ON THE STABILITY OF THE SOLUTIONS IN THE STEADY THEORY OF A THERMAL EXPLOSION

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The theory of a thermal explosion in a vessel with exothermic chemical reactions has been developed in [1-3]. For the description of the thermal explosion Semenov [1] employed the values of the temperature and heat output averaged over the vessel. He established that for dimensions of the vessel less than a certain critical dimension, two regimes are possible for the course of the chemical reactions. For the critical dimension of the vessel these solutions degenerate into one, whilst for dimensions greater than critical a steady solution does not exist – a thermal explosion occurs.

The qualitative study of the two regimes of the chemical reaction for vessels of small dimensions, carried out by Semenov, showed that the only one of them which is stable is that which corresponds to the lower temperature of the reacting mixture in the vessel.

Frank-Kamenetskii [2,3] in the steady theory of the thermal explosion solved exactly the problem of the distribution of temperature in the vessel and the critical condition for a thermal explosion. (A very full account of the steady theory of the thermal explosion, from the standpoint of mathematical treatment, is given by Barenblatt in [4].) In this theory, just as in Semenov's theory, with dimensions of the vessel less than critical, several different steady distributions of temperature are possible: for plane and cylindrical vessels there are two solutions, for spherical vessels the number of solutions can vary from one to infinity depending on the dimension of the vessel.

The stability of the solutions of the steady theory of the thermal explosion has not been investigated. By analogy with Semenov's results

[1], the proposition was put forward in [2] that in the case of plane and cylindrical vessels the distribution of temperature corresponding to the lower temperature at the centre of the vessel is stable, whilst the higher is unstable. Indications on the stability of the solutions in this case are also contained in [4]. However, carrying through the analogy for the spherical vessel with a large family of solutions presents significant difficulties, and therefore no conclusions at all concerning the stability of the solutions in the spherical vessel have been drawn.

Below we carry out an investigation of the stability of the solutions of the steady theory of the thermal explosion for vessels of various shapes. We apply a method, similar in certain respects to the method applied by Barenblatt and Zel'dovich for the explanation of the stability of propagation of a laminar flame [5,6]. It will be shown that, of all possible regimes of the chemical reaction, the only regime which is stable is that with the lowest temperature at the centre of the vessel.

1. Fundamental propositions of the steady theory of the thermal explosion. Let us reproduce briefly from first principles the fundamental propositions of the steady theory of the thermal explosion.

With the usual assumptions of this theory [2,3] in the case of symmetric vessels the problem reduces to the solution of the steady equation of heat conduction with a heat production function

$$\frac{1}{\xi^\nu}\frac{d}{d\xi}\left(\xi^\nu\frac{dU}{d\xi}\right)+2e^U=0$$
$$\left(U=\frac{(T-T_0)E}{RT_0^2}, \quad \xi=\left[\frac{QZE}{2kRT_0^2}\exp\left(-\frac{E}{RT_0}\right)\right]^{1/2}x\right) \qquad (1.1)$$

Here U is the dimensionless temperature, T is the temperature in the vessel, T_0 is the temperature of the walls, E is the energy of activation, R is a universal constant, ξ is the dimensionless coordinate (measured from the centre of the vessel), Q is the heat effect of the reaction, Z is a multiplying factor, k is the thermal conductivity of the reacting mixture and the index $\nu = 0, 1, 2$, for plane, cylindrical and spherical vessels, respectively. The boundary conditions (ξ_0 is the dimensionless radius of the vessel) are

$$\xi=0, \quad dU/d\xi=0, \qquad \xi=\xi_0, \quad U=0 \qquad (1.2)$$

As was first shown in [7], equation (1.1) with the first of the boundary conditions (1.2) is invariant with respect to the group of transformations

$$U(\xi)=\alpha+U_0(\xi e^{\alpha/2}) \qquad (1.3)$$

Here $U(\xi)$ is the general solution of equation (1.1), whilst $U_0(\xi)$ is the particular solution satisfying the conditions

$$\xi = 0, \qquad U_0 = 0, \qquad dU_0/d\xi = 0 \qquad (1.4)$$

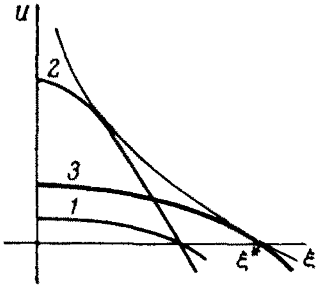

Fig. 1.

The parameter α is the value of the temperature at the centre of the vessel.

