ON THE THEORY OF STATIONARY VELOCITY OF PROPAGATION OF AN EXOTHERMIC REACTION FRONT IN A CONDENSED MEDIUM

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It has been demonstrated experimentally that in the combustion of many explosives and powders in the condensed phase (k-phase) an exothermic chemical reaction occurs. Although the heat release in the k-phase is usually small in comparison with the calorific value, it may play an important role in the multistage reaction in the combustion zone.

Analysis of the heat balance of the k-phase reveals that in a number of cases heating of the substance before gasification is primarily due to self-heating. According to the thermocouple measurements made by A. A. Zenin,[1] the heat release in the k-phase during combustion of nitroglycerine N powder is more than 80% of the total quantity of heat in the heated layer of the k-phase (pressure ~ 50 atm). This makes it possible to speak of the propagation of the exothermic reaction front in a condensed medium as the first stage in the combustion of condensed systems. Cases are also known where the propagation of the reaction front is maintained only by self-heating (flameless combustion [1]), and there are cases when such propagation is not accompanied by gasification (combustion of thermites, sometimes the polymerization process). Theoretical investigations of stationary propagation of a reaction front in a condensed medium were made in [2–6]. We note that this problem is also of interest in relation to the study of various nonstationary phenomena associated with the combustion of powders [7–9]. One of the principal theoretical problems is the derivation of a formula for the velocity of propagation of the reaction front in the k-phase. The Zel'dovich–Frank-Kamenetskii method [10] was used in [2–5] in the solution of this problem.

This paper is an investigation of the applicability of the Zel'dovich–Frank-Kamenetskii method to the case of propagation of a zero-order reaction front in the k phase. A method is proposed for deriving a formula for the propagation velocity of the front leading in the case of a zero-order reaction to a formula identical to that obtained using the Zel'dovich–Frank-Kamenetskii method, and this method is then used to derive a formula for the propagation velocity of a first-order reaction front in the k-phase. The upper and lower limits of the velocity given by this formula are investigated.

The propagation of a reaction front in a condensed medium differs from the propagation of a flame front in a homogeneous gas mixture. In a condensed medium the diffusion of reagents may be neglected and the diffusion coefficient D may be considered equal to zero. As a result of gasification, the chemical reaction in the k-phase cannot go to completion, and therefore the quantity Q of heat released prior to gasification may be not equal to the thermal effect h of the reaction in the k-phase.

In the case of multistage combustion at the gasification surface, there is a finite heat flux q_s. Finally, in the case of a first-order reaction in the k-phase the equation describing the thermal processes has a form appreciably different from that of the equation describing the thermal processes during the combustion of gases. This difference can be attributed to the fact that the condition D = 0 in the k-phase, in contrast to the condition of equality of heat conductivity and diffusion coefficient in a gas, obviously cannot lead to similarity of the concentration and temperature fields.

First, we will consider the propagation of a zero-order reaction front.

The heat conduction equation and the boundary conditions have the form

$$\lambda \frac{d^2T}{dx^2} - mc\frac{dT}{dx} + h\Phi(T) = 0 \qquad (-\infty \leqslant x \leqslant 0), \tag{1}$$

$$T(-\infty) = T_0, \qquad T(0) = T_s, \qquad \lambda \frac{dT}{dx}\Big|_{x=0} = q_s. \tag{2}$$

Here T is temperature, λ the heat conductivity, c the specific heat, m the mass velocity of the reaction front, h the thermal effect of the reaction in the k-phase, and Φ (T) the dependence of the rate of the chemical reaction on temperature. We assume that the reaction in the k-phase proceeds at a considerable rate at temperatures close to the temperature T_s at the gasification surface. This corresponds to the assumption of high activation energy for an Arrhenius relation Φ (T).

Equation (1) formally coincides with the equation describing the thermal processes during combustion of a homogeneous gas mixture [10].

We will now obtain an approximate expression for the mass velocity m of the front by the Zel'dovich-Frank-Kamenetskii method. Dividing the region of temperature change into two subregions $T_0 \le T \le T_\varepsilon$ and $T_\varepsilon \le T \le T_s$ in such a way that heat release can be neglected in the first subregion, and convective heat transfer can be neglected in the second, and integrating the equations in each zone, we can derive expressions for the heat flux on the boundary of the subregions.

