

STATIONARY PROPAGATION OF AN EXOTHERMIC-REACTION FRONT IN A CONDENSED MEDIUM

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UDC 534.2

The problem of the propagation of an exothermic-reaction front in a condensed medium has been examined in a number of reports [1-8], in which various statements of the problem have been analyzed, the conditions of existence and uniqueness of a solution determined, and different approximate methods of determining the propagation velocity of the front suggested. In [1-6] the examination was conducted for a specific class of heat-release functions corresponding to the kinetics of exothermic transformation in homogeneous condensed systems. The propagation of the reaction front in heterogeneous systems (condensed mixtures) was studied in [7, 8] for particular forms of the heat-release function corresponding to certain simplifying assumptions concerning the structure of the heterogeneous medium. In connection with the complexity of the structures of real condensed systems [9-11] and the diversity of the kinetic laws of interaction, in the present report the available results on a broader class of heat-release functions are generalized, and the possible approximate methods of determining the propagation velocity are analyzed.

1. Statement of Problem

The stationary propagation of an exothermic-reaction front in condensed systems which are homogeneous in a thermal respect is examined, i.e., it is assumed that the temperature distribution is one-dimensional in the direction along the propagation of the front. Such a situation occurs not only for systems which are homogeneous in a chemical respect (or are homogenized in the warm-up zone), where the heat release has a volumetric nature, but also for the case, important in a practical respect, of condensed mixtures which interact heterogeneously. As shown in [12], condensed mixtures can be considered as homogeneous in a thermal respect independently of the degree of dispersion of the particles, since the heat release in such mixtures (determined by the intermixing of the components) takes place much more slowly than the process of thermal relaxation in the particles. The chemical heterogeneity inherent to such systems is manifested in the particular form of the kinetic function characterizing the heat release in an effectively homogeneous medium. Below we will use the concept of the effective reaction rate which determines the rate of transformation of the components per unit volume of the homogeneous medium under consideration.

A stationary mode of propagation of a reaction front in a condensed medium assumes the presence of a sample, infinite in both directions, at one end of which ($x = -\infty$) is given the initial state of the substance (the temperature and composition), while the final state is determined by the thermodynamic conditions of equilibrium. For a one-stage transformation $A \rightarrow B$, where A and B are the set of initial substances and reaction products, respectively, the propagation of the front is described by two differential equations: an equation for the propagation of heat and an equation for the rate of heat release. In a coordinate system moving along with the front with a velocity u these equations have the form

$$\frac{d}{dx} \left(\sum_1^N u \rho^i H_i - \lambda \frac{dT}{dx} \right) = 0 \quad (1.1)$$

$$u \frac{d\eta}{dx} = w(\eta, T), H_i(T) = H_i(T_-) + \int_{T_-}^T c_i dT \quad (1.2)$$

Moscow. Translated from *Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, No. 3, pp. 96-105, May-June, 1974. Original article submitted April 18, 1973.

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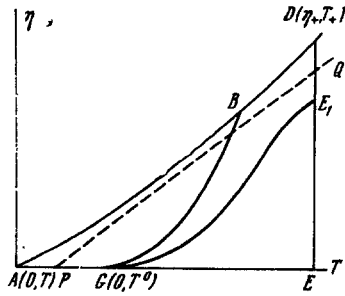


Fig. 1

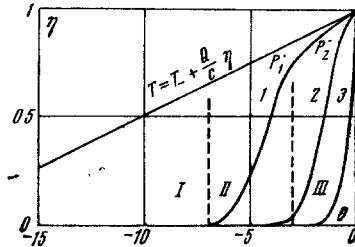


Fig. 2

The equation of heat conduction (1.1) is written in the form of the conservation of the total enthalpy flux. In (1.1) and (1.2) $\eta = (\rho_-^1 - \rho^1) / \rho_-^1$ is the depth of transformation ($0 < \eta < \eta_+$), w is the reaction rate, x is the coordinate along the direction of propagation, ρ^i is the amount of the i -th component per unit volume of the medium, ρ^1 is the amount of one of the initial components, $H_i(T)$ is the enthalpy of a unit mass of the i -th component at the temperature T , $c_i(T)$ is the specific heat capacity of the i -th component, N is the number of components, the indices minus and plus correspond to the conditions at the "cold" ($x = -\infty$) and "hot" ($x = \infty$) ends, respectively. The thermal conductivity coefficient λ , generally speaking, can vary along with the temperature and composition of the medium: $\lambda = \lambda(\eta, T)$.

