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Abstract

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THERMAL EXPLOSION WITH HEAT REMOVAL BY CONVECTION AND CONDUCTION

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The condition for thermal self-ignition was first formulated by N. N. Semenov ([1]) for an exothermic reaction proceeding in a vessel inside which the temperature is equalized by convection, while heat transfer to the surrounding medium occurs purely by convection according to Newton' s law. In works by one of us ([2], [3]) it was shown that Semenov' s condition can be reduced to the form

$$t_p \leq e \frac{E}{RT_0} \frac{q}{cT_0} t_e, \tag{1}$$

where t_p is the time of complete combustion at constant rate and initial temperature, and t_e is the time of thermal relaxation, i.e., the cooling time of an initially heated and nonreacting system by a factor of $e = 2.7$. For the present case t_e is expressed through the heat-transfer coefficient α_k, the heat capacity per unit volume c, and the ratio of the heat-exchange surface to the volume S/V:

$$t_e = cV/\alpha_k S. \tag{2}$$

In an earlier work ([4]) an attempt was made to formulate the condition for thermal ignition as the loss of stability of the stationary temperature distribution during heat transfer within the reacting volume by pure heat conduction. The result was obtained in a very general, but not very transparent, form. Subsequently D. A. Frank-Kamenetskii ([5]), introducing certain simplifications, carried this problem through to completion for the cases of a vessel with plane-parallel walls, an infinite cylinder, and a sphere, on the outer surface of which a constant temperature T_0 is maintained.

In analyzing Frank-Kamenetskii' s results we established that, to within several percent, they can be reduced to the form (1), if t_e is understood as the time of thermal relaxation characterizing the regular cooling regime of the system. In particular, for a spherical vessel of radius L, with thermal conductivity of the reacting mixture k, we have

$$t_e = \frac{c}{k}\frac{L^2}{\pi}. \tag{3}$$

These conclusions were subsequently included in N. N. Semenov' s review article ([6]) on thermal explosion.

The calculations we have now carried out for the conditions of thermal self-ignition under the joint action of convection and conduction, as well as for more complex geometrical configurations, have shown that formula (1) gives a sufficiently good approximation in all cases. Here t_e should in each case be understood as the time of thermal relaxation characterizing the regular cooling regime of the given particular system. Subsequent mathematical analysis made it possible to confirm, in general form, the applicability of formula (1) as a first approximation. We present this derivation here.

To begin with, let us consider a one-dimensional problem. The nonstationary heating of the system is described by the equation

$$c\,\partial T/\partial t = k\,\partial^2 T/\partial x^2 + qw(T), \tag{4}$$

where q is the heat effect per unit volume, $w(T)$ is the reaction rate

$$w(T) = 1/t_p(T) = A\exp\{-E/RT\}, \tag{5}$$

with boundary conditions at both boundaries, for $x = \pm L$,

$$\mp k\,\partial T/\partial x = \alpha(T - T_0). \tag{6}$$

For the usually large values of the activation energy E, the pre-explosion heating is small, and dependence (5) can be linearized near any intermediate temperature $T_i > T_0$. Then

$$w(T) \simeq w(T_i) + w'(T_i)[T - T_i] = w(T_i)\frac{E}{RT_i^2}\left[T - T_i + \frac{RT_i^2}{E}\right]. \tag{7}$$

We choose this temperature T_i so that equation (4) with boundary conditions (6) becomes homogeneous. For this one must set

$$T_i - RT_i^2/E = T_0. \tag{8}$$

In the first approximation it follows from this that

$$T_i \simeq T_0 + \frac{RT_0^2}{E}, \qquad \frac{E}{RT_i^2} w(T_i) \simeq \frac{E}{RT_0^2} e w(T_0), \tag{9}$$

which corresponds to the Frank-Kamenetskii approximation for $w(T)$. Then equation (4) takes the form

$$\frac{\partial T}{\partial t} = \frac{k}{c}\frac{\partial^2 T}{\partial x^2} + e\,\frac{q}{cT_0}\,\frac{E}{RT_0}\,\frac{T - T_0}{t_p}. \tag{10}$$

