Theoretical Aspects of Self-Propagating Reaction Fronts in Condensed Medium

Victor M. Ilyashenko, Stanislav E. Solovyov, and John A. Pojman
Dept. of Chemistry and Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406

Exothermic chemical reactions are capable of autocatalytic self-propagation in a condensed reactive medium as a thermal wave. These take place in self-propagating high-temperature synthesis, frontal polymerization, curing of epoxy resins, and various solid-phase reaction processes. The lack of accurate analytical solutions for the front velocity and spatial parameter distributions has led to a period of approximate analytical solutions based on the infinitely narrow reaction zone assumption. A more accurate reaction zone approximation is presented that results in new equations for temperature and concentration spatial distributions as well as the wave velocity. Necessary conditions for nondegeneration of the combustion wave were also obtained.

Introduction

Many exothermic chemical reactions are capable of self-propagation in a reactive medium as a thermal wave. Besides well-known processes of gaseous combustion such regimes also occur when both reactants and products of the reaction are in condensed phase, for example, self-propagating high-temperature synthesis (SHS) (Merzhanov, 1990), frontal polymerization (Chechilo et al., 1972; Pojman et al., 1994), curing of epoxy resins (Arutiunian et al., 1975), and various solid-phase chemical reactions (Maksimov et al., 1965). Calculation of self-propagation velocity for such processes is based on the simultaneous solution of the thermal conductivity equation with heat source and kinetic equations for chemical reactions. Mass transfer due to diffusion is usually neglected for processes in condensed phase.

There are many approximate analytical solutions for the stationary front velocity of first-order chemical reaction (Novozhilov, 1961; Margolis, 1983, Puszynski et al., 1987; Merznanov and Khaikin, 1988; Varma et al., 1991; Volpert and Volpert, 1991). The majority of them is based on the infinitely narrow reaction zone approximation. In this article we present a new approach to the description of reaction zone that results in an approximate analytical solution of the problem. Other developments include analytical solutions for the spatial temperature and concentration distributions. Necessary conditions for wave propagation without thermal runaway were also obtained.

Governing Equations

We consider heat and mass balance equations for an infinitely long reactor. Adiabatic conditions on the boundaries are assumed, and the chemical reaction is of first order. Basic stationary one-dimensional equations describing the system take the following form

$$a\frac{d^2T}{dx^2}+u\frac{dT}{dx}+u\frac{\Delta H}{c_p}\frac{dc}{dx}=0 \tag{1}$$

$$\frac{dc}{dx}=\frac{k_0}{u}\exp\left(\frac{-E_a}{RT}\right)c \tag{2}$$

with boundary conditions:

$$x=-\infty:\quad \frac{dT}{dx}=0 \tag{3}$$

$$x=+\infty:\quad T=T_0,\quad c=c_0. \tag{4}$$

Analytical Solution

Integrating Eq. 1 with respect to x with conditions 3 and 4, we obtain a relationship for the temperature gradient vs. the concentration of the reactive medium:

$$-\frac{dT}{dx}=\frac{u}{a}(T-T_m)+\frac{u}{a}\frac{\Delta H}{c_p}c. \tag{5}$$

Correspondence concerning this article should be addressed to J. A. Pojman.

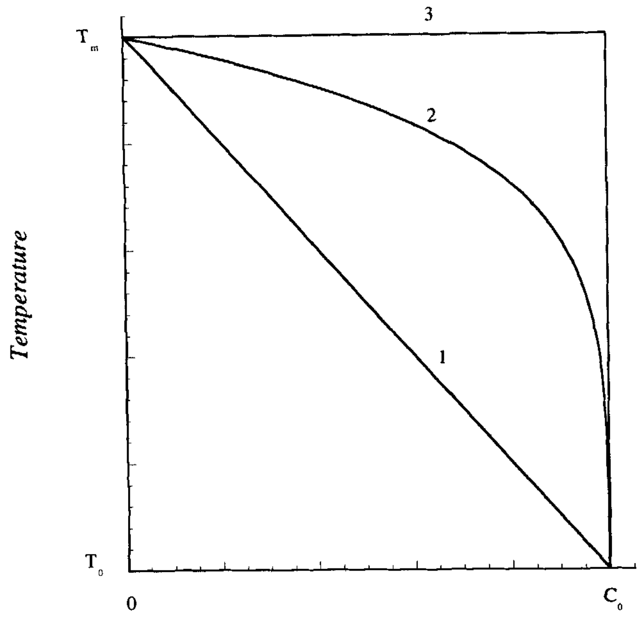

Figure 1. Typical phase diagrams for wave propagation.