With allowance for the stoichiometric relationships between the reacting components the values ρ^i can be expressed through the depth of conversion:

$$d\rho^i / d\rho^1 = \nu_i, \quad \rho^1 \nu_i \eta = \rho_-^i - \rho^i, \quad i = 1, 2, \dots, N \quad (1.3)$$

where ν_i are the stoichiometric coefficients of the reaction.

The integration of (1.1) in the limits from $-\infty$ to x gives

$$\lambda dT / dx = u\rho [c(T)(T - T_-) - Q(T)\eta], \quad \rho = \sum_{i=1}^N \rho^i \quad (1.4)$$

$$c(T) = \frac{1}{T - T_-} \sum_{i=1}^N \int_{T_-}^T c_i dT \quad (1.5)$$

$$Q(T) = \frac{\rho_-^1}{\rho} \sum \nu_i H_i(T) = Q(T_-) + \frac{\rho_-^1}{\rho} \sum_{i=1}^N \nu_i \int_{T_-}^T c_i dT \quad (1.6)$$

Here $c(T)$ is the mean heat capacity of the medium, and $Q(T)$ is the calorific effect of the reaction per unit mass of the substance.

For a strongly exothermic reaction the last term in (1.6), as a rule, has the nature of a correction and reflects the dependence of the calorific effect on the temperature, connected with the difference in heat capacities of the initial substances and the reaction products (the Kirchhoff effect). The temperature T_+ after the completion of the reaction is determined from (1.4):

$$x = \infty, \quad dT / dx = 0, \quad \eta = \eta_+, \quad T_+ = T_- + Q(T_+)\eta_+ / c(T_+) \quad (1.7)$$

The dependence $Q(T)c^{-1}(T)$ is henceforth assumed to be such that in accordance with the physical meaning the combustion temperature is a monotonically increasing continuous function of the final depth of transformation η_+ .

Equations (1.2) and (1.4) together with the boundary conditions at $x = \pm\infty$ completely determine the propagation of an exothermic-reaction front in a condensed medium. For further consideration it is convenient to represent the problem on the propagation of the front in the form

$$\frac{d\eta}{dT} = \frac{\varphi(\eta, T)}{u^2 [(T - T_-) - Q(T)c^{-1}(T)\eta]}, \quad \varphi(\eta, T) = \frac{\lambda w}{cp} \quad (1.8)$$

$$\eta = 0, \quad T = T_-; \quad \eta = \eta_+, \quad T = T_+ \quad (1.9)$$

In general, Eq. (1.8) does not have an analytical solution and therefore it is often necessary to resort to a numerical calculation to solve the problem (1.8), (1.9). Here the question of the existence and uniqueness of a solution acquires fundamental significance.

2. Existence and Uniqueness of Stationary Mode of Propagation of an Exothermic-Reaction Front in a Condensed Medium

The question of the existence and uniqueness of a stationary mode of propagation of an exothermic-reaction front in the condensed phase was examined in [1, 2, 5] on the assumption that the reaction rate can be represented in the form

$$w(\eta, T) = (1 - \eta)^n k(T) \quad (2.1)$$

The theorem of the existence and uniqueness of a solution was proven in [1, 2] for the cases $n = 0, 1$ and in [5] for an arbitrary value of n . Equation (2.1) corresponds to the kinetics of an exothermic transformation in homogeneous condensed systems. The proof of the existence and uniqueness of the stationary propagation of a reaction front was conducted in [8] for heterogeneous systems when the heat-release function is not reduced to zero at the moment of completion of the reaction

$$w(\eta, T) > 0, 0 < \eta < \eta_+; w(\eta, T) = 0, \eta > \eta_+ \quad (2.2)$$

which corresponds to certain simplifying assumptions concerning the structure of the heterogeneous system. In many cases a more complex kinetics, not corresponding to (2.1) and (2.2), occurs for reactions in the condensed phase. In connection with this let us examine the question of existence and uniqueness for more general assumptions concerning the chemical reaction rate.

