the aim of determining the boundaries of existence of the self-ignition regime and certain regularities of the transition to ignition. An essential feature of the problem considered, in comparison with ordinary problems on self-ignition, is the inclusion of the stage of heating (the initial temperature of the system is lower than the ambient temperature), which makes it possible to establish the upper boundary of self-ignition and to investigate the transition to ignition. The paper gives results obtained for a cylindrical form of the system under the simplest thermokinetic conditions (constancy of the temperature on the surface of the system, zero-order reaction).

The initial differential equation in dimensionless variables has the form

$$\frac{\partial\theta}{\partial\tau} = e^{\theta/(1+\beta\theta)} + \frac{1}{\delta}\left(\frac{\partial^2\theta}{\partial\xi^2} + \frac{1}{\xi}\frac{\partial\theta}{\partial\xi}\right), \qquad 0 \leqslant \xi \leqslant 1, \quad 0 \leqslant \tau < \infty.$$

The initial and boundary conditions are specified:

$$\theta(\xi, 0) = -\theta_0; \qquad \theta(1, \tau) = 0; \qquad \left.\frac{\partial\theta}{\partial\xi}\right|_{0,\tau} = 0.$$

Here

Fig. 1. Nonstationary temperature profiles at $\theta_0 = 11.7$. The numbers indicate the corresponding values of τ. a—$\delta = 2.5$; b—$\delta = 12.0$; v—$\delta = 20.0$.

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$$\theta = \frac{E}{RT_0^2}(T - T_0); \quad \xi = \frac{x}{r}; \quad \tau = \frac{Q}{c\rho}\,\frac{E}{RT_0^2}\,k_0 e^{-E/RT_0} t; \quad \delta = \frac{Q}{\lambda}\,\frac{E}{RT_0^2} \times$$

$$\times r^2 k_0 e^{-E/RT_0}; \quad \beta = \frac{RT_0}{E}; \quad \theta_0 = \frac{E}{RT_0^2}(T_0 - T); \quad x\text{—radial coordinate}$$

(cm); t—time (sec.); $T(x,t)$—temperature (°K); T_0—ambient temperature (°K); T—initial temperature of the system (°K); r—radius of the cylinder (cm); E—activation energy (cal/mole); k_0—pre-exponential factor (1/sec.); Q—heat effect of the reaction (cal/cm^3); λ—thermal-conductivity coefficient (cal/cm·sec.·deg); c—heat capacity (cal/g · deg); ρ—density (g/cm^3).

The problem contains three dimensionless parameters: δ, θ_0, and β. The Frank-Kamenetskii criterion ([2]), δ, is the principal parameter in the theory of thermal explosion, determining the position of the self-ignition limit; θ_0 characterizes the thermal head of the surrounding medium and is specific to the given problem. As for the parameter β, as Frank-Kamenetskii showed, in processes of inflammation and combustion it should have a very weak influence on the behavior of the system.

Using an implicit difference scheme, the original differential equation was approximated by a system of finite-difference equations

$$\theta_{l+1}^{n+1} - B_l\theta_l^{n+1} + C_l\theta_{l-1}^{n+1} = -D_l^n \quad (l = 0, 1, \dots, N),$$

whose solution at each time step was obtained by the sweep method (3). Here

$$B_l = 1 + \frac{\delta\Delta\xi^2}{\Delta\tau} + C_l; \quad C_l = \frac{l-1}{l}\,\varepsilon(l); \quad D_l^n = \frac{\delta\Delta\xi^2}{\Delta\tau}\theta_l^n +$$

$$+\delta\Delta\xi^2 e^{\theta_l^n/(1+\beta\theta_l^n)}; \quad \Delta\xi \text{ is the space step;} \quad \Delta\tau \text{ is the time step;}$$

$$\theta_l^n = \theta(l\Delta\xi, n\Delta\tau), \quad \varepsilon(l) = 0 \text{ for } l = 0; \quad \varepsilon(l) = 1 \text{ for } l \neq 0.$$

Fig. 1. Nonstationary temperature profiles at $\theta_0 = 11.7$.
The numbers indicate the corresponding values of τ. a–$\delta = 2.5$;
b–$\delta = 12.0$; v–$\delta = 20.0$.

