AUTOWAVE PROPAGATION OF CHEMICAL REACTIONS IN DISPERSED MEDIA

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1. Models of autowave propagation of chemical reactions in homogeneous media were investigated in [1-6]. It is shown in [6] that an immobile front of a polymerization reaction (accompanied by a sharp increase in the viscosity) in a moving medium has a strongly distorted (singular) form. In this connection it is of interest to study autowave propagation of a polymerization reaction in dispersed media, consisting of a carrying, low-viscosity phase and particles of a dispersed phase, in which the polymerization reaction occurs. In this case an increase in the viscosity of the material in the particles in the course of the reaction will have no effect on the hydrodynamic flow of the medium as a whole and the reaction front can be regarded as being flat. The results of the study are useful for analysis of not only polymerization processes, but also any other exothermal chemical reactions, satisfying the conditions of the problem. A simplified model of the propagation of a combustion wave in a chemically inert medium, containing gas bubbles in which combustion occurs, was proposed in [7, 8]. In [9, 10] this model is used to analyze a polymerization wave in a liquid medium with liquid particles of a monomer distributed in it. The model studied in [7-10], however, has significant drawbacks. The main drawback is that the asymptotically decaying chemical reaction in the trailing edge of the wave is neglected. This reaction is important in any chemical-technological processes. According to the boundary conditions employed in [7-10], the temperature profiles in continuous and dispersed phases have discontinuous derivatives, and the proposed qualitative form of the profiles was not confirmed either computationally or by means or qualitative studies of differential equations.

In this paper it is shown that taking into account the decaying chemical reaction in the trailing edge of the wave and using boundary conditions corresponding to a smooth temperature profile in a continuous medium leads to fundamentally new qualitative and quantitative results. In particular, it is found that for the parameters adopted in [7-10] for the problem a stationary wave solution does not exist. The conditions for existence of waves of chemical reaction in dispersed media are found, and the velocities of the waves and their structure are calculated. It is shown that waves in dispersed media can have two qualitatively different types of structures.

2. We shall study the one-dimensional, steady-state motion of a continuous medium, containing particles of a dispersed phase, in which an exothermal chemical reaction can occur. It is assumed that the sizes of the particles and their volume content are low enough that the velocity of the carrying phase equals that of the particles and the particles do not collide with one another, transfer of the heat of reaction from particle to particle occurs by means of heat conduction in the carrying phase, the chemical reaction is quite active, and a stationary self-maintained wave forms in the dispersed medium.

We shall write down the equation for the conservation of energy and mass in terms of coordinates fixed in the wave. The energy equation for the dispersed phase is the equation for the temperature T_1 in a separate particle (regarded as an ideal mixing reactor), moving along the axis of the channel x with the velocity of the wave u:

$$\rho_1 c_1 u \frac{dT_1}{dx} = \rho_1 Q w (C, T_1) - \frac{\alpha S}{v} (T_1 - T_2). \tag{2.1}$$

Here ρ_1 and c_1 are the density and specific heat capacity of the particle material; Q is the specific heat of reaction; w is the reaction rate; S and v are the surface and volume of the particles; α is the coefficient of heat transfer at the surface of the particle; T_2 is the temperature of the continuous medium; and, C is the concentration (mass fraction) of the reagent in the particle.

The equations for the concentration of the reagent in the particle and the energy for the continuous phase have the form

$$u \frac{dC}{dx} = -w(C, T_1); \tag{2.2}$$

$$(1 - \varphi) \lambda_2 \frac{d^2 T_2}{dx^2} - (1 - \varphi) \rho_2 c_2 \frac{dT_2}{dx} + \varphi \frac{\alpha S}{v}(T_1 - T_2) = 0, \tag{2.3}$$

where φ is the volume content of the particles; λ_2, ρ_2, and c_2 are the thermal conductivity, density, and specific heat capacity of the continuous medium.*

Substituting (2.1) and (2.2) into (2.3) and integrating the equation obtained from the instantaneous section to $+\infty$ with $T_1 = T_2 = T_m$, $C = 0$, $dT/dx = 0$ and $x = +\infty$ we obtain

$$\lambda_2 \frac{dT_2}{dx} = u\rho_2 c_2 (T_m - T_2) + \frac{\varphi}{1 - \varphi} u\rho_1 c_1 (T_1 - T_m) + \frac{\varphi}{1 - \varphi} \rho_1 QuC. \tag{2.4}$$