We will assume that the function $\varphi(\eta, T)$ in (1.8) is bounded above and is positive everywhere except for some interval in the vicinity of the initial temperature, where it is identically reduced to zero:

$$\varphi \equiv 0; T_- < T < T^0, \eta = 0 \quad (2.3)$$

$$M > \varphi > 0; T^0 < T < T_+, 0 < \eta < \eta_+, \varphi(\eta_+, T_+) = 0 \quad (2.4)$$

where T^0 is the temperature at the start of the reaction ($T_- < T^0 < T_+$). As is known [13], the condition (2.3) is necessary for the existence of a stationary mode of propagation of an exothermic-reaction front. In addition to (2.3) and (2.4), we will assume that the properties of the function $\varphi(\eta, T)$ are such that the differential equation (1.8) has a unique solution at all internal points of the region $0 < \eta < \eta_+, T_- < T < T_+$.

An important fact for the analysis is that the function $\varphi(\eta, T)$ is reduced to zero at the moment of completion of the reaction ($\eta = \eta_+, T = T_+$). In this case, as seen from (1.7) and (1.8), the point η_+, T_+ is a singular point of the differential equation, with the type of singularity and the behavior of the integral curves in the vicinity of this point being determined by the properties of the function $\varphi(\eta, T)$. We can show that if $\varphi(\eta, T)$ has the properties (2.3), (2.4), then one can always find a value of the parameter u at which the integral curve (1.8) satisfies the boundary conditions (1.9).

The existence of a stationary mode of propagation of an exothermic-reaction front in the condensed phase will be proven on this basis. It should be noted that in the case under consideration one cannot use the method of proof of existence and uniqueness used in [1-3, 5] in which the form of the function $\varphi(\eta, T)$ was assumed to be known, which permitted a direct determination of the nature of the singular point (η_+, T_+) and the behavior of the integral curves in its vicinity.

In the case of an arbitrary function $\varphi(\eta, T)$ the principal aspect of the proof is the question of the existence of integral curves passing through the point (η_+, T_+).

Let us consider an increasing sequence of values η_+^i and the values T_+^i corresponding to them [from (1.7)]:

$$\eta_+^i < \eta_+^{i+1} < \eta_+, \quad T^0 < T_+^i < T_+^{i+1} < T_+$$

An analysis of (1.8) shows [8] that there is a unique value of the parameter u^i at which the integral curve emerging from the point G passes through the chosen point B(η_+^i, T_+^i) (Fig. 1), with the value of the parameter u^i increasing together with η_+^i

$$\eta_+^{i+1} > \eta_+^i, \quad u^{i+1} > u^i$$

Values of $u > u_1 = \sqrt{M_0/b}$, where b is the slope of some straight line PQ intersecting a segment AG and lying below the line AD and M_0 is the greatest value of the function $\varphi/[T - T_- - Q\eta c^{-1}]$ on the segment PQ, do not belong to the sequence u^i , since $d\eta/dT < b_0$ holds for these values of the parameter u , i.e., the integral curves pass below the straight line PQ. Consequently, with the approach of η_+^i to η_+ the increasing sequence of η_+^i corresponds to an increasing sequence of values u^i bounded above and having the limit

$$u^- = \lim u^i, \quad \eta_+^i \rightarrow \eta_+$$

It is not hard to show the existence of a limit for the decreasing sequence $\{u^j\}$, corresponding to the integral curve AE₁, passing through the point E₁(η_+^j, T_+) of the segment DE (any of the u^j can be taken as the value of u bounding the decreasing sequence $\{u^j\}$ from below):

$$u^+ = \lim u^j, \quad \eta_+^j \rightarrow \eta_+, \quad \eta_+^{j+1} > \eta_+^j$$

TABLE 1

RT_+/E	m	s	n	u_0/u^0	u_+/u^0
0.05	20	—	—	1.26	1.08
0.10	10	—	—	1.4	1.16
0.10	40	—	—	1.14	1.0
0.15	15	—	—	1.21	1.01
0.05	—	20	—	1.07	1.0
0.10	—	10	—	1.02	0.94
0.10	—	20	—	1.04	0.97
0.15	—	10	—	1.02	0.9
0.15	—	4	—	1.31	1.23
0.05	—	—	5	1.53	1.10
0.10	—	—	5	1.5	1.03
0.15	—	—	5	1.47	1.02
0.05	—	—	2	2.3	1.22
0.10	—	—	2	2	1.06
0.15	—	—	2	2	1.04

