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Abstract

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ON THE THEORY OF IGNITION

§ 1. Statement of the problem.

In a computational study of the course of an exothermic chemical reaction in a vessel with a constant wall temperature, A. G. Merzhanov and his coworkers ([1]) discovered the existence of different reaction regimes. For a given wall temperature T_c and a given initial temperature of the substance T_0 (with $T_0 < T_c$), the following occurs depending on the vessel radius r:

a) attainment of a steady regime, in which the temperature of the substance everywhere exceeds the wall temperature only slightly,—for $r < r_1$;

b) ignition of the substance as a whole, i.e., a nonstationary rapid rise of temperature, with the temperature becoming maximal in the volume of the vessel far from its walls,—for $r_1 < r < r_2$;

c) ignition of the substance by the vessel walls, i.e., again a nonstationary rapid rise of temperature, but the maximum temperature is reached near the vessel walls, and only afterward does a heat wave (flame propagation) bring a high temperature to the center of the vessel. Such a regime occurs for $r > r_2$.

The existence of two possibilities—a stationary reaction or a nonstationary temperature rise, i.e., a thermal explosion—has long been known. A qualitative consideration of thermal explosion using mean values of temperature and heat transfer was given in the classical work of N. N. Semenov ([2]); D. A. Frank-Kamenetskii solved exactly the problem of the critical condition for thermal explosion ([3]) and obtained an expression for r_1.

The finer distinction between the two nonstationary regimes—ignition and kindling—remained unnoticed until recently. The critical value r_2 for the transition from ignition to kindling in ([1]) is determined by numerical integration.

§ 2. Qualitative considerations.

In the present note an attempt is made to develop an approximate theory of kindling and, in particular, to give an expression for the critical value r_2. The basis is the author' s work ([4]), in which the stationary theory of ignition by a heated surface was considered. In that work it was shown that, for a given surface temperature T_c, a stationary state, i.e., absence of kindling, is possible only if the temperature gradient far from the surface provides sufficient heat removal. The critical heat removal corresponds to the release of chemical-reaction energy in the temperature field that is obtained when the temperature gradient at the surface is zero. Thus, in the critical regime the heat flux from the igniting surface itself turns to zero; all the removed heat is generated by the reaction.

Now, considering nonstationary kindling, in the first approximation we shall neglect the release of chemical energy and calculate the heating of the cold substance by the hot walls of the vessel. With time, the temperature gradient at the wall decreases. It is easy to find the time required for the temperature gradient to reach the critical value, below which the stationary theory has no solution and kindling occurs. This time will give the **induction period** of kindling.

However, in order for this calculation to make sense, it is necessary that during the indicated time the entire substance not be heated. We impose the condition that the temperature rise at a given wall, depending on the heat flux, be small.

of the heat flux coming from the opposite wall. This condition will give the critical value of the vessel size r_2, above which ignition takes place.

It should be especially emphasized that both the wall temperature and the initial temperature of the substance enter essentially into the ignition condition and into the expression for r_2. This is the difference between the ignition condition and the inflammation condition: in particular, the expression for r_1 depends only on T_c, but not on T_0 under the condition $T_0 < T_c$. In the particular case $T_0 = T_c$, ignition will not occur for any vessel size, since if at the instant $t = 0$ the temperature $T = T_0 = T_c$, then subsequently, for $t > 0$, one will have $T > T_c$; the vessel walls only cool the substance, and the temperature maximum is necessarily located at the center of the vessel.

§ 3. **Approximate calculation.** Let us first reproduce the stationary ignition condition. To find an expression for the critical gradient, we solve the equation

$$\varkappa \frac{d^2T}{dx^2} = -Ae^{-E/RT} \tag{1}$$

with the boundary condition

$$x = 0, \qquad T = T_c, \qquad \frac{dT}{dx} = 0. \tag{2}$$

We replace the Arrhenius expression for the rate of heat release approximately by the Frank-Kamenetskii exponential; we measure temperature from T_c, taking RT_c^2/E as the unit of temperature scale, so that the dimensionless temperature is

$$\theta = (T - T_c)\, E/RT_c^2. \tag{3}$$

We choose the dimensionless coordinate

$$\xi = x\sqrt{\frac{AEe^{-E/RT_c}}{\varkappa RT_c^2}}. \tag{4}$$

As a result, from (1) and (2) we obtain the equation and boundary conditions

$$\frac{d^2\theta}{d\xi^2} = -e^{\theta}, \qquad \xi = 0, \qquad \theta = 0, \qquad \frac{d\theta}{d\xi} = 0. \tag{5}$$