In the first subregion

$$\lambda \frac{dT}{dx}\Big|_{T_\varepsilon - 0} = mc(T_\varepsilon - T_0)\ . \tag{3}$$

In the second subregion

$$\lambda \frac{dT}{dx}\Big|_{T_\varepsilon + 0} = [q_s^2 + \Theta(s, \varepsilon)]^{1/2}, \qquad \Theta(s, \varepsilon) = 2\lambda h \int_{T_\varepsilon}^{T_s} \Phi(T)\, dT. \tag{4}$$

From (3), (4) we find

$$m = \frac{[q_s^2 + \Theta(s, \varepsilon)]^{1/2}}{c(T_\varepsilon - T_0)}\ . \tag{5}$$

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[1] A. A. Zenin, Candidate's Dissertation, Institute of Chemical Physics, Moscow, 1962.

Making the assumption that the temperature interval in which heat release occurs is narrow, we exclude from (5) the indefinite quantity T_ε and obtain a formula for the mass velocity of the front of a zero-order exothermic reaction in the k-phase (the velocity of the gasification front)

$$m = \frac{[q_s^2 + \Theta(s, 0)]^{1/2}}{c(T_s - T_0)}. \qquad (6)$$

Under conditions of flameless combustion it is necessary to assume in formula (6) that $q_S = 0$, $c(T_S - T_0) = Q$. We will show that (6) can be derived by a somewhat different method. As before, we divide the region of temperature change into two subregions, and after integration of the heat conduction equation in the first subregion, we arrive at formula (3).

The quantity Q of heat released in the second subregion is

$$Q = \frac{h}{m} \int_{T_\varepsilon}^{T_s} \Phi(T) \left[\frac{dT}{dx}\right]^{-1} dT.$$

The temperature gradient in the integrand is replaced by its mean value in the chemical reaction zone; then

$$mQ = \frac{\Theta(s, \varepsilon)}{q_s + \lambda\,[dT/dx]_{T_\varepsilon}}. \qquad (7)$$

On the other hand, the heat release in the reaction zone is

$$mQ \approx \lambda \frac{dT}{dx}\bigg|_{T_\varepsilon} - q_s. \qquad (8)$$

Using formulas (3), (7), (8), we find an expression for mass velocity m, which after elimination of the indefinite quantity T_ε, as in the Zel'dovich-Frank-Kamenetskii method, assumes the form (6).

Thus, in deriving the formula for the velocity of the zero-order reaction front in the k-phase, the Zel'dovich-Frank-Kamenetskii method and the method using averaging of the temperature gradient in the reaction zone lead to an identical result. Gradient averaging is used below for finding a formula for the velocity of a first-order reaction front.

It was shown in [11] that the accuracy of the formula for the flame velocity in a gas increases with decrease of the temperature interval in which the chemical reaction proceeds. Formula (6) also possesses this property.

We introduce the notation

$$\tau = \frac{T - T_0}{T_s - T_0}, \qquad p_s = \frac{q_s}{T_s - T_0}, \qquad \omega = mc, \qquad \varphi(\tau) = \frac{\lambda h \Phi(T)}{T_s - T_0}.$$

In addition, besides the function T(x), we introduce the function $p(\tau) = \lambda d\tau/dx$. Then (1) and the boundary conditions (2) can be represented in the form

$$p\frac{dp}{d\tau} - \omega p + \varphi(\tau) = 0, \qquad p(0) = 0, \qquad p(1) = p_s. \quad (9)$$

Here $\varphi(\tau) = 0$ when $0 < \tau < \varepsilon$ and $\varphi(\tau) > 0$ when $\varepsilon < \tau < 1$.

