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Abstract

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A BOUNDARY-VALUE PROBLEM IN THE THEORY OF THERMAL EXPLOSION

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In studying the thermal explosion of substances in the condensed phase, we observed that constancy of temperature at the interface between the substance and the surrounding medium* can be maintained only under special experimental conditions. Under ordinary conditions, more complicated heat exchange occurs at the interface. This is possible because the heat capacity of a unit volume of a substance in the condensed phase is comparable with, or much greater than, the heat capacity of a unit volume of the surrounding medium. The heat released in the reaction heats the adjacent layers of the surrounding medium, and the temperature at the surface of the substance becomes different from the temperature of the medium at infinity.

In the present work we consider the critical conditions for thermal explosion under such, more complicated, heat exchange. In this case the boundary conditions have the form:

$$\lambda \left(\frac{\partial T}{\partial n} \right)_S = -\alpha (T_S - T_0),$$

where λ is the coefficient of thermal conductivity of the explosive substance, T_0 is the temperature of the surrounding medium far from the interface, α is the heat-transfer coefficient, and n is the normal to the interface S. The heat-transfer coefficient α depends on the nature of the contacting surfaces, the character of heat exchange with the surrounding medium, and the surface temperature (the latter dependence is usually neglected), and does not depend on the temperature distribution in the substance. The presence of a wall does not mathematically complicate the problem. In this case the total thermal resistance $1/\alpha$ will include the thermal resistance of the wall.

Todes and Kontorova ([2]) solved the problem of thermal explosion with analogous boundary conditions, but did not obtain a satisfactory solution. We shall solve the problem by the Frank-Kamenetskii method, using his transformation of the exponent in the Arrhenius law. In our case the stationary heat-conduction equation with boundary conditions has the form**:

$$\frac{d^2\theta}{d\xi^2} + \frac{m}{\xi}\frac{d\theta}{d\xi} = -\delta e^{\theta}, \tag{1}$$

$$\text{at } \xi = 1 \qquad \left(\frac{d\theta}{d\xi}\right)_S = -\mathrm{Bi}\,\theta_S. \tag{2}$$

For an infinite plane-parallel vessel $m = 0$, for an infinite cylinder $m = 1$, and for a spherical vessel $m = 2$.

Analysis of the equation and boundary conditions shows that the Frank-Kamenetskii criterion δ at the explosion limit is a function of the criterion

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* As Frank-Kamenetskii showed ([1]), in the case of a thermal explosion in the gas phase the temperature of the surrounding medium T_0 may be regarded as specified at the inner surface of the wall of the reaction vessel.

** In Frank-Kamenetskii' s notation.

$\mathrm{Bi} = \alpha r/\lambda$. As $\mathrm{Bi} \to \infty$, i.e., for such intense heat exchange between the surface of the substance and the surrounding medium that no heating of the surface relative to the medium is permitted, $\theta_s \to 0$, and the problem reduces to the Frank-Kamenetskii problem. By varying Bi from infinity to zero, we thereby cover all possible cases of heat exchange, beginning with ideal heat removal from the surface and ending with the absence of heat exchange (the adiabatic case).

Let us find the stationary temperature distributions and the critical conditions for the vessel shapes indicated above.

For an infinite cylindrical vessel the problem is solved analytically to the end. The general integral of equation (1) for $m = 1$ was found by Lemke ([3]) and has the form:

$$\theta = \ln\frac{8-b}{\delta} - 2\ln\left(a\xi^{k_1} + \frac{1}{a}\xi^{k_2}\right),$$

where a and b are integration constants, and k_1 and k_2 are the roots of the equation:

$$k^2 - 2k + \frac{b}{8} = 0.$$

From the condition $d\theta/d\xi = 0$ at $\xi = 0$ we have $b = 0,\ k_1 = 2,\ k_2 = 0$. The form of the solution is simplified:

$$\theta = \ln\frac{8}{\delta} - 2\ln\left(a\xi^2 + \frac{1}{a}\right). \tag{3}$$

The constant a is found from the transcendental equation

$$\mathrm{Bi}\left[\ln\frac{8}{\delta} - 2\ln\left(a + \frac{1}{a}\right)\right] = \frac{4a^2}{a^2+1}, \tag{4}$$

which is obtained using the boundary conditions (2). Below the explosion limit this equation gives two values $a(\delta, \mathrm{Bi})$, corresponding to two stationary temperature distributions—stable and unstable. At the explosion limit the two distributions merge, and a becomes a function of only one parameter,

$$a_{\mathrm{cr}} = \sqrt{\sqrt{\frac{4}{\mathrm{Bi}^2} + 1} - \frac{2}{\mathrm{Bi}}}. \tag{5}$$

The critical condition has the form:

$$\delta = \frac{8a_{\mathrm{cr}}^2}{(a_{\mathrm{cr}}^2+1)^2}\exp\left[-\frac{4a_{\mathrm{cr}}^2}{(a_{\mathrm{cr}}^2+1)\mathrm{Bi}}\right]. \tag{6}$$

It is easy to see that for $\mathrm{Bi} = \infty$, $a_{\mathrm{cr}} = 1$, $\delta = 2$, and the distribution at the explosion limit is as follows:

$$\theta = \ln\frac{4}{(\xi^2+1)^2}.$$

As is seen from expressions (3), (5), (6), the maximum heating at the explosion limit decreases with decreasing Bi, which indicates the regularity of the transformation of the exponent for any Bi.

Knowing (3) and (4), one can find, for any heat exchange, all quantities connected with the distribution (mean heating, heat flux, etc.).

For an infinite plane-parallel vessel the general integral of equation (1) was given by Frank-Kamenetskii. Using the boundary conditions, we calculated the critical dependence $\delta(\mathrm{Bi})$.

The general integral of equation (1) for a spherical vessel could not be found. It is possible that it does not exist at all. With the substitution

$$x = \xi^2 e^{\theta}, \qquad y = \xi\frac{d\theta}{d\xi},$$

equation (1) is reduced to the first-order equation

$$\frac{dy}{dx} = -\frac{y+\delta x}{(y+2)x},$$

which is easily integrated numerically. The critical relation $\delta(\mathrm{Bi})$ was found from the condition of tangency of the integral curve and the curve $y = -\mathrm{Bi}\ln x$, obtained from the boundary conditions.

It was observed that the curves of the dependence $\delta(\mathrm{Bi})$ at the explosion limit for the vessel shapes considered are transformed well into one another (to an accuracy of 1–2%) and can be expressed by the general formula

$$\delta = \delta_\infty \varphi(\mathrm{Bi}),$$

where δ_∞ is the critical value of the parameter δ at $\mathrm{Bi} = \infty$, and $\varphi(\mathrm{Bi})$ is a universal function, independent of the shape of the vessel, whose form is clear from (6).

It should be noted that the critical dependence $\delta(\mathrm{Bi})$ can be obtained approximately within the framework of the nonstationary theory by adding the effective heat-transfer coefficient, determined by the Frank-Kamenetskii method, to the heat-exchange coefficient α. The dependence obtained in this way has the form:

$$\frac{1}{\delta} = \frac{1}{\delta_\infty} + \frac{e\beta}{\mathrm{Bi}}$$

with $\beta = 1$ for a plane-parallel vessel, $\beta = 1/2$ for an infinite cylinder, and $\beta = 1/3$ for a sphere.

Comparison of this approximate formula with the exact solution obtained shows that the maximum discrepancy reaches 5% for a plane vessel, 9% for an infinite cylinder, and 16% in the case of a sphere.

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[3] N. Lemke, J. f. Math., **142**, 118 (1913).

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