We seek a particular solution of equation (10) by the method of separation of variables, setting

$$T - T_0 = e^{-\lambda t} f(x). \tag{11}$$

Substituting (11) into (10), introducing the thermal diffusivity of the substance $a = k/c$ and, for brevity of notation, the dimensionless parameter

$$\sigma = e\,\frac{q}{cT_0}\,\frac{E}{RT_0}, \tag{12}$$

which usually has a numerical value of the order of 100, we obtain

$$a d^2 f/dx^2 + [\lambda + \sigma/t_p] f = 0. \tag{13}$$

Taking into account the symmetry of the boundary conditions,

$$f(x) = C \cdot \cos\left(\sqrt{\frac{\lambda + \sigma/t_p}{a}}\, x\right). \tag{14}$$

Substituting (11) and (14) into boundary condition (5), we obtain a transcendental equation for determining λ:

$$\sqrt{\frac{\lambda + \sigma/t_p}{a}}\, L^2 \ \mathrm{tg} \sqrt{\frac{\lambda + \sigma/t_p}{a}}\, L^2 = \frac{\alpha L}{k}. \tag{15}$$

The quantity $\alpha L/k = \mathrm{Bi}$ is the so-called Biot criterion, and equation (15) has an infinite number of increasing positive roots

$$(\lambda_i + \sigma/t_p) L^2/a = \mu_i, \qquad \mu_1 < \mu_2 < \cdots, \tag{16}$$

whose values depend on Bi. Hence

$$\lambda_i = \mu_i a/L^2 - \sigma/t_p. \tag{17}$$

In the absence of heat release ($q = 0$), $\sigma = 0$, and the cooling of the initially heated system is expressed by the formula

$$T - T_0 = \sum_{i=1}^{\infty} C_i \exp\left\{-\frac{\mu_i a}{L^2} t\right\} \cos\left(\sqrt{\mu_i}\,\frac{x}{L}\right), \tag{18}$$

where the coefficients C_i are determined from the expansion of the initial temperature distribution in a cosine series. Owing to the rapid decay

of the exponential factors, after a short time it is necessary to take into account only the first term of series (18), and the cooling of the system proceeds according to the law of the regular regime

$$T - T_0 \simeq C_1 \cos\left(\sqrt{\mu_1}\,x/L\right) \exp\{-\mu_1 a t/L^2\}. \tag{19}$$

Over the time interval

$$t_e = L^2/a\mu_1 \tag{20}$$

the heating at all points of the system decreases by $e = 2.7$ times. This is the time of thermal relaxation of the system.

Returning to the linearized equation of nonstationary thermal explosion (10), we see that its general solution can also be represented in the form of a series

$$T - T_0 = \sum_{i=1}^{\infty} P_i \exp\{-\lambda_i t\} \cos\left(\sqrt{\mu_i}\,x/L\right). \tag{21}$$

If all λ_i are positive, then any initial heating dissipates and $T(x,t) \to T_0$. This is due to the approximation (8) made, corresponding to neglect of heat release from the reaction at $T = T_0$.

If, however, the first of the roots changes sign, i.e. $\lambda_1 = 0$, then any initial heating will grow without bound and a thermal explosion will occur ($e^{-\lambda_1 t} = e^{+|\lambda_1| t} \to \infty$ as $t \to \infty$).

Using (17) and (20), we can rewrite the condition of self-ignition in the form

$$\lambda_1 = \mu_1 a/L^2 - \sigma/t_p = 1/t_e - \sigma/t_p \leqslant 0 \quad \text{or} \quad t_p \leqslant \sigma t_e, \tag{22}$$

which coincides with condition (1).