Because of the monotonic dependence of the solution of (1.8) on the parameter we have

$$u^i < u^- \leq u^+ < u^j, \quad u^{i+1} > u^i, \quad u^{j+1} < u^j$$

The integral curves $\eta(T, u^-)$ and $\eta(T, u^+)$ cannot intersect either the curve AD or the segment DE (intersection with AD corresponds to the value u^i and intersection with DE corresponds to u^j), consequently, they pass through the point D, i.e., they are the solutions of the problem (1.8), (1.9). When the values u^- and u^+ coincide the point D has a singularity of the saddle type. In this case there is a unique curve corresponding to the value $u = u^- = u^+$ passing through the points A and D. In the general case [the form of $\varphi(\eta, T)$ is arbitrary] the inequality $u^- \leq u^+$ is satisfied between u^- and u^+ . It can be shown that if u^- and u^+ are such that $u^- < u^+$, then for any interval of values $u^- < u < u^+$ the integral curve emerging from the point A passes through the point D, i.e., is also a solution of the problem (1.8), (1.9).

In the latter case from the set of values $u^- < u < u^+$ corresponding to the solution of the problem (1.8), (1.9) one must select as the velocity of stationary propagation of the front the value $u = u^-$ which is the limit of the u^i corresponding to solutions of the problem (1.8), (1.9) when $\eta_+^i < \eta_+$ ($T_+^i < T_+$), since it is clear from physical considerations that the stationary propagation velocity of the reaction front must vary continuously with a decrease in the parameter η_+ . We note here that the mode of stationary propagation of the reaction front is an asymptotic representation (as $t \rightarrow \infty$) of the real nonstationary propagation.

In a number of cases, for example, when $\varphi(\eta, T) = (1-\eta)^n k(\Gamma)$, $n \geq 1$, the values $\eta = \eta_+$ and $T = T_+$ are not reached in any finite time t , i.e., the actual propagation of the reaction front takes place with $\eta < \eta_+$ and $T < T_+$.

3. Approximate Determination of Velocity of Stationary Propagation of a Combustion Front

The specific properties of the function $\varphi(\eta, T)$ are usually used in the construction of approximate solutions. One of these properties is the strong temperature dependence

$$\varphi(\eta, T) = \lambda(\eta, T) w(\eta, T) / c(T)\rho = a(\eta, T) k_0 f(\eta) e^{-E/RT}$$

Here $a = \lambda / c\rho$ is coefficient of thermal diffusivity of the medium, k_0 is the preexponent, E is the activation energy, R is the universal constant, and the function $f(\eta)$ characterizes the dependence of the reaction rate on the depth of transformation.

At high activation energies ($E/RT \gg 1$) the reaction rate falls off rapidly with temperature, which makes it possible to use the approximation of a narrow reaction zone [14] in the calculation of the combustion velocity.

By considering (1.8) in a narrow temperature interval of the reaction zone, where one can neglect all the temperature dependences which are weakly exponential, one can obtain for the square of the velocity

$$u^2 = k_\eta k_0 e^{-E/RT+a(\eta_+, T_+)} (RT_+^2 c(T_+) / Q(T_+)) \tag{3.1}$$

$$k_\eta = \left[\int_0^{\eta_+} \frac{(1-\eta) a(\eta_+, T_+)}{f(\eta) a(\eta, T_+)} d\eta \right]^{-1}$$

The approximation of a narrow zone is not always valid, however, even when $E/RT_+ \gg 1$. An important factor limiting the applicability of (3.1) in a number of cases is the dependence $f(\eta)$ of the reaction rate on the depth of transformation. The function $f(\eta)$ can have different forms. For example, in heterogeneous condensed mixtures, the components of which interact through a solid layer of the product, the dependence of the velocity on the depth of transformation is described by laws of the type [15, 16]

$$f(\eta) = (\eta + \eta_-)^{-s} e^{-m\eta}, \quad \eta < 1 \tag{3.2}$$

where m and s are kinetic parameters, and η_- characterizes the initial depth of transformation ($\eta_- \ll 1$).

The dependence (1.4) reflects the slowing of the reaction in a condensed mixture in proportion to the growth of the layer of product separating the reacting components. In the case of strong slowing of the re-

action [large m and s in (3.2)] the approximation of a narrow zone is incorrect even for high activation energies [7, 8].