From Eq. (2.4) with $T_1 = T_2 = T_0$, $C = C_0$, $dT_2/dx = 0$ and $x = -\infty$ we find a relation between the starting and final parameters of the system:

$$\rho_2 c_2 (T_m - T_0) + \frac{\varphi}{1 - \varphi} \rho_1 c_1 (T_m - T_0) - \frac{\varphi}{1 - \varphi} \rho_1 Q C_0 = 0. \tag{2.5}$$

For small particles (we assume that they are spherical and have a radius r) the ratio $\alpha S/v = 3\lambda_2/r^2$, $Nu = \alpha 2r/\lambda_2 = 2$. We introduce dimensionless variables and system parameters:

$$\chi = \frac{3x\lambda_2}{u\rho_1 c_1 r^2}, \quad \Theta = \frac{Tc_1}{Q}, \quad \gamma = \frac{Ec_1}{RQ}, \quad \psi = \frac{\rho_2 c_2}{\rho_1 c_1} \frac{1 - \varphi}{\varphi}, \quad U = \left(\frac{\varphi/3}{1 - \varphi}\right)^{1/2} \frac{\rho_1 c_1 ur}{\lambda_2}.$$

Then Eqs. (2.1), (2.2), and (2.4) assume the form

$$d\Theta_2/d\chi = \psi U^2 (\Theta_2 - \Theta_m) + U^2 (\Theta_1 - \Theta_m) + U^2 C; \tag{2.6}$$

$$d\Theta_1/d\chi = W(C, \Theta_1) - (\Theta_1 - \Theta_2); \tag{2.7}$$

$$dC/d\chi = -W(C, \Theta_1) \tag{2.8}$$

(W is the dimensionless reaction rate).

3. The system (2.6)-(2.8), with the function w given, is autonomous; its solutions can be represented by trajectories in a three-dimensional phase space (Θ_1, Θ_2, C). We shall assume that the chemical reaction is of first order (in the case of polymerization this corresponds to thermal polymerization):

$$w = k_0 C \exp(-E/RT_1).$$

Here k_0 is the rate constant of the reaction; E is the activation energy; and, R is the universal gas constant.

In accordance with the well-known principle of truncating the kinetic function [11] in (2.7) and (2.8) we shall assume that the function

$$W = kC \exp(-\gamma/\Theta_1) \quad (k = \rho_1 k_0 c_1 r^2/(3\lambda_2)) \tag{3.1}$$

equals zero in a neighborhood of the starting values of the temperature Θ_0. For the conditions adopted, taking into account (2.5), the system (2.6)-(2.8) in the part of the phase space $\Theta_2 \geq \Theta_0$, $\Theta_1 \geq \Theta_0$, $C \geq C_0$ has two singular points — the starting position of equilibrium ($\Theta_1 = \Theta_0$, $\Theta_2 = \Theta_0$, $C = C_0$) and the final position of equilibrium ($\Theta_1 = \Theta_m$, $\Theta_2 = \Theta_m$, $C = 0$). The characteristic numbers of the starting position of equilibrium are

$$\lambda_{01,2} = \frac{U^2 \psi - 1}{2} \pm \left[\left(\frac{U^2 \psi - 1}{2}\right)^2 + U^2 (\psi + 1)\right]^{1/2}, \tag{3.2}$$

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*The coefficient $1 - \varphi$ in (2.3) in front of the second derivative of T_2 was omitted in [7-10], while it was included in front of the first derivative of T_2.
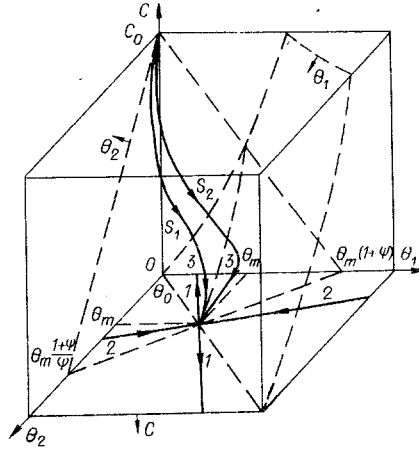
Fig. 1

i.e., the equilibrium position is of the saddle type and lies in the plane $C = C_0$.