According to the indicated scheme, the temperature distribution as a function of time and of the system parameters $\theta = \theta(\xi, \tau, \delta, \theta_0)$ was calculated on an electronic computer. The value of the parameter β in all the main calculations was equal to 0.03. The remaining parameters were varied within the limits $0 < \delta < 1000$, $0 < \theta_0 < 16$.

Analysis of numerous curves of the nonstationary temperature distribution (some of them are shown in Fig. 1) makes it possible to establish the following picture of ignition. For values of δ close to δ_{cr}, heating of all points of the system to the ambient temperature occurs practically simultaneously, and the maximum temperature throughout the entire heating stage is located at the center (on the axis of the cylinder), where ignition also begins (Fig. 1a). As δ increases, the nonuniformity of heating of the system becomes more and more pronounced. Even before the moment when the center reaches the ambient temperature, a heating maximum arises near the surface; it then increases and moves toward the center, i.e., a heat wave of increasing amplitude moves from the surface toward the center. If δ is not very large, this wave reaches the center, and ignition occurs in the same way as in the case without a wave (Fig. 1b). At large values of δ, the wave does not have time to reach the center, and ignition begins at some distance from it, the greater the larger δ is (Fig. 1v). At very large values of δ, ignition occurs in the surface layers, while the temperature at the center practically does not change and remains equal to the initial temperature.

Of great interest in the picture described are the regularities governing the formation and displacement of the heating maxima. The formation of a maximum is caused by intense heat release in the hotter surface layers, while its displacement is associated with the "asymmetry of the maximum," i.e., with the inequality of the temperature gradients on the two sides of the maximum; moreover, the displacement occurs toward the smaller gradient. As the maxi-

"symmetrized," and its position is stabilized, i.e., the abscissa of the maximum tends to a definite value ξ_{ign} (Fig. 2).

The quantity ξ_{ign} is a convenient characteristic of the ignition process. Figure 3 shows the dependence of ξ_{ign} on δ, which clearly illustrates the regularities of the transition from self-ignition to ignition. For $\delta_{\text{cr}} < \delta < \delta'_{\text{cr}}$, $\xi_{\text{ign}} = 0$, and the self-ignition regime occurs. In the transition region, for $\delta > \delta'_{\text{cr}}$, ξ_{ign} rapidly increases with increasing δ, asymptotically approaching the curve $\xi_{\text{ign}} = 1 - \frac{\text{const}}{\sqrt{\delta}}$,* which describes the other limiting regime–ignition. According to Siger' s data ([4]), the value of const is ~ 1.3. Ignition does not have such sharp boundaries as self-ignition (the existence of δ_{cr} and δ'_{cr}). The values of the parameter δ at which ignition occurs are very large–of the order of hundreds.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

The critical values of δ for self-ignition are as follows: $\delta_{\text{cr}} = 2.07\,(^{5})$, $\delta'_{\text{cr}} = 12.0 \div 12.5$. These data indicate that self-ignition exists in a comparatively narrow region of parameters. A change in δ from δ_{cr} to δ'_{cr} corresponds to an increase in diameter by only a factor of 2.4, or to an increase in temperature by only several tens of degrees (approximately by $1.8\,RT_0^2/E$). It is interesting to note that the quantity δ'_{cr}, over a wide range of values, does not depend on θ_0 (within the indicated accuracy of determining δ'_{cr}). The dependence $\delta'_{\text{cr}}(\theta_0)$ appears only for $0 < \theta_0 < 1.8$ (as $\theta_0 \to 0$, $\delta'_{\text{cr}} \to \infty$). It is curious that this interval corresponds to the interval between $T'_{0\text{cr}}$ and $T_{0\text{cr}}$. Thus it follows that $T'_{0\text{cr}}$ depends on T_{h} (or δ'_{cr} on θ_0) only when $T_{\text{h}} > T_{0\text{cr}}$, i.e., in cases encountered rather rarely in ignition problems. The value δ_{cr} does not depend on θ_0.