Dividing Eq. 5 by Eq. 2 we get a differential relationship between temperature and concentration while the space coordinate is excluded:

$$\frac{dT}{dc} = -\frac{u^2}{k_0 a}\left(\frac{T - T_m}{c} + \frac{\Delta H}{c_p}\right)\exp\left(\frac{E_a}{RT}\right). \tag{6}$$

Differential Eq. 6 is basic for an approximate calculation of the front velocity. However, separation of variables is possible only after some simplifications and additional assumptions. Although Novozhilov's equation (Novozhilov, 1961) was derived using another approach, his simplifications are reduced to neglecting the term $(T - T_m)/c$ in Eq. 6 by equating the current temperature T to the combustion temperature T_m. It is assumed that the reaction zone is narrow, and the reaction occurs only at temperatures close to T_m.

An approximate estimate of the term $(T - T_m)/c$ allows us to "widen" the reaction zone while still obtaining a solution of Eq. 6 by separation of variables. For this purpose let us consider a typical phase diagram of a first-order reaction wave. It can be seen from Figure 1 (curve 2) that in the combustion zone the temperature dependence on the concentration is close to a linear function, that is, the term $(T - T_m)/c$ in this zone changes weakly. Thus it is possible to assume this term to be constant for the entire combustion zone, and equal to the derivative of the phase curve at $T = T_m$:

$$\frac{T - T_m}{c} \approx \left(\frac{dT}{dc}\right)_{T = T_m,\, c = 0}. \tag{7}$$

In other words, we approximate the temperature dependence on concentration in the reaction zone by the straight line going through the point T_m with the slope given by the phase diagram at this point. Noting that

$$\left(\frac{T - T_m}{c}\right)_{T \to T_m,\, c \to 0} = \left(\frac{dT}{dc}\right)_{T = T_m,\, c = 0}, \tag{8}$$

we can find the derivative of the phase curve at the temperature T_m from Eq. 6 as

$$\left(\frac{dT}{dc}\right)_{T = T_m,\, c = 0} = -\frac{u^2}{k_0 a \exp(-E_a/RT_m) + u^2}\,\frac{\Delta H}{c_p}. \tag{9}$$

By substituting Eq. 9 into Eq. 6 along with relation 7, after simple transformations we can separate variables in Eq. 6 and integrate it with boundary conditions 3 and 4:

$$\frac{dT}{dc} = -\frac{u^2}{k_0 a}\left(1 - \frac{u^2}{k_0 a \exp(-E_a/RT_m) + u^2}\right)\frac{\Delta H}{c_p}\exp\left(\frac{E_a}{RT}\right) \tag{10}$$

$$\frac{\Delta H}{c_p}\,\frac{u^2 k_0 a \exp(-E_a/RT_m)}{u^2 + K_0 a \exp(-E_a/RT_m)}\int_{c_0}^{0} dc = k_0 a \int_{T_0}^{T_m} \exp\left(-\frac{E_a}{RT}\right) dT. \tag{11}$$

The well-known Frank-Kamenetskii (F-K) approximation (Frank-Kamenetskii, 1969) can be used to integrate the right part of Eq. 11, resulting in

$$\frac{\Delta H}{c_p}\,\frac{u^2 c_0}{u^2 + k_0 a \exp(-E_a/RT_m)} = \frac{RT_m^2}{E_a}. \tag{12}$$

Noting that

$$\frac{\Delta H}{c_p} c_0 = T_m - T_0, \tag{13}$$

we finally obtain the equation for the square of the wave velocity from Eq. 12:

$$u^2 = \frac{RT_m^2 k_0 a}{E_a(T_m - T_0) - RT_m^2}\exp\left(-\frac{E_a}{RT_m}\right). \tag{14}$$

Results and Discussion

All analytical relationships in this article were verified by comparison with the results of numerical simulations. The nonstationary one-dimensional problem was considered:

$$\begin{cases} \dfrac{\partial T}{\partial t} = a\dfrac{\partial^2 T}{\partial x^2} - (T_m - T_0)\dfrac{\partial \xi}{\partial t} \\ \dfrac{\partial \xi}{\partial t} = -k_0 \exp\left(-\dfrac{E_a}{RT}\right)\xi \end{cases}$$