Linearizing the system (2.6)-(2.8) in a neighborhood of the final position of equilibrium, from the discriminant

$$\begin{vmatrix} \psi U^2 - \lambda_m, & U^2, & U^2 \\ 1, & -1 - \lambda_m, & k \exp\left(-\dfrac{\gamma}{\Theta_m}\right) \\ 0, & 0, & -k \exp\left(-\dfrac{\gamma}{\Theta_m}\right) - \lambda_m \end{vmatrix} = 0 \tag{3.3}$$

we find $\lambda_{m1} = \lambda_{01} > 0$, $\lambda_{m2} = \lambda_{02} < 0$, $\lambda_{m3} = -k \exp(-\gamma/\Theta_m) < 0$, i.e., the final position of equilibrium, based on the classification of Sideriadis [12], is a stable saddle.

The possibility of a transition from the starting position of equilibrium to the final position is determined by the characteristic directions at the singular points and the position of three zero surfaces in phase space: $C = \Theta_m - \Theta_1 + (\Theta_m - \Theta_2)\psi$, $C = k^{-1}(\Theta_1 - \Theta_2) \cdot \exp(\gamma/\Theta_1)$, $C = 0$, at the points of which $d\Theta_2/d\chi = 0$, $d\Theta_1/d\chi = 0$, $dC/d\chi = 0$, respectively.

The characteristic directions at the singular points are found by calculating the derivatives $d\Theta_2/d\Theta_1$, $dC/d\Theta_1$ there. Dividing (2.8) by (2.7) and evaluating the indefinite form by l'Hospital's method at the final singular point we find

$$\left(\frac{dC}{d\Theta_1}\right)_m = -k \exp\left(-\frac{\gamma}{\Theta_m}\right)\left(\frac{dC}{d\Theta_1}\right)_m \left[-1 + \left(\frac{d\Theta_2}{d\Theta_1}\right)_m + k \exp\left(-\frac{\gamma}{\Theta_m}\right)\left(\frac{dC}{d\Theta_1}\right)_m\right]^{-1}. \tag{3.4}$$

It follows from (3.4) that one of the two values of the derivative $(dC/d\Theta_1)_m$ equals zero. It can be shown, by performing analogous transformations, that it corresponds to two values of the derivative:

$$\left(\frac{d\Theta_2}{d\Theta_1}\right)_{m1,2} = \frac{1 + \psi U^2}{2} \pm \left[\left(\frac{1 + \psi U^2}{2}\right)^2 + U^2\right]^{1/2}. \tag{3.5}$$

We obtain the second value of the derivative $(dC/d\Theta_1)_m$ from (3.4) and the equation

$$\left(\frac{d\Theta_2}{d\Theta_1}\right)_{m3} = \left[1 - k^2 U^{-2} \exp\left(-\frac{2\gamma}{\Theta_m}\right) - \psi k \exp\left(-\frac{\gamma}{\Theta_m}\right)\right]^{-1}, \tag{3.6}$$

found after evaluating the indeterminate form of the derivative $d\Theta_2/d\Theta_1$ at the final point with $(dC/d\Theta_1)_m = 0$. Substituting (3.6) into (3.4) we obtain

$$\left(\frac{dC}{d\Theta_1}\right)_{m3} = \left[-1 + \left(k U^{-2} e^{-\gamma/\Theta_m} + \psi\right)\left(k e^{-\gamma/\Theta_m} - 1\right)\right]\left(\frac{d\Theta_2}{d\Theta_1}\right)_{m3}. \tag{3.7}$$

Thus at the final singular point there exist three characteristic directions, two of which lie in the plane $C = 0$.
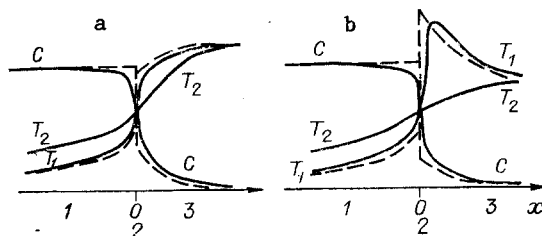
Fig. 2

By performing a similar analysis for the starting singular point it can be shown that at this point there are two characteristic directions, lying in the plane C = 0, and in addition

$$(d\Theta_2/d\Theta_1)_{01,2} = (d\Theta_2/d\Theta_1)_{m1,2}$$

(3.8)

(the numbers of the characteristic directions correspond to the numbers of the characteristic values).