Fig. 2. Curves of displacement of the heating maximum at $\theta_0 = 11.7$

Fig. 3. Dependence of ξ_{ign} on δ at $\theta_0 = 11.7$. The dashed line shows the limiting curve for ignition

An analysis of the time characteristics was carried out mainly for the self-ignition regime. The purpose of the analysis was to clarify the possibility of separating the total self-ignition delay time τ_{ign} into the heating time τ_{pr} and the induction period τ_{ind} ($\tau = \tau(\xi, \theta)$; $\tau_{\text{ign}} = \tau(0, \infty)$; $\tau_{\text{pr}} = \tau(0, 0)$; $\tau_{\text{ind}} = \tau_{\text{ign}} - \tau_{\text{pr}}$). Owing to the presence of temperature waves, the possibility of such a separation is not obvious.

Figure 4 presents the dependences of τ_{ign}, τ_{pr}, and τ_{ind} on δ at $\theta_0 = 11.7$. For comparison, the dependence $\tau_{\text{ind}}(\delta)$ at $\theta_0 = 0$ is given ($\tau_{\text{pr}} = 0$). The discrepancy between the induction periods is due to the nonuniformity of heating. The larger δ is, the greater the nonuniformity of heating, and the greater the discrepancy. However, throughout the entire region of self-ignition this

* This dependence was obtained from considerations of similarity theory.

the discrepancy is small. Even in the worst case (for $\delta = \delta'_{\text{cr}}$), it does not exceed 20%. This makes it possible, throughout the entire autoignition region, to separate τ_{ign} into τ_{pr} and τ_{ind} and to neglect (with satisfactory accuracy) the dependence of τ_{ind} on θ_0. It is interesting to note that the separation of τ_{ign} into τ_{pr} and τ_{ind} proved possible even when $\tau_{\text{pr}} > \tau_{\text{ind}}$, although from general considerations it had seemed that the necessary condition for such a separation is $\tau_{\text{pr}} \ll \tau_{\text{ign}}$.

The dependences $\tau_{\text{pr}}(\theta_0, \delta)$ and $\tau_{\text{ind}}(\delta)$ in the region $0 < \theta_0 < 16$, $0 < \delta < 12$

are approximated with good accuracy ($\sim 1\%$) by the formulas

$$\tau_{\text{pr}} = 0.48\,\theta_0^{0.22}\delta^{0.85-0.6/\theta_0},$$

$$\tau_{\text{ind}} = 1 + \frac{1}{(\delta-2)^{0.92}} \quad (\text{for } \theta_0 = 0).$$

Fig. 4. Time characteristics in the autoignition regime at $\theta_0 = 11.7$. Curve 1 –for $\theta_0 = 0$.

It was stated above that all calculations were carried out at $\beta = 0.03$, and that the ignition characteristics should depend only weakly on the value of β. The presence of a weak dependence on β is confirmed by the calculation whose results are given in Table 1.

Table 1

β	$\theta_0 = 0$: δ_{cr} according to (5)	$\theta_0 = 0$: τ_{ad}	$\theta_0 = 11.7$: τ_{ign} at $\delta = 6$	$\theta_0 = 11.7$: δ'_{cr}	$\theta_0 = 11.7$: τ_{ign} at $\delta = 16$	$\theta_0 = 11.7$: ξ_{ign} at $\delta = 16$
0.01	2.01	1.02	4.47	11.5–12.0	8.10	0.44
0.03	2.07	1.07	4.50	12.0–12.5	8.15	0.44
0.05	2.11	1.11	4.64	12.5–13.0	8.27	0.40

At present, calculations according to the scheme considered are being carried out for autocatalytic reactions, and the effect of external heat exchange on the regularities of the transition from autoignition to ignition is also being clarified.

Institute of Chemical Physics
Academy of Sciences of the USSR

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