The value μ_1 is the first root of the transcendental equation

$$\sqrt{\mu_1}\ \mathrm{tg}\sqrt{\mu_1} = \mathrm{Bi}. \tag{23}$$

If Bi $\ll 1$ (poor heat transfer at the surface or high thermal conductivity inside the system), then the temperature gradients in the system will be small and the temperature distribution is close to the case considered by Semenov. Replacing approximately $\mathrm{tg}\,\beta \simeq \beta$, we have $\mu_1 \simeq \mathrm{Bi} = \alpha L/k$ and

$$t_e = \frac{L^2}{a}\,\frac{k}{\alpha L} = \frac{cL}{\alpha} = \frac{c}{\alpha}\,\frac{V}{S} = t_{e,\mathrm{conv}}, \tag{24}$$

in accordance with expression (2).

In the second limiting case Bi $\gg 1$ (very intensive heat transfer or poor thermal conductivity), the temperature at the surface is established practically equal to T_0. In this case, since Bi $\to \infty$, then also $\mathrm{tg}\sqrt{\mu_1} \to \infty$, i.e. $\mu_1 \to \pi^2/4$. This gives

$$t_e = \frac{4}{\pi^2}\,\frac{L^2}{a} = t_{e,\mathrm{cond}}, \tag{24'}$$

which, after substitution into (22), gives the critical condition of self-ignition, differing from the exact solution of Frank-Kamenetskii by 2.4%.

In intermediate cases of neither very small nor very large values of the Biot criterion, one can solve the transcendental equation (23) numerically or use the approximate interpolation dependence

$$\mu_1 \simeq \pi^2\mathrm{Bi}/(\pi^2 + 4\mathrm{Bi}). \tag{25}$$

The example considered admits an exact solution by the methods of the stationary theory of thermal explosion. Solving, in the Frank-Kamenetskii approximation, the stationary problem

$$k\,\frac{d^2T}{dx^2} + qw(T_0)\exp\left\{\frac{E}{RT_0^2}(T - T_0)\right\} = 0 \tag{26}$$

with allowance for boundary conditions (6), more general than those of Frank-Kamenetskii, we determined the critical conditions for different values of Bi. The maximum deviation from equation (22) did not exceed $\sim 3\%$.

The characteristic features revealed in the consideration of the one-dimensional problem can readily be extended to the general case of a reacting body of arbitrary shape (solid or with internal cavities), placed in a medium of given temperature T_0. The equation of nonstationary thermal explosion

$$c\,\partial T/\partial t = k^2\nabla^2 T + q\omega(T) \tag{27}$$

with boundary conditions

$$-k\,\partial T/\partial n = \alpha(T - T_0) \tag{28}$$

can be approximately reduced to the homogeneous equation

$$\frac{\partial T}{\partial t} = a\nabla^2 T + \frac{\sigma}{t_p}(T - T_0). \tag{29}$$

Solving it by the same method of separation of variables, one can show that the critical condition for self-ignition has the form

$$t_p \leqslant e\,\frac{q}{cT_0}\,\frac{E}{RT_0}\,t_e, \tag{30}$$

where t_e is the time of thermal relaxation of the system in the absence of combustion, determined from the equation

$$a\nabla^2 f + \frac{1}{t_e} f = 0 \tag{31}$$

with the boundary condition

$$-k\,df/dn = \alpha f \tag{32}$$

and characterizing the regular cooling regime

$$T - T_0 = C_1 f_1(x, y, z)\exp\{-t/t_e\}. \tag{33}$$

In this way we were able to verify, on a number of examples (cylinder, sphere, hollow cylinder) admitting an exact solution, that the solution of the approximate equation (29), i.e., the basic formula (30), as a rule differs from the exact one by no more than 2-3%.

The conclusion obtained in (30) makes it possible to greatly simplify the problem of finding the critical conditions of thermal self-ignition for bodies of arbitrary shape under mixed cooling conditions—conduction and convection. When using computers, instead of the exact nonlinear equation it is sufficient to solve the approximate linear homogeneous equation for the regular cooling regime (31) with boundary conditions (32). In addition, in many cases the quantity t_e is easier to determine experimentally on a model made of a nonreacting substance with similar geometrical and thermal parameters.

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