It follows from (2.6)-(2.8) and (3.1) that the trajectories exhibit distinctive behavior in a neighborhood of the starting and final points. It consists of the fact that the plane C = C_0, in which the characteristic directions of the starting singular point lie, is not integral, while the plane C = 0, in which the characteristic directions of the final singular point lie, is integral. This means that the solutions lying in the plane C = 0 in a neighborhood of the final singular point lie wholly in this plane (i.e., there are no parts unique to them that lie in the open part of the phase space). On the other hand, the trajectories lying in the plane C = 0 in a neighborhood of the starting singular point lie mostly in the open phase space. It follows from this that the wave solution of interest to us can be found from the starting singular point along the characteristic direction 1 and by entering the final position of equilibrium only along the characteristic direction 3, making a finite angle with the plane C = 0. The characteristic directions 1 and 2 of the final singular point are not related with the wave solution. Neglecting the chemical reaction in the final part of the wave, as done in [7-10], corresponds to neglecting the characteristic direction 3 at the final singular point, i.e., it essentially leads to throwing away the wave solution sought.

As one can see from (3.6) the slope angle of the projection of the characteristic direction 3 on the plane C = 0 can have a different sign depending on the parameters

$$\left(\frac{d\Theta_2}{d\Theta_1}\right)_{m3} > 0 \quad \text{for} \quad \psi < k^{-1} \exp\frac{\gamma}{\Theta_m} - U^{-2}k \exp\left(-\frac{\gamma}{\Theta_m}\right);$$

(3.9a)

$$\left(\frac{d\Theta_2}{d\Theta_1}\right)_{m3} < 0 \quad \text{for} \quad \psi > k^{-1} \exp\frac{\gamma}{\Theta_m} - U^{-2}k \exp\left(-\frac{\gamma}{\Theta_m}\right),$$

(3.9b)

i.e., the wave solution can enter the final singular point in two different ways. To represent them we shall examine the arrangement of the zero surfaces $d\Theta_1/d\chi = 0$, $d\Theta_2/d\chi = 0$ in the phase space ($\Theta_1 \geq \Theta_0$, $\Theta_2 \geq \Theta_0$, $C \leq C_0$). The zero surface $d\Theta_1/d\chi = 0$ is a plane intersecting the three coordinate planes. The zero surface $d\Theta_2/d\chi = 0$ is a surface passing through the straight line $\Theta_1 = \Theta_2$, C = 0 (Fig. 1). The arrows on the zero surfaces in Fig. 1 mark the regions where the corresponding variables increase. The wave solution emanates from the point C = C_0, $\Theta_1 = \Theta_2 = \Theta_0$ along the characteristic direction 1, lying above the plane $d\Theta_1/d\chi = 0$, and enters the point C = 0, $\Theta_1 = \Theta_2 = \Theta_m$, either always remaining between the surfaces $d\Theta_1/d\chi = d\Theta_2/d\chi = 0$ (solution S_1) or first crossing the surface $d\Theta_1/d\chi = 0$ (solution S_2). In both cases the solutions cross the plane $\Theta_1 = \Theta_2$ and as the final singular point is approached $\Theta_1 > \Theta_2$. In the first case, in a neighborhood of the final singular point the temperatures of the continuous and dispersed phases increase [the values of the parameters satisfy the inequality (3.9a)]; in the second case the temperature of the continuous phase increases while that of the dispersed phase decreases [the value of the parameters satisfy the inequality (3.9b)].

Graphs of the change in the parameters corresponding to the solutions S_1 and S_2 are presented in Figs. 2a and b (solid lines), respectively. The remaining solutions of the
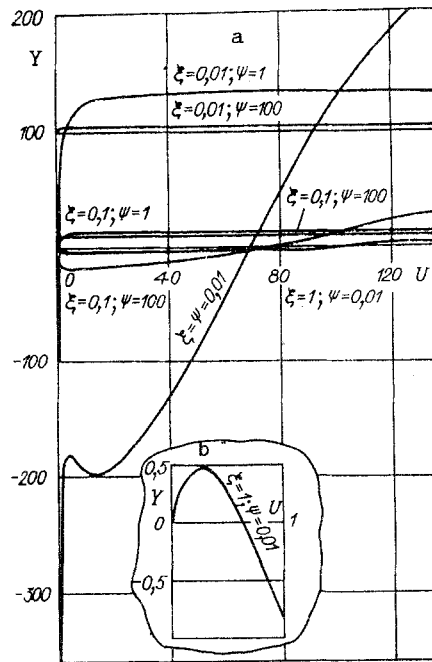
Fig. 3

system (2.6)-(2.8) and (3.1), evidently, are of no interest. The existence of a solution of the type S_2 was proposed in [7] based on physical considerations. It does exist, however, as follows from the foregoing discussion, when the chemical reaction in a neighborhood of the final singular point is taken into account.