Making use of the general form of the solution (1.3), we can find the envelope of the solutions. The equation of the envelope in the general case has the form

$$U = 2\ln\frac{s^*}{\xi} + U_0(s^*) \qquad (1.5)$$

Here s^* is the root of the equation

$$2 + s^*\frac{dU_0(s^*)}{ds} = 0 \qquad (1.6)$$

The envelope (1.5) in the $u\xi$-plane ($U > 0$, $\xi > 0$) divides the region where there are solutions of the equation (1.1), from the region where solutions do not exist. The intersection of the envelope with the axis of ξ cuts off a segment ξ^* corresponding to the maximum dimension of the vessel for which a steady distribution of temperature is still possible

$$\xi^* = s^*\exp\frac{U_0(s^*)}{2} \qquad (1.7)$$

For larger dimensions of the vessel solutions do not exist: an explosion occurs.

The particular solution $U_0(\xi)$ can be obtained in closed form [4]:

for a plane vessel ($\nu = 0$)

$$U_0(\xi) = -2\ln\cosh\xi \qquad (1.8)$$

for a cylindrical vessel ($\nu = 1$)

$$U_0(\xi) = -2\left[\ln\xi + \ln\cosh\ln\frac{2}{\xi}\right] \qquad (1.9)$$

Equations (1.6) and (1.7), determining s^* and the maximum dimension of the vessel ξ^*, for these cases take the forms

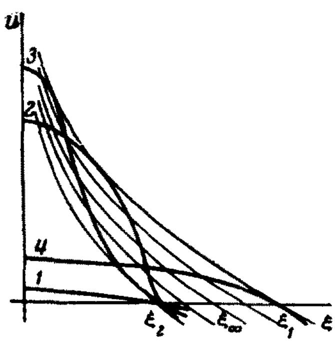

Fig. 2.

$$(\nu = 0) \quad 1 = s^*\tanh s^*, \quad \xi^* = s^*/\cosh s^* \qquad (1.10)$$

$$(\nu = 1) \qquad s^* = 2, \qquad \xi^* = 1 \qquad (1.11)$$

In Fig. 1 we depict the forms of the envelope and the curves of temperature distribution for plane and cylindrical vessels. For dimensions of the vessel $\xi < \xi^*$ there are two possible solutions with different values of the quantity α (curves *1* and *2*). The values of α are determined in the general case (ν is arbitrary) by solution of the equation

$$\alpha + U_0(s) = 0, \qquad s = \xi e^{\alpha/2} \tag{1.12}$$

When $\xi = \xi^*$ both solutions degenerate into one (curve *3*), and for this solution

$$\alpha^* = -U_0(s^*), \qquad s^* = \xi^* e^{\alpha/2} \tag{1.13}$$

From the form of the solutions (1.8) and (1.9) and the expression (1.12) for α it is easy to see that $\alpha < \alpha^*$ when $s < s^*$, and $\alpha > \alpha^*$ when $s > s^*$.

For the spherical vessel ($\nu = 2$) we have not succeeded in integrating equation (1.1). However, study of the behavior of the solution [4] shows that in this case equation (1.6) has a non-denumerable family of roots s_i^* and consequently in the $U\xi$-plane there is a non-denumerable family of envelopes. In Fig. 2 is shown the distribution of some of these envelopes (all the envelopes are distributed between the points ξ_1 and ξ_2, being dense in the neighborhood of the point $\xi_\infty = 1$), and some temperature distributions have also been drawn. All the solutions as ξ grows at first touch the extreme right-hand envelope, and subsequently the extreme left-hand envelope, then the second from the right, and then the second from the left, and so on. In the same order we shall denote the points of intersection of the corresponding envelopes with the axis of ξ as the points ξ_1, ξ_2, ξ_3, ξ_4, etc. The critical dimension of the vessel is determined by $\xi^* = \xi_1$. Through the point ξ_1 and in the region $0 < \xi < \xi_2$, through each point there passes one solution. When $\xi_2 \leqslant \xi < \xi_1$ several solutions are possible. Thus, with $\xi_3 \leqslant \xi < \xi_1$ there are two of them; with $\xi_2 \leqslant \xi < \xi_4$ there are three; when $\xi_5 \leqslant \xi < \xi_3$ there are four, and so on. Close to $\xi_\infty = 1$ the solutions become infinitely numerous. The curves touching the envelopes at the points ξ_1, ξ_2, ξ_3, ..., are characterized by the parameters α_i^*, determined according to (1.13) for different roots s_i^*.