Figure 2 shows integral curves of Eq. (1.8) obtained through a numerical solution of the problem (1.8), (1.9) with strong (curve 1) and weak (curve 3) dependences of the velocity on the depth of transformation. As seen from Fig. 2, curves 1 and 3 have an essentially different nature. With a strong dependence of the velocity on the depth of transformation the integral curves have an inflection, the zone of transformation is not narrow compared with the warm-up zone, and there is a certain section on the integral curves adjoining the straight line $T = T_- + Q\eta c^{-1}$ (here and later the ratio Q/c is taken as constant: $\eta_+ = 1$). The behavior of the integral curves at different values of the parameter u is illustrated by the dashed curves 1' and 1'',* corresponding to the values $u' = 0.85 u_1$ and $u'' = 1.1 u_1$, where u_1 is the value of the parameter u corresponding to curve 1.

It is shown in [7, 8] that with strong slowing of the reaction the propagation velocity of the front is determined by the heat release in a certain part of the reaction zone — the zone of propagation (zone II in Fig. 2), and the later transformation of the substance in the burn-out zone (zone III) and the heat release connected with it have almost no effect on the combustion velocity. Let us examine the possibility of constructing approximate equations for the velocity u which are connected with the properties of the field of directions of the differential equation (1.8) for several heat-release functions.

In differential form the equation of isoclines has the form

$$\frac{d\eta}{dT} = \frac{\varphi - (T - T_- - Q\eta c^{-1}) \varphi_T'}{(T - T_- - Q\eta c^{-1}) \varphi_{\eta'}' + Q\varphi c^{-1}} \quad (3.3)$$

As seen from (3.3), the field of directions of the differential equation (1.8) can have a singular point whose coordinates T_0, η_0 are determined by the equations

$$(\varphi_T')_{T_0, \eta_0} = -cQ^{-1}(\varphi_{\eta'}')_{T_0, \eta_0}, \quad T_0 = T_- + Qc^{-1}\eta_0 + (\varphi / \varphi_T')_{T_0, \eta_0} \quad (3.4)$$

It is interesting to note that the values T_0, η_0 are close to the values T_*, η_* corresponding to the maximum of $\varphi(\eta, T)$ under conditions where the reaction proceeds adiabatically and are determined by the equations

$$(\varphi_T')_{T_*, \eta_*} = -cQ^{-1}(\varphi_{\eta'}')_{T_*, \eta_*}, \quad T_* = T_- + Qc^{-1}\eta_* \quad (3.5)$$

The first equations of (3.4) and (3.5) which determine the values η_0, T_0 and η_*, T_* coincide, while for a strong dependence of the velocity on the temperature the second equations of (3.4) and (3.5) differ by the small value ($\varphi \sim \exp(-E/RT)$, $\varphi / \varphi_T' = RT_0^2 E^{-1} \ll T_0$).

The closeness of the values η_0, T_0 and η_*, T_* indicates that the presence of the singular point η_0, T_0 in the region $0 < \eta < 1, T_- < T < T_+$, just like the presence of the point η_*, T_* , is connected with the strong dependence of the reaction rate on the depth of transformation.

An analysis of the behavior of the integral curves obtained through the numerical solution of (1.8) with different types of function $\varphi(\eta, T)$ shows that the start of the section of the integral curve adjoining the straight line $T = T_- + Qc^{-1}\eta$ and corresponding to the burn-out zone III corresponds to the vicinity of the singular point $P(\eta_0, T_0)$ of the field isoclines (in Fig. 2 the points P_1 and P_2 pertain to curves 1 and 2). This circumstance makes it possible to obtain an approximate expression for the propagation velocity of the front in the presence of a burn-out zone. As seen from (1.8), it is easy to calculate u^2 if $d\eta/dT$ is known at any of the points η_1, T_1 of the integral curve $\eta(T, u)$:

$$u^2 = \frac{\varphi(T_1, \eta_1)}{T_1 - T_- - Qc^{-1}\eta_1} \left(\frac{dT}{d\eta} \right)_{T_1, \eta_1} \quad (3.6)$$

Considering that in the vicinity of the point T_0, η_0 the integral curve $\eta(T, u)$ approaches the straight line $T = T_- + Qc^{-1}\eta$, we have

$$\left(\frac{dT}{d\eta} \right)_{\eta_0, T_0} \approx \frac{Q}{c}, \quad u^2 \approx \frac{\varphi(T_0, \eta_0)}{T_0 - T_- - Qc^{-1}\eta_0} \frac{Q}{c} \quad (3.7)$$

Keeping in mind the second of Eqs. (3.4), the expression (3.7) can be represented in the form

$$u_0^2 = \varphi(T_0, \eta_0) Qc^{-1} (\partial \ln \varphi / \partial T)_{T_0, \eta_0} \quad (3.8)$$

* As in Russian original, curves 1' and 1'' are not labeled in the figure — Publisher.