4. To obtain analytical expressions for calculating the structure of the wave and its velocity we shall separate three zones in the wave: 1) no chemical reaction, heat exchange occurs between phases, and heat transfer occurs by means of heat conduction along the continuous medium; 2) the rate of the chemical reaction greatly exceeds all transport processes, the temperature of the particles in it increases sharply and the concentration of reagents in them decreases, and we assume that the thickness of the wave equals zero (the particles are significantly smaller than the characteristic dimensions of the channel and the width of the wave); 3) we assume that the solution linearized in a neighborhood of the singular point of the system (2.6)-(2.8) and (3.1) is valid, chemical reaction and heat exchange between the phases as well as heat transfer by means of heat conduction occur simultaneously (dashed lines in Fig. 2).

Integrating the equations (2.6) and (2.7) in the first zone we find

$$\Theta_{11} = B \exp\left(\lambda_{01}\chi\right) + \Theta_m - C_0(\psi + 1)^{-1}; \tag{4.1}$$

$$\Theta_{21} = B(\lambda_{01} + 1) \exp\left(\lambda_{01}\chi\right) + \Theta_m - C_0(\psi + 1)^{-1}; \tag{4.2}$$

the second index for the temperature corresponds to the number of the zone. It follows from (2.7) and (2.8) that in zone 2 the temperature of the particles and the concentration are related by the equation

$$\Theta_{12} = -C_2 + A. \tag{4.3}$$

In the zone 3 the system (2.6)-(2.8), (3.1) after linearization has the solution

$$\Theta_{13} = \Theta_m + D \frac{\lambda\left(\lambda U^{-2} + \psi\right) - 1}{(1 - \lambda)\left(\lambda U^{-2} + \psi\right) + 1} \exp\left(-\lambda\chi\right); \tag{4.4}$$

$$C_3 = D \exp\left(-\lambda\chi\right); \tag{4.5}$$

$$\Theta_{23} = \Theta_m - \frac{D \exp\left(-\lambda\chi\right)}{(1 - \lambda)\left(\lambda U^{-2} + \psi\right) + 1}. \tag{4.6}$$

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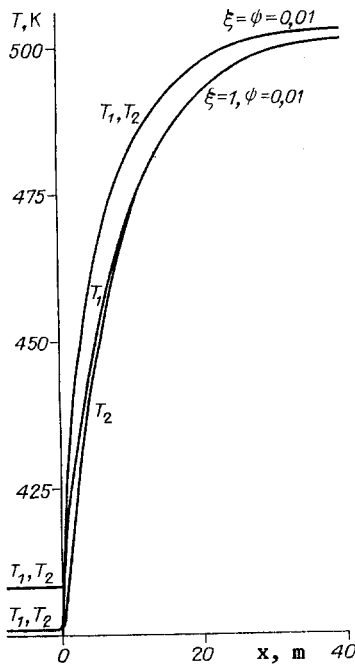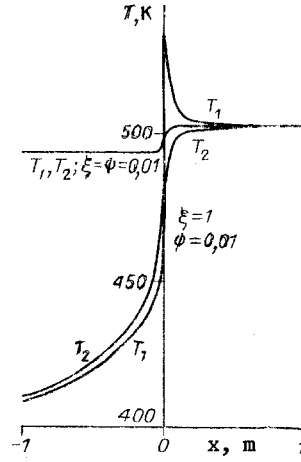
Fig. 4

Fig. 5

In deriving Eqs. (4.1)-(4.6) the boundary conditions at x = ± ∞ were employed; A, B, and D are constants of integration;

$$\lambda = |\lambda_{m3}| = k \exp\left(-\gamma/\Theta_m\right). \tag{4.7}$$

We shall employ the boundary conditions for joining the solutions at the boundaries of the zones, fixing the origin of coordinates in the zone 2 (we call it the reaction front):

$$\Theta_{11}(\chi = 0) = \Theta_{120}, \ \Theta_{21}(\chi = 0) = \Theta_{22}, \ C_3(\chi = 0) = C_k, \ \Theta_{21}(\chi = 0) =$$
$$= \Theta_{23}(\chi = 0), \ \Theta_{13}(\chi = 0) = \Theta_{12k}. \tag{4.8}$$