In the interval $0 < \tau < \varepsilon$ solution of (9) has the form $p(\tau) = \omega\tau$. The upper and lower bonds for ω, which we denote by ω^+ and ω^-, can be expressed in terms of the upper and lower bonds for the ordinates of the curve $p(\tau)$ at the point $\tau = \varepsilon$ ($p^+(\varepsilon)$ and $p^-(\varepsilon)$). To determine $p^+(\varepsilon)$ we will consider (9) in the interval $\varepsilon < \tau < 1$. An upper bond of the solution of (9), satisfying the condition $p(1) = p_S$, on this interval is the solution of the equation $p^+ dp^+/d\tau = -\varphi(\tau)$ with the condition $p^+(1) = p_S$. It has the form

$$p^+(\tau) = [p_s^2 + 2\vartheta(1, \tau)]^{1/2} \qquad \vartheta(1, \tau) = \int_\tau^1 \varphi(t)\,dt.$$

Therefore, as an upper bond for $p(\varepsilon)$ we can take

$$\omega^+ = \varepsilon^{-1}[p_s^2 + 2\vartheta(1, 0)]^{1/2}, \quad p^+(\varepsilon) = [p_s^2 + 2\vartheta(1, 0)]^{1/2}. \quad (10)$$

The lower bound of the solution $p(\tau)$ will be the solution of the equation

$$dp^-/d\tau = \omega - \varphi(\tau)/p^+(\tau), \quad p^-(1) = p_s.$$

It has the form $p^-(\tau) = -\omega(1 - \tau) + \sqrt{2\vartheta(1, \tau) + p_s^2}$. Accordingly, the lower bound for ω is

$$\omega^- = \frac{p^-(\varepsilon)}{\varepsilon} = \frac{-\omega(1 - \varepsilon) + \sqrt{p_s^2 + 2\vartheta(1, \varepsilon)}}{\varepsilon}.$$

It follows from the explicit form of the upper and lower bounds for ω that with decrease of the temperature interval within which the chemical reaction occurs, that is, as $\varepsilon \to 1$, both bounds tend to a single limit

$$\omega = \sqrt{p_s^2 + 2\vartheta(1, 0)}.$$

This formula is obviously equivalent to (6).

The description of the chemical reaction in the k-phase in terms of zero-order reaction kinetics is valid only when the quantity of heat released in the k-phase is considerably less than the thermal effect of the reaction in the k-phase. The physical picture corresponds more precisely to the assumption that the reaction in the k-phase is a first-order reaction.

We now obtain a formula for the velocity of propagation of a first-order exothermic reaction front in the k-phase by approximate integration with averaging of the temperature gradient in the reaction zone.

The equations describing the stationary propagation of a first-order reaction front in the k-phase in the case of completion of the reaction as $x \to \infty$ have the form

$$\lambda \frac{d^2T}{dx^2} - mc\frac{dT}{dx} + ha\Phi(T) = 0, \qquad (11)$$

$$m\frac{da}{dx} + a\Phi(T) = 0, \qquad -\infty \leqslant x \leqslant +\infty, \qquad (12)$$

$$T(-\infty) = T_0, \qquad a(-\infty) = a_0,$$
$$T(\infty) = T_1 = T_0 + ha_0/c. \qquad (13)$$

Here a is the concentration; the remaining notation is the same as before.

After eliminating the heat release function from equations (11), (12), ana integrating between the limits $-\infty$, x, we obtain

$$a(x) = a_0 - \frac{c}{h}(T - T_0) + \frac{\lambda}{mh}\frac{dT}{dx}. \qquad (14)$$

Integrating (11) in the region $T_0 \leq T \leq T_\varepsilon$, in which heat release can be neglected, and using the boundary condition at the "cold" boundary, we obtain (3) for the heat flux at the point with temperature $T = T_\varepsilon$.