Integrating,

$$\frac{d\theta}{d\xi} = -\sqrt{2(1 - e^{\theta})}, \tag{6}$$

whence it is seen that, in the limit as $\xi \to \infty$, $\theta \to -\infty$ and

$$\lim_{\xi\to\infty} \frac{d\theta}{d\xi} = -\sqrt{2}. \tag{7}$$

We now construct the solution of the planar nonstationary heat-conduction problem without taking the chemical reaction into account. We solve the equation

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} \tag{8}$$

with the conditions

$$\xi = 0, \quad \theta = 0; \qquad \tau = 0, \quad \theta = \theta_0 < 0. \tag{9}$$

This form of the equation is obtained for θ and ξ specified by formulas (3) and (4), with

$$\theta_0 = (T_0 - T_c)\, E/RT_c^2, \qquad \tau = \frac{tAEe^{-E/RT_c}}{RT_c^2}. \tag{10}$$

As is known,

$$\theta(\xi, \tau) = \theta_0 \left[1 - \frac{1}{\sqrt{\pi\tau}} \int_{\xi}^{\infty} e^{-\eta^2/4\tau}\, d\eta\right], \tag{11}$$

whence

$$\left.\frac{\partial\theta}{\partial\xi}\right|_{\xi=0} = \frac{\theta_0}{\sqrt{\pi t}}. \tag{12}$$

The condition that the temperature gradient reach the critical value (7) gives the approximate value of the induction period of ignition

$$\tau_i = \theta_0^2/2\pi. \tag{13}$$

Let us consider a vessel with plane-parallel walls located at a distance ξ_2 (in units of (4)) from the plane of symmetry. Let us impose the condition that at the time τ_i the heating at one wall due to the heat flux from the other wall be small and equal to k units of temperature RT_c^2/E, where k is of order unity:

$$\frac{|\theta_0|}{\sqrt{\pi\tau_i}} \int_{2\xi_2}^{\infty} e^{-\eta^2/4\tau_i}\, d\eta = k. \tag{14}$$

Substitute τ_i from (13) and use the asymptotic expression

$$\int_a^{\infty} e^{-\zeta^2}\, d\zeta \simeq \frac{1}{2a} e^{-a^2}, \qquad a \gg 1. \tag{15}$$

We obtain for ξ_2 the transcendental equation

$$e^{-2\pi\xi_2^2/\theta_0^2} = k\pi\sqrt{2}\,\xi_2/\theta_0^2, \tag{16}$$

which we solve by successive approximations: the first approximation

$$\frac{2\pi\xi_2^2}{\theta_0^2} = 1, \qquad r_2 = \frac{|\theta_0|}{\sqrt{2\pi}}\sqrt{\frac{\varkappa RT_c^2}{AEe^{-E/RT_c}}}; \tag{17}$$

the second approximation

$$\frac{2\pi\xi_2^2}{\theta_0^2} = \ln\frac{|\theta_0|\sqrt{\pi}}{k}, \qquad r_2 = \frac{|\theta_0|}{\sqrt{2\pi}}\sqrt{\frac{\varkappa RT_c^2}{AEe^{-E/RT_c}}\ln\frac{|\theta_0|\sqrt{\pi}}{k}}. \tag{18}$$

Thus, r_2, as was assumed, depends on T_0. The quantity k cannot be specified within the framework of the approximation under consideration and may be different for vessels of different shapes (plane, cylindrical, spherical). The uncertainty of the quantity k is connected with the absence of a sharp transition from ignition in the volume to ignition near the wall. However, this quantity enters under the square-root sign from a logarithm, and therefore one may hope for a reasonable result by taking, for example, $k = 1/2$.

The entire calculation is meaningful, of course, for $|\theta_0| \gg 1$.

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