Substituting (4.8) into (4.1)-(4.6) we obtain

$$\tag{4.9}$$

$$B + \Theta_m - C_0(\psi + 1)^{-1} = \Theta_{120};$$

$$B(\lambda_{01} + 1) + \Theta_m - C_0(\psi + 1)^{-1} = \Theta_{22}; \tag{4.10}$$

$$D = C_k; \tag{4.11}$$

$$B(\lambda_{01} + 1) - C_0(\psi + 1)^{-1} = -D\left[(1 - \lambda)(\lambda U^{-2} + \psi) + 1\right]^{-1}; \tag{4.12}$$

$$\Theta_m + D\left[\lambda(\lambda U^{-2} + \psi) - 1\right]\left[(1 - \lambda)(\lambda U^{-2} + \psi) + 1\right]^{-1} = \Theta_{12k}. \tag{4.13}$$

Here, as follows from (4.3),

$$\Theta_{120} = A - C_0; \tag{4.14}$$

$$\Theta_{12k} = A - C_k. \tag{4.15}$$

We shall assume that at the start of the zone 2 the heat flux released in the chemical reaction equals the heat flux flowing to the particles from the continuous phase:

$$kC_0 \exp\left(-\gamma/\Theta_{120}\right) = \Theta_{22} - \Theta_{120}, \tag{4.16}$$

while at the end of zone 2 the heat flux released in the chemical reaction equals the heat flux flowing from the particles into the continuous phase:

$$kC_k \exp\left(-\gamma/\Theta_{12k}\right) = \Theta_{12k} - \Theta_{22}. \tag{4.17}$$

TABLE 1

Mixture	β	ρ_1	ρ_2	c_1	c_2	$k_0, \sec^{-1}$	Q, J/kg	E, J/mole	λ_2, W/(m·K)
		kg/m³		J/(Kg·K)					
Styrene–water	0,0494	$9,06 \cdot 10^2$	10^3	$1,75 \cdot 10^3$	$4,19 \cdot 10^3$	$4,53 \cdot 10^6$	$7,2 \cdot 10^5$	$8,46 \cdot 10^4$	0,68
Styrene–air	0,0494	$9,06 \cdot 10^2$	0,747	$1,75 \cdot 10^3$	1,025	$4,53 \cdot 10^6$	$7,2 \cdot 10^5$	$8,46 \cdot 10^4$	0,0393
Oxygen–hexane	0,0454	17,7	550	$3,4 \cdot 10^3$	$1,7 \cdot 10^3$	$2,26 \cdot 10^{11}$	$4,2 \cdot 10^7$	$1,26 \cdot 10^5$	2,1

The equations (3.2), (4.7), and (4.9)-(4.17) contain the parameters U, k, B, Θ_m, C_0, ψ, Θ_{120}, λ_{01}, Θ_{22}, D, C_k, λ, Θ_{12k}, A, γ, three of which (γ, k, ψ) are determined by the thermophysical and kinetic properties of the system under study and can be regarded as given. Therefore it is sufficient to give one more parameter so that the system of equations can be solved. For example, this parameter could be the final temperature Θ_m. After the system is solved with the given Θ_m the dimensionless velocity of the wave U is determined. An important property of the model developed is that the condition that the temperature of the continuous phase before the front is equal to the temperature after the front (4.12) and the ratios of the temperatures of the particles and concentrations on the front (4.9), (4.11), and (4.13)-(4.15) imply that the derivatives of the temperature of the continuous phase with respect to the coordinate χ vanish on both sides of the front.

Indeed, eliminating the parameters A, C_0, Θ_{120}, Θ_{12k} from (4.9), (4.11)-(4.15) we obtain the relation

$$B = C_k \lambda (\lambda_{01} + 1)^{-1} [(1 - \lambda)(\lambda U^{-2} + \psi) + 1]^{-1}, \tag{4.18}$$

which, as one can easily verify by differentiating Eq. (4.2) and (4.6), shows that the derivatives of the temperature of the continuous phase with respect to χ on both sides of the front are equal. Thus the temperature profile in the continuous phase, obtained with the help of this model, is smooth.