In the case of a first-order reaction, the equation for the quantity of heat release in the k-phase has the form

$$mQ = h\int_{-\infty}^{\infty} a(x)\,\Phi[T(x)]\,dx. \qquad (15)$$

After replacing in (15) integration with respect to the coordinate by integration with respect to temperature, taking into account that in this case $Q = ha_0$, and substituting the expression for $a(x)$, given by (14), we obtain

$$ma_0 = \int_{T_\varepsilon}^{T_1}\left[a_0 - \frac{c}{h}(T - T_0) + \frac{\lambda}{mh}\frac{dT}{dx}\right]\left[\frac{dT}{dx}\right]^{-1}\Phi(T)\,dT. \qquad (16)$$

Then averaging the temperature gradient over the reaction zone in (16), just as in the case of the zero-order reaction considered above, from (3), (8), (16) for the velocity of the reaction front we find

$$m = \left[\frac{\lambda}{a_0 h}\int_{T_0}^{T_1}\Phi(T)\,dT + \frac{2\lambda c}{a_0^2 h^2}\int_{T_0}^{T_1}(T_1 - T)\,\Phi(T)\,dT\right]^{1/2}. \qquad (17)$$

The accuracy of this formula can be estimated after finding estimates for m, the eigenvalue of problem (11)-(13).

In determining the upper and lower bounds, we convert from the unknown function T(x) to the function $p(\tau) = \lambda\, d\tau/dx$, and we introduce the notation

$$\omega = mc, \quad \tau = (T - T_0)/(T_1 - T_0), \quad \varphi(\tau) = \lambda c\Phi(T).$$

With (14) taken into account, equation (11), conditions (13) and formula (17) reduce to the form

$$\frac{dp}{d\tau} = \omega - \frac{\varphi(\tau)}{\omega} - \frac{(1-\tau)\varphi(\tau)}{p(\tau)},$$

$$p(0) = 0, \quad p(1) = 0 \quad (0 \leqslant \tau \leqslant 1),$$

$$\omega = [\vartheta(1, 0) + 2\mu(1, 0)]^{1/2},$$

$$\left(\mu(1, 0) = \int_0^1 (1-\tau)\,\varphi(\tau)\,d\tau\right). \qquad (18)$$

First we will obtain an upper bound for ω.

For this purpose we use not only (18), but also the equation

$$\frac{dp^+}{d\tau} = \omega^+ - \frac{\varphi(\tau) + (1-\tau)\varphi(\tau)}{p^+}, \quad p^+(0) = p^+(1) = 0. \qquad (19)$$

In view of the properties of $\varphi(\tau)$, in accordance with [12] it can be assert3d that (19) always has a unique solution $p^+(\tau, \omega^+)$.

We will now compare the relative position on the plane p, τ of the curve $p^+(\tau, \omega^+)$ and the integral curve (18), passing through the point $p(1) = 0$, when $\omega = \omega^+$. It can be stated that the curve $p(\tau, \omega^+)$ passes below the curve $p^+(\tau, \omega^+)$, that is, $p^+(\tau, \omega^+) \geq p(\tau, \omega^+)$.

In fact, the curve $p^+(\tau, \omega^+)$, issuing from the point $p = 0$, $\tau = 1$ at a larger angle than the curve $p(\tau, \omega^+)$ ($\tau = 1$, $dp^+/d\tau = -\infty$, $dp/d\tau = -\varphi(1)/\omega^+$), thereafter cannot intersect the latter, because at the point of intersection we would have $dp^+/d\tau \geq dp/d\tau$. But this inequality occurs only if $p^+(\tau) > \omega^+$. However, the latter relation does not occur.

The following relation between the ordinates at the point $\tau = \varepsilon$ follows from the relative postion of the $p^+(\tau, \omega^+)$ and $p(\tau, \omega^+)$ curves

$$p^+(\varepsilon, \omega^+) > p(\varepsilon, \omega^+). \qquad (20)$$

As pointed out in [13], the value $p(\varepsilon, \omega)$ does not decrease with decrease of ω. It follows from this property of the $p(\tau, \omega)$ curves and the inequality (20) that the eigenvalue ω of (18) satisfies the inequality $\omega < \omega^+$.