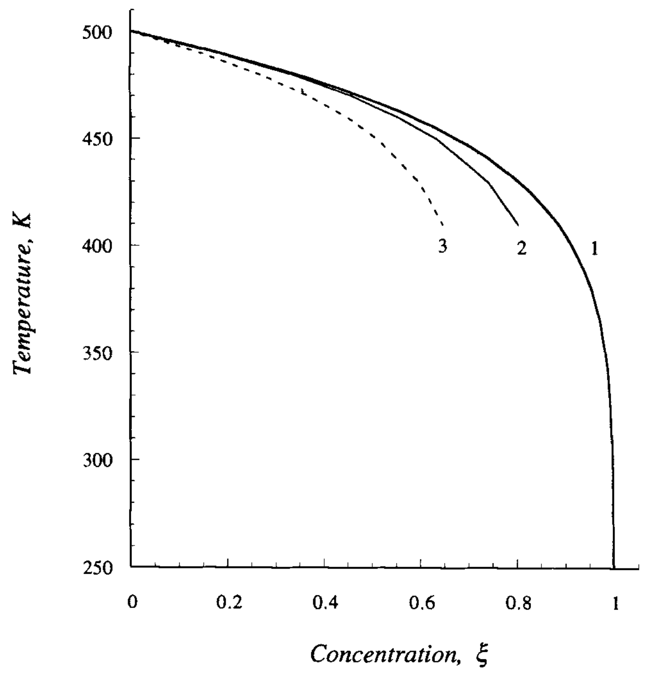

Figure 2. Analytical combustion zone approximations vs. diagram obtained numerically.

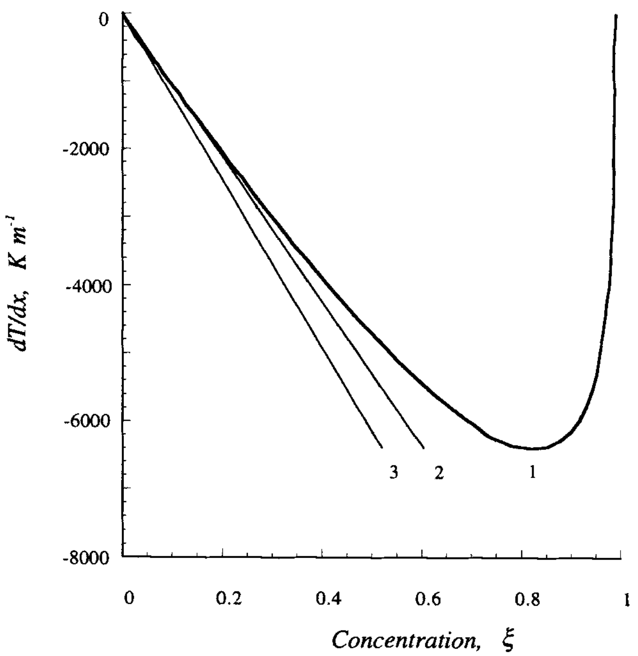

Figure 3. Approximation of temperature gradient in combustion zone by different analytical solutions.

with initial and boundary conditions:

$$T(0)=\begin{cases}T_m, & 0<x\le x_f\\ T_0, & x_f<x<L\end{cases}\qquad \xi(0)=\begin{cases}0, & 0<x\le x_f\\ 1, & x_f<x<L\end{cases}$$

$$0\le x\le L,\qquad \frac{dT}{dx}=0\quad \text{for}\quad x=0\quad\text{and}\quad x=L,$$

where $\xi = c/c_0$ is the dimensionless concentration, $L = 0.2$ m is the reactor length, and x_f is the length of the ignition zone (usually $0 \le x_f \le 0.05\cdot L$).

Solutions were obtained for the following set of constants that relate to frontal polymerization processes:

$$T_0 = 250\ \text{K},\qquad T_m = 500\ \text{K}$$
$$\frac{E_a}{R} = 5{,}000\ \text{K},\qquad k_0 a = 2.2\ \text{m}^2\cdot\text{s}^{-1}.$$

All presented numerical results including calculated velocity of front propagation were taken after a steady solution of the system had been reached. Conservative finite difference schemes on an adapting space grid with a constant integration time step were used for the numerical solution of the problem.

Figure 2 represents the system phase portraits, obtained numerically (curve 1), obtained with Eq. 10 (curve 2), and its simplified form (curve 3) corresponding to the infinitely narrow reaction zone approximation. It is also important to show how the numerically simulated temperature gradient (curve 1, Figure 3) is approximated in the combustion zone by our solution (curve 2), and Novozhilov's approximation (curve 3). Thus, comparative analysis clearly shows a higher accuracy of the new reaction zone approximation.