Eliminating systematically the unknown parameters from (4.7) and (4.9)-(4.17) we obtain an equation for calculating the velocity of the wave:

$$\frac{\Theta_m}{\gamma} = \frac{1 - V}{\ln w_2} + \frac{V}{\ln w_1}, \tag{4.19}$$

where

$$V = \frac{1}{\lambda} \frac{\lambda_{01}(\lambda + U^2 \psi) + U^2(1 + \psi)}{\lambda_{01}(1 + \psi \lambda + \psi^2 U^2) + (1 + \psi)(\lambda + \psi U^2)};$$

$$w_1 = \frac{\lambda_{01}(\psi + 1)^{-1}}{U^2 + (\lambda_{01} + 1)(\lambda + \psi U^2)}; \quad w_2 = \frac{\lambda + \psi U^2}{(\lambda + U^2 \psi)(1 - \lambda) + U^2}.$$

Equation (4.19) can be solved graphically based on the intersection of the right side of this equation with the straight line Θ_m/γ as a function of U.* After U has been determined λ_{01} is calculated from (3.2). From (4.7) and (4.16) we obtain

$$C_0 = \frac{\Theta_m(\psi + 1)}{1 - \gamma(\Theta_m \ln w_1)^{-1}} \frac{U^2 + (\lambda_{01} + 1)(\lambda + U^2 \psi)}{U^2 - \lambda + (\lambda_{01} + 1)(\lambda + U^2 \psi)} \tag{4.20}$$

and the constants of integration are

$$D = C_0 \frac{\psi + 1 + \lambda_{01} \psi}{\psi + 1} \frac{U^2 + (\lambda + U^2 \psi)(1 - \lambda)}{U^2 + (\lambda + U^2 \psi)(\lambda_{01} + 1)}; \tag{4.21}$$

$$B = \frac{C_0}{\psi + 1} \frac{\lambda}{U^2 + (\lambda_{01} + 1)(\lambda + U^2 \psi)}. \tag{4.22}$$

Once U, λ_{01}, C_0, D, B are known the profile of the temperatures and concentrations in the wave can be calculated from (4.1), (4.2), and (4.4)-(4.6).

5. The determination of the velocity of the wave reduces to constructing the right side of Eq. (4.19) (denoting it by Y) as a function of U, which depends on the parameters ψ and λ. The function $Y(U)$ was calculated for a wide range of parameters ($\psi = 10^{-2}$ -10^2, $\lambda = 10^{-4}$ -10). Figure 3a shows the results of the calculation, giving an idea of the character of the dependence $Y(U; \psi, \lambda)$. It has a horizontal asymptote in the limit $\varphi \to \infty$, equal to $Y_\infty = [1 - (\lambda \psi)^{-1}]/[\ln \psi - \ln(\psi - \psi \lambda + 1)]$, and crosses the ordinate axis at $Y_0 = -\ln^{-1}(1 - \lambda)$. For large values of $\psi(\psi \gg 1)$ the dependence Y becomes a straight line,

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*We note that the first term on the right side of (4.19) is indefinite — the numerator and denominator vanish at $U^2 = \lambda^2(1 - \lambda \psi)^{-1}$.

TABLE 2

λ	r, m	u_1	u_2	C_{01}	C_{02}	T_{01}	T_{02}
		m/sec				K	
0,01	$0{,}318 \cdot 10^{-3}$	0,0464	$1{,}23 \cdot 10^{-1}$	0,233	0,021	408,05	494
1	$3{,}18 \cdot 10^{-3}$	0,0633	$3{,}84 \cdot 10^{-4}$	0,25	0,233	401	408,1

parallel to the abscissa axis in virtually the entire domain of U. For values of λ close to unity Y lies in a neighborhood of the abscissa axis and for $\lambda = 1$ passes through the origin (Fig. 3b); it has a maximum in the positive and a minimum in the negative quadrant of the half-plane (Y, U). Decreasing λ causes a stronger curvature of the dependence Y(U), while for $\lambda > 1$ the function Y vanishes for small and large U. Since the ratio $\Theta_m/\gamma = T_m R/E = \beta$ for most substances varies in the range from several hundredths to several tenths, the points of intersection of Y and the straight line Θ_m/γ sought practically coincide (in the scale of Fig 3a) with the points of intersection of the function Y and the abscissa axis. It follows from Fig. 3a that there can be 2, 3 ($\lambda \approx 1$) or no ($\psi \gg 1$) such intersections. The parameter ψ is the ratio of the heat capacities of the masses of the continuous phase and the particles contained per unit mass of the mixture. It is obvious that if the heat capacity of the mass of continuous phase is much greater than the heat capacity of the mass of particles, then the heat of reaction released in the particles will be absorbed by the continuous phase without any appreciable changes in the temperature of the continuous phase, and under these conditions the chemical reaction cannot propagate through the medium.