It is interesting to note that (3.8) can also be obtained by another means — the linearization of the function $\varphi(\eta, T)$ in the zone of propagation, if the point T_0, η_0 is chosen as the point of the expansion. In [8] such a method was used to obtain the following approximate equation for the propagation velocity of the front:

$$u_*^2 = \varphi(T_*, \eta_*) Qc^{-1} (\partial \ln \varphi / \partial T)_{T_*, \eta_*} e \quad (3.9)$$

The coordinates T_*, η_* of the point of the expansion of $\varphi(\eta, T)$ are determined by Eqs. (3.5). With a strong dependence of the reaction rate on the depth of transformation the values u_0 and u_* practically coincide. For example, for kinetic functions corresponding to exponential ($\varphi_1 \sim e^{-m\eta}$) and power-law ($\varphi_2 \sim \eta^{-s}$, $s \gg 1$) slowings of the reaction rate the respective ratios of velocities u_0 and u_* are

$$(u_0 / u_*)_1 = 1, \quad (u_0 / u_*)_2 = e / (1 + s^{-1})^s \approx 1, \quad s \gg 1$$

A comparison of the approximate velocities with the results of numerical calculations is presented in Table 1, where the ratios of u_0 to u° determined through a numerical solution of the problem ($T_- cQ^{-1} = 0.01$) are given. For the heat-release functions under consideration

$$\varphi_1 = k_0 e^{-m\eta} e^{-E/RT}, \quad \varphi_2 = k_0 \eta^{-s} e^{-E/RT}, \quad \varphi_3 = k_0 (1 - \eta)^n e^{-E/RT}$$

the propagation velocities determined by (3.8), as well as by Eq. (3.9) which is equivalent to it, are somewhat overstated.

More exact correspondence with the results of the numerical calculation is obtained if it is assumed that the slope of the integral curve in the vicinity of the singular point (η_0, T_0) of the field of directions corresponds approximately to the slope of the isocline passing through this point. The closeness of the directions of the integral curve and the isocline is indicated by the small variation in the slope of the integral curve in the burn-out zone:

$$(d\eta / dT)_{\eta_0, T_0} = p, \quad p = (\varphi_{\eta T}'' \pm \sqrt{(\varphi_{\eta T}''^2 - \varphi_{TT}'' \varphi_{\eta\eta}''}) / \varphi_{\eta\eta}'' \quad (3.10)$$

For the kinetic functions φ_1, φ_2 , and φ_3 the expression under the radical in (3.10) is greater than zero, i.e., the point η_0, T_0 is a saddle point of the field of directions. The values p_+ and p_- determine the slope of the separatrices at this point. Substituting into (3.6) the values

$$T_1 = T_0, \quad \eta_1 = \eta_0; \quad (dT / d\eta)_{\eta_0, T_0} = p_+^{-1}$$

we have

$$u^2 = \varphi(T_0, \eta_0) Qc^{-1} (\partial \ln \varphi / \partial T)_{T_0, \eta_0} \xi \quad (3.11)$$

where ξ is a coefficient close to unity which is determined by the kinetic parameters of the function φ :

$$\begin{aligned} \xi_{\varphi_1} &= \frac{1}{1 + \sqrt{2RT_0/E}} \\ \xi_{\varphi_2} &= \frac{1+s}{s} \left[1 + \sqrt{\frac{1+s^{-1}}{1+s}} \right]^{-1}, \quad T_- \ll E/Rs \\ \xi_{\varphi_3} &= \frac{n-1}{n + \sqrt{n[1 + 2RT_0 E^{-1}(n-1)]}} \end{aligned}$$

The velocities determined by the approximate expression (3.11) agree well with the numerical results (Table 1) if the dependence of the reaction rate on the depth of transformation is strong enough.