Further discussion is greatly simplified with an introduction of the following dimensionless variables:

$$\gamma=\frac{E_a}{RT_m},\qquad \beta=\frac{T_m-T_0}{T_m},\qquad \vartheta=\frac{T}{T_m},$$
$$w^2=u^2/k_0 a\exp\left(\frac{-E_a}{RT_m}\right).$$

In this case, Eq. 12 takes the following form:

$$w_a^2=\frac{1}{\gamma\beta-1}\tag{15}$$

and Novozhilov's equation looks like

$$w_N^2=\frac{1}{\gamma\beta}.\tag{16}$$

Both Eq. 15 and Eq. 16 contain two compensating errors. The first one is caused by an incomplete description of the reaction zone and lowers the calculated front velocity. The second one is a result of the approximate integration from using the F-K technique, and it increases the front velocity. For an estimation of the role of each approximation we write Eq. 15 and Eq. 16 without the F-K approximation and use the tilde sign to discriminate from previous results:

$$\frac{\tilde{w}_a^2}{1+\tilde{w}_a^2}=\frac{e^\gamma}{\beta}\int_{1-\beta}^{1}\exp\left(\frac{-\gamma}{\vartheta}\right)d\vartheta.\tag{17}$$

$$\tilde{w}_N^2=\frac{e^\gamma}{\beta}\int_{1-\beta}^{1}\exp\left(\frac{-\gamma}{\vartheta}\right)d\vartheta.\tag{18}$$

Table 1. Comparison of Analytical and Numerical Calculations of the Front Velocity

β	γ	w_E	w_N	w_a	$\tilde{w}_N$	$\tilde{w}_a$
0.2	40	0.390	0.353	0.378	0.345	0.368
0.33	20	0.428	0.389	0.423	0.372	0.401
0.5	15	0.384	0.365	0.392	0.344	0.366
0.5	12	0.436	0.408	0.447	0.380	0.410
0.5	10	0.487	0.447	0.500	0.410	0.451
0.625	10	0.416	0.400	0.436	0.367	0.395
0.7	10	0.386	0.378	0.408	0.346	0.369

In Table 1 we present the results of numerical calculations of the velocity w_E published in Varma et al. (1991). The values of the front velocity obtained by using Eqs. 15–17 and 18 are added to the table. As seen from Table 1 the value of $\tilde{w}_a$ is always more accurate than that of $\tilde{w}_N$ because of a better reaction zone approximation. The error of the F-K approximate integration distorts the picture. At small values of $\gamma \approx 10$ the accuracy of Eq. 16 increases due to mutual compensation of errors. As γ increases, the integration error decreases much faster than error from the infinitely narrow reaction zone approximation. That is why Novozhilov's equation has a higher relative error at higher γ despite the fact that both the infinitely narrow zone and F-K approximation become more valid as $\gamma \to \infty$. The effect of β on the F-K approximation accuracy becomes significant only when $\gamma < 15$, $\beta < 0.3$, and $\gamma > 15$, $\beta < 0.2$. (This estimation was obtained by numerical calculation of the F-K integration error.) We do not include the analysis of the β effect here because of a narrow range of its significance.

On average, Eq. 15 has a higher accuracy than Eq. 16, but at $\gamma \leq 18$ it leads to results exceeding numerical values of front velocity due to more accurate reaction zone approximation and, correspondingly, weaker compensation of the F-K integration error. Equations for the front velocity obtained in Puszynski et al. (1987) and Varma et al. (1991) are built on the infinitely narrow reaction zone approximation and more accurate integration than F-K. As a result the error of thin zone assumption was not compensated, and those more strict equations lose in accuracy compared to Novozhilov's equation.

In conclusion of the comparative analysis of front velocity equations in some way based on Novozhilov's expression, we should note the equation obtained in Margolis (1983) by using the perturbation expansion technique:

$$w_M^2 = \left(\beta\gamma + 2\beta - \frac{\pi^2}{6} \right)^{-1}. \tag{19}$$

It is the most accurate solution for the front velocity of a first-order reaction thermal wave in condensed medium.