The calculations were performed for three mixtures of substances: water—styrene ($p = 10^5$ N/m^2, $T_m = 503$ K, $r = 1.3 \cdot 10^{-4}$ m, $\varphi = 0.2$); air—styrene ($p = 10^5$ N/m^2, $T_m = 503$ K); liquid hexane—oxygen ($p = 5 \cdot 10^6$ N/m^2, $T_m = 687$ K, $r = 10^{-4}$ m, $\varphi = 0.064$). The values of the thermophysical and kinetic parameters of these mixtures are presented in Table 1 [8, 13].

For the styrene—water mixture we obtained for the conditions chosen the following values of the determining parameters: $\psi = 10$, $\lambda = 10^{-4}$. A graph of the function Y, in this case, is a line that for very large values of Y ($Y_\infty = 10{,}481$, $Y_0 = 9{,}984$) lies close to a straight line parallel to the U-axis. There are no wave solutions for these conditions and conditions close to them, namely, they correspond to real conditions under which the process of polymerization of styrene in water is conducted.

For a system of oxygen bubbles in liquid hexane $\psi = 227$, $\lambda = 0.0056$. Wave solutions likewise do not exist for these values of the parameters. The main reason for the nonexistence of wave solutions in these cases is that the value of ψ is large; this is attributable primarily to the high density of the continuous phase.

The parameter ψ decreases by several orders of magnitude, if the reaction of thermal polymerization of styrene is conducted in a gas phase. Thus even with a comparatively low volume content of styrene droplets in air $\varphi = 0.046$, $\psi = 0.01$. For a radius of the drops $r = 0.318 \cdot 10^{-3}$ m $\lambda = 0.01$ and, according to Fig. 3a, there exist two wave solutions with velocities $u_1 = 0.0464$ m/sec and $u_2 = 1.23 \cdot 10^{-4}$ m/sec. For $r = 3.18 \cdot 10^{-3}$ m $\lambda = 1$ and, according to Fig. 3, there exist three wave solutions with $u_1 = 0.0633$ m/sec, $u_2 = 3.84 \cdot 10^{-4}$ m/sec, and $u_3 = 1.23 \cdot 10^{-5}$ m/sec. The calculation showed that the third wave solution is physically meaningless, since the starting concentration of monomer in the droplets corresponding to it $C_0 > 1$.

Graphs of the structure of the wave corresponding to the wave solutions u_1 and u_2 obtained are shown in Figs. 4 and 5, respectively. It follows from the calculation that for every solution pair $u_{1,2}$ there exist starting parameters C_0 and T_0 that differ from the values of these parameters for other solutions (Table 2); in addition $C_0 < 1$. The latter means that the liquid in the starting state is a mixture of a monomer with an inert substance, for example, polystyrene. Of the four wave solutions only one u_2 with $r = 3.18 \cdot 10^{-3}$ m is of the type 2; the others are of the type 1. The width of the wave u_1 equals several tens of meters, while the width of the wave u_2 is smaller and varies from 0.1 to 2 m. In both cases the width of the wave is many times greater than the diameter of the particles. Solutions of the type 1 have a temperature profile that is characteristic for spontaneous combustion regimes. There is virtually no discontinuity in the temperature of the particles

in the zone 2 of these solutions. For solutions of the type 2 there is a significant discontinuity in the temperature of particles in zone 2. They correspond to the combustion regime.

We shall evaluate the validity of the condition, adopted in Sec. 2, for the temperature to be independent of the instantaneous radius in a particle for the wave solutions obtained (the condition of an ideal mixing reactor). For this we compare the characteristic time for the release of heat from a particle to the carrying phase $t_1 = 2r\rho_1 c_1/(6\alpha)$ with the characteristic time for the transfer of heat by means of heat conduction within the particle $t_2 = \rho_1 r^2 c_1/(\pi\lambda_1)$ [14]. Taking into account the fact that the value of the coefficient of heat transfer α equals exactly λ_2/r for particles that are at rest relative to the carrying phase (see, e.g., [14, 15] for the system styrene—air we obtain $t_1/t_2 \approx 11$, i.e., the time required for heat transfer in a particle is many times shorter than the time necessary for heat to be removed from the surface of the particle. The value of the ratio t_1/t_2 for other systems, studied in this work, but not having wave solutions, is also greater than unity. There is no basis for studying forms of heat transfer in a particle other than heat conduction, since the known circulation of mass in liquid and gaseous particles is caused by the motion of the particles [16], which is absent in this formulation. If, however, they do exist, they will merely reduce the time for equalizing the temperature over the volume of a particle.

The stability of waves solutions in a dispersed medium must be studied separately. This analysis must be performed (unlike [7-10]) based on an investigation of nonstationary differential equations.

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