2. Formulation of the problem of stability Study of the stability of the different solutions in the steady theory of the thermal explosion is carried out by the method of small perturbations. We consider the non-steady equation of heat conduction

$$\frac{\partial u}{\partial \tau} = \frac{1}{\xi^\nu}\frac{\partial}{\partial \xi}\xi^\nu\frac{\partial u}{\partial \xi} + 2e^u \qquad \left(\tau = \frac{\varkappa QZEt}{2RT_0^2k}\exp\left(-\frac{E}{RT_0}\right)\right) \tag{2.1}$$

Here $u(\xi, \tau)$ is the dimensionless temperature, depending upon the time, τ is the dimensionless time, t is the time and κ is the thermal conductivity of the reacting mixture.

It will be assumed that the unsteady solution varies only slightly from the steady solution (produced by a small perturbation of the steady solution)

$$u(\xi, \tau) = U(\xi) + \varphi(\xi, \tau) \qquad (2.2)$$

where $\varphi(\xi, \tau)$ is a small increment, and $U(\xi)$ has the form (1.3).

Making use of the smallness of $\varphi(\xi, \tau)$, let us linearize equation (2.1)

$$\frac{1}{e^{\alpha}} \frac{\partial\varphi}{\partial\tau} = \frac{1}{s^{\nu}} \frac{\partial}{\partial s} s^{\nu} \frac{\partial\varphi}{\partial s} + 2e^{U_0(s)}\varphi \qquad (s = \xi e^{1/2\,\alpha}). \qquad (2.3)$$

Here we have made use of expression (1.3) for $U(\xi)$.

The boundary conditions for the solution of the equation (2.3) are

$$s = s_0 = e^{\alpha/2}\xi_0, \qquad \varphi = 0; \qquad\qquad s = 0, \qquad \frac{\partial\varphi}{\partial s} = 0 \qquad (2.4)$$

(the perturbation is assumed symmetric). The solution of (2.3) is sought in the form

$$\varphi(s, \tau) = T(\tau) P(s) \qquad (2.5)$$

The temporal dependence of the solution is determined by the factors

$$T_n(\tau) = e^{-\lambda_n e^{\alpha}\tau} \qquad (2.6)$$

Here λ_n are the eigenvalues of the Sturm-Liouville problem

$$\frac{1}{s^{\nu}} \frac{d}{ds} s^{\nu} \frac{dP}{ds} + (2e^{U_0(s)} + \lambda) P = 0 \qquad (2.7)$$

with the conditions

$$s = 0, \qquad \frac{dP}{ds} = 0; \qquad\qquad s = s_0, \qquad P = 0 \qquad (2.8)$$

If in the spectrum of eigenvalues of the problem all the $\lambda_n > 0$, then the solution under study is stable, whilst, if there is at least one $\lambda_n < 0$, the solution is unstable. The direct determination of the whole spectrum of eigenvalues $\lambda_n (n = 0, 1, 2, \ldots)$ presents significant difficulties. However, there is no need for this. To answer the question of the stability we need only know the sign of the zero-th eigenvalue λ_0, since from the theory of Sturm-Liouville boundary problems [8] it is known that with increasing number the magnitude of the eigenvalue increases.

For study of the stability of the solution we can also employ the method applied by Barenblatt and Zel'dovich to the problem of stability of propagation of a one-dimensional laminar flame [5,6]. This method is based on the property of eigenfunctions, that the number of zeros of an eigenfunction is equal to the number of its eigenvalue. For laminar flames it turns out that the eigenfunction corresponding to the eigenvalue $\lambda_n = 0$ has no zero anywhere, apart from infinity, and therefore the eigenvalue $\lambda_n = 0$ is the zero-th eigenvalue. Since all the other eigenvalues are positive, the propagation of the flame is stable.

For study of the stability of the solutions of the steady theory of the thermal explosion we shall seek the general solution of equation (2.7) corresponding to $\lambda = 0$. The solution of the equation will satisfy the boundary conditions (2.8), i.e. they are eigenfunctions for the eigenvalue $\lambda_n = 0$ only for certain discrete values $s_{0i} = s_i^*$. The boundary of stability of the solution of the problem with regard to s_0 is given by the smallest value $s_{0i} = s_i^*$. In fact, in the interval $0 \leqslant s \leqslant s_1^*$ the function does not vanish anywhere, i.e. it is the zero-th eigenfunction. With decrease of the segment $[0, s_0]$, according to the property of eigenfunctions [8] the zero-th eigenvalue λ_0 does not diminish, and consequently the stability of the solution is guaranteed. With increase of $[0, s_0]$ the eigenvalue λ_0 decreases: if λ_0 increased with increasing s_0, then this would contradict the stated property of eigenvalues; also λ_0 cannot equal zero, since all the eigenfunctions for $\lambda_n = 0$ are contained in the general solution of equation (2.7), whilst all successive points, at which the general solution is an eigenfunction, correspond to the non-zero-th eigenvalues ($n \neq 0$) – the eigenfunctions, apart from the end of the segment, vanish in the segment itself.