An analysis of the field of isoclines of the differential equation (1.8) in the region $T_- < T < T_+, 0 < \eta < \eta_+$ under consideration makes it possible to predict from the form of the function $\varphi(\eta, T)$ the nature of the integral curves and thereby to predetermine the means of calculating the combustion velocity. The absence of a singular point of the field of directions in the region $T_- < T < T_+, 0 < \eta < 1$ points to a monotonic variation in the slope of the integral curves. In this case the reaction zone is narrow (for a strong dependence of the velocity on the temperature) and one can use (3.1) to calculate the combustion velocity. The presence of a singular point T_0, η_0 of the field of directions in the region $T_- < T < T_+, 0 < \eta < \eta_+$ indicates a nonmonotonic variation in the slope of the integral curve $\eta(T, u)$. For values of T_0 differing considerably from T_+ the reaction zone is not narrow: the combustion velocity is determined by Eqs. (3.8) and (3.11).

As an illustration let us examine the kinetic dependence for a reaction of n -th order

$$\varphi = ak_0(1 - \eta)^n e^{-E/RT} \quad (3.12)$$

For this heat-release function the coordinates of the singular point $P(T_0, \eta_0)$ of the field of directions are determined by the equations

$$T_0 = T_+ - RT_0^2 E^{-1} (n - 1), \quad \eta_0 = 1 - nRT_0^2 c (EQ)^{-1}$$

When $n < 1$ the point T_0, η_0 does not belong to the region $T_- < T < T_+, 0 < \eta < 1$, the variation in the slope of the integral curves has a monotonic nature (curve 3 in Fig. 2; $n=0, RT_+/E=0.05$), and the velocities determined from the approximate equation (3.1) agree well with those calculated numerically. When $n > 1$ the point T_0, η_0 falls in the region of variation in T and η and the nature of the integral curves changes: an inflection appears on the curves, and the temperature interval of the reaction zone increases (curve 2, $n=2$). For values considerably greater than unity T_0 differs from T_+ by many characteristic intervals RT_0^2/E and clearly expressed sections are observed on the integral curve corresponding to the zones of warm-up (zone I), propagation (zone II), and burn-out (zone III) [7, 8] (curve 3; $n=5$). In this case the propagation velocity can be determined from Eq. (3.11). The correspondence of the velocities obtained using (3.11) and calculated numerically is the better, the larger the value of n . We note that in contrast to (3.8), Eq. (3.11) gives good results even for small n ($n=2$).

In conclusion, let us dwell on the temperature coefficient of the propagation velocity which is an important experimental and theoretical characteristic of the combustion process and characterizes the change in the propagation velocity of the front with a change in the combustion temperature $T_+ = T_- + Qc^{-1}$. The coefficients k_- and k_+ can be analyzed in accordance with the two possible means of variation in the combustion temperature: by a change in the initial temperature T_- and in the calorific effect Q (through dilution of the system of products, for example)

$$k_- = \partial \ln u / \partial T_-, \quad k_+ = \partial \ln u / \partial (Q / c) \quad (3.13)$$

With a weak dependence of the reaction rate on the depth of transformation the reaction zone is narrow, and the combustion velocity is practically determined by the value T_+ ; in this case the coefficients k_- and k_+ coincide:

$$k_- \approx k_+ = E / 2 RT_+^2$$

We can use (3.9) to determine the temperature coefficients in the case of a strong dependence of the reaction rate on the depth of transformation (wide reaction zones). We have

$$k_+ \approx E / 2 RT_* T_+, \quad k_- \approx E / 2 RT_*^2, \quad T_- \ll T_+ \quad (3.14)$$

With strong slowing of the reaction the temperature T_* is considerably less than the combustion temperature, which corresponds to a higher coefficient k_- compared with k_+ . It follows from Eqs. (3.14) that the experimental determination of k_- and k_+ can provide information on the kinetics of heat release in the system studied. Equality of the coefficients k_- and k_+ shows that the transformation of the substance is accomplished in a narrow temperature interval near the combustion temperature T_+ . A value of k_+ lower than k_- indicates the strong slowing of the reaction with greater depth of transformation, and the ratio $k_- / k_+ \approx T_+ / T_*$ permits an estimate of the temperature T_* corresponding to the start of the burn-out zone.

The author is grateful to B. I. Khaikin and K. G. Shkadinskii for constant assistance and attention to the work performed and to T. M. Martem'yanova for compiling the program for the computer calculations.

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