Using the formal analogy of the problem (19) to the problem of the propagation of a zero-order reaction front in the k-phase considered above, it is possible to write an explicit expression for the upper bound for ω

$$\omega^+ = \sqrt{2\vartheta(1,0) + 2\mu(1, 0)}. \qquad (21)$$

We will now obtain a lower bound for ω. We consider the equations

$$\omega^* - \frac{\vartheta(1, 0)}{\omega^*} = \int_0^1 \frac{(1-\tau)\,\varphi(\tau)\,d\tau}{p(\tau, \omega^*)}$$

$$\omega_1 - \frac{\vartheta(1, 0)}{\omega_1} = \frac{\mu(1, 0)}{\omega^*}, \quad \omega^- - \frac{\vartheta(1, 0)}{\omega^-} = \frac{\mu(1, 0)}{\omega^-} \qquad (22)$$

Here ω^* is the eigenvalue of the problem (18). The first of equations (22) was obtained by integration of (18), with the boundary conditions taken into account.

The second of equations (22) was derived by the substitution of ω^* into the integrand on the right-hand side of the first of equations (22) in place of the function $p(\tau, \omega^*)$. With respect to $p(\tau, \omega^*)$, the solution of problem (18), it can be asserted that $p(\omega^*, \tau) < \omega^*$. Therefore, the value ω_1, determined by the second of equations (22), satisfies the inequality $\omega_1 < \omega^*$.

The quantity ω_1 is still not the lower bound for ω^*, since its equation contains ω^*. As such an estimate it is possible to use ω^-, determined from the third of equations (22)

$$\omega^{-} = \sqrt{\vartheta(1, 0) + \mu(1, 0)}. \qquad (23)$$

This assertion follows from a comparison of the second and third of equations (22). In fact, let us postulate the opposite. Assume $\omega^{-} > \omega^{*}$; then the right-hand side of (22) is smaller than the right-hand side of the second of equations (22), and $\omega_1 > \omega^{*}$, which contradicts the previously established inequality $\omega_1 < \omega^{*}$.

Thus, the quantity ω^{*}, proportional to the velocity of propagation of a first-order exothermic reaction front in the k-phase, lies in the range

$$\omega^{-} < \omega^{*} < \omega^{+}. \qquad (24)$$

The values ω^{+} and ω^{-} are given by (21), (23). It can be seen that the value of ω, given by (18), which was obtained by averaging the temperature gradient in the combustion zone, lies within the mentioned limits. We note that the formula for the velocity of a polymerization front, established in [3], leads to velocity values falling within the determined bounds.

If it is assumed that in equations (11), (12) the rate constant of the chemical reaction has the form $\Phi(T) = B\exp(-E/RT)$, after substitution into (17) and approximate integration by the Frank-Kamenetskii method we obtain

$$m^2 = \frac{B\lambda RT_1^2}{hE}\exp\frac{-E}{RT_1}. \qquad (25)$$

When the processes in the k-phase constitute the first stage of a multistage combustion process and the k-phase occupies the region $-\infty < x \leq 0$, in deriving the formula for the velocity of the reaction front it is necessary to use as a point of departure equations (11), (12) with other boundary conditions, which in this case have the form

$$T(-\infty) = T_0, \qquad a(-\infty) = a_0,$$

$$T(0) = T_s, \qquad \lambda \left.\frac{dT}{dx}\right|_{x=0} = q_s \qquad (26)$$

Here q_s is the heat flux from the products of gasification in the k-phase. Using the system of equations (11), (12) with the boundary conditions (26), by approximate integration with averaging of the temperature gradient in the reaction zone it is possible to obtain the following algebraic equation for the mass velocity m of the reaction front, that is, the gasification rate:

$$m^2c^2(T_s - T_0)^2 - q_s^2 = \lambda\left[c(T_s - T_0) + \frac{q_s}{m}\right]\times$$
$$\times\int\limits_{T_0}^{T_s}\Phi(T)\,dT + 2c\lambda\int\limits_{T_0}^{T_s}\left(T_0 + \frac{ha_0}{c} - T\right)\Phi(T)\,dT. \qquad (27)$$

We note that our formulas for the velocity of the front of zero- (6) and first-order reactions (27) in the k-phase were derived on the assumption that the temperature at the gasification surface is a given quantity (T_s-regime [12, 13]). As pointed out in [13], another formulation of the problem of the propagation of an exothermic reaction front in the k-phase in the presence of gasification (Q-regime) is possible. The problem of determining the velocity of the reaction front in this regime is not considered in this paper.

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