Accordingly, the investigation of stability amounts to finding the general solution of equation (2.7) with $\lambda = 0$ and determining the minimum segment s_1^*, on which the boundary conditions (2.8) are fulfilled.

3. Stability of the temperature distributions in a plane reaction vessel. In the plane case the problem reduces to the solution of an equation of the following form (λ has here already been set equal to zero)

$$\frac{d^2P}{ds^2} + \frac{2}{\cosh^2 s} P = 0 \tag{3.1}$$

with the boundary conditions (2.8). This equation reduces to

$$\frac{d}{dy}\left[2(1-e^y)\frac{dP}{dy}+e^yP\right]=0 \qquad \left(e^y=\frac{1}{\cosh^2 s}\right) \tag{3.2}$$

with the new variable y, related to s by the relation given in brackets.

Integration of (3.2) gives

$$P = C_1 \tanh s + C_2(1 - s\tanh s) \qquad (C_1, C_2 = \text{const}) \tag{3.3}$$

The first of the conditions (2.8) determines $C_1 = 0$. Accordingly, the function P is an eigenfunction for the segment s^*, for which

$$1 - s^* \tanh s^* = 0 \tag{3.4}$$

This expression completely coincides with equation (1.10), determining the envelope of the solutions (1.5).

As already mentioned in Section 1, $\alpha < \alpha^*$ when $s < s^*$ and consequently solutions with small α are stable solutions. (We notice that α is the temperature at the centre of the vessel.) Unstable solutions with $s > s^*$ correspond to distributions with $\alpha > \alpha^*$ – high temperature at the centre of the vessel.

4. Proof of stability in the general case. The results obtained in Section 3, indicating that the general solution of the equation of the boundary problem (3.1) is the expression serving to determine the root s^* appearing in the equation of the envelope, suggests that this property is true also in the general case (for arbitrary ν).

This fact is actually not fortuitous, as was shown by Zel'dovich. Since the envelope can be considered as the geometrical locus of the points of intersection of two infinitely close steady solutions, the difference of these solutions is a stationary perturbation, i.e. a perturbation with $\lambda = 0$.

Let us convince ourselves that the equation (2.7) with $\lambda = 0$ is satisfied by the function

$$P = C\left(s\frac{dU_0(s)}{ds}+2\right), \qquad \frac{dU_0(s)}{ds} = -\frac{2}{s^\nu}\int_0^s \zeta^\nu e^{U_0(\zeta)}\,d\zeta, \qquad C = \text{const} \tag{4.1}$$

The expression for dU_0/ds is obtained by direct integration of equation (1.1) with the condition $dU_0/ds = 0$ for $s = 0$.

Remembering that $dP/ds = 0$ when $s = 0$, let us rewrite equation (2.7) as

$$\frac{dP}{ds} = -\frac{2}{s^\nu}\int_0^s \zeta^\nu e^{U_0(\zeta)} P(\zeta)\, d\zeta \qquad (4.2)$$

Calculating the derivative dP/ds on the left-hand side and the integral on the right-hand side of equation (4.2) and using (4.1), we find that equation (4.2) is satisfied.

Accordingly, the function (4.1) is an eigenfunction of the boundary value problem for those values of s_i^* which are roots determining the envelopes of the solutions. As has already been said, the stable solutions correspond to solutions with s_0 less than the minimum root of equation (1.6). But corresponding to the minimal value s_1^* there is the minimal value α_1^*, since s is a monotonically increasing function of α. In fact, let us differentiate the relation (1.12)

$$\frac{ds}{d\alpha} = -\frac{1}{dU_0/ds} = s^\nu\left(\int_0^s \zeta^\nu e^{U_0(\zeta)} d\zeta\right)^{-1} > 0 \qquad (4.3)$$

The critical value α_1^* is calculated according to the formula

$$\alpha_1^* = -U_0(s_1^*) \qquad (4.4)$$

Let us illustrate what has been said, using the example of a spherical vessel. The temperature distributions and the envelopes of the solutions are depicted in Fig. 2. Curve *4*, starting at the point of intersection of the extreme right-hand envelope with the axis of ξ has $\alpha = \alpha_1^*$. All the curves *1* relate to curves with $\alpha < \alpha_1^*$ and are therefore stable. Curves *2* and *3* with $\alpha > \alpha_1^*$ are unstable.

It is interesting that the qualitative character of the stability of the solutions can be assessed from the following arguments: if we perturb curve *1*, then everywhere we move into a region where there are steady solutions. But if we perturb curves *2* and *3* close to their points of tangency with the extreme right-hand envelope, then we may find ourselves in a region where steady solutions do not exist, and suspicion arises as to the instability of the solution.

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