Temperature and concentration profiles

One of the advantages of the reaction zone approximation described earlier is the possibility to determine the temperature profile in the combustion zone. The differential equation relating temperature and spatial coordinate can be derived by combining Eqs. 5, 7 and 9:

$$\frac{dT}{dx} = \frac{k_0}{u} \exp\left(-\frac{E_a}{RT_m} \right)(T - T_m). \tag{20}$$

To integrate Eq. 20 it is necessary to choose some initial space coordinate. The most convenient in this case is to accept that the temperature at the initial coordinate $x = 0$ is one degree less than combustion temperature T_m. Considering this it is possible to integrate Eq. 20

$$\int_0^{\ln(T_m - T)} d\ln(T_m - T) = \frac{k_0}{u} \exp\left(-\frac{E_a}{RT_m} \right) \int_0^x dx \tag{21}$$

$$\ln(T_m - T) = \frac{k_0}{u} \exp\left(-\frac{E_a}{RT_m} \right) x. \tag{22}$$

The equation for the temperature profile in the reaction zone has the following form:

$$T = T_m - \exp\left[\frac{k_0}{u} \exp\left(-\frac{E_a}{RT_m} \right) x \right]. \tag{23}$$

The comparison of the results calculated according to Eq. 23 (dots) with numerical results (line) is shown in Figure 4. Because the heat conductivity effect was only partially taken into account, the analytical temperature profile is always sharper than the numerical one. However, as can be seen from Figure 4, at least a 10–20 degree range in the combustion zone is approximated satisfactory for the case considered.

The entire temperature profile picture can be drawn by matching combustion and heat conductivity curves. Assuming $x = 0$ in the matching point (point of equal derivatives) and

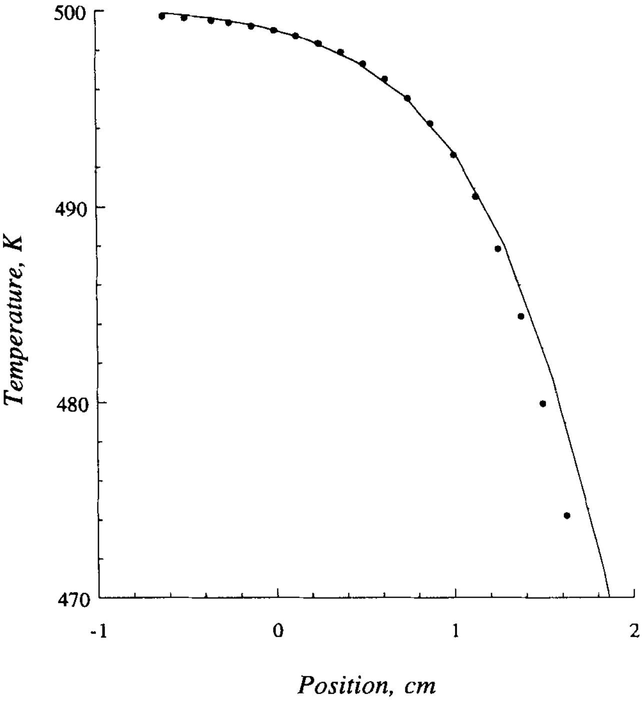

Figure 4. Analytical and numerical temperature profiles in combustion zone.

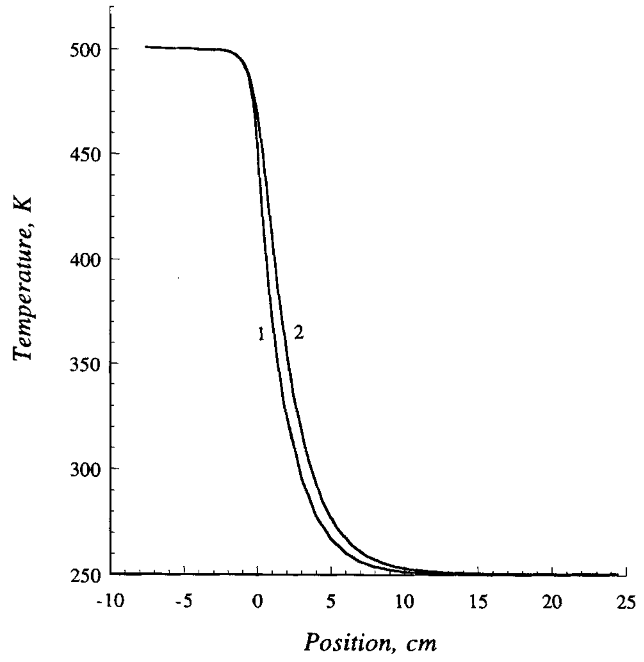

Figure 5. Analytical (1) vs. numerical (2) temperature profiles in propagating reaction wave.

omitting routine steps, it is possible to write the temperature distribution as

$$\begin{cases} T = T_m\left(1 - \dfrac{1}{\gamma}\exp\left[\dfrac{k_0}{u}\exp(-\gamma)x\right]\right), & \text{for } x < 0 \\ T = T_0 + \left(\dfrac{\gamma - 1}{\gamma}T_m - T_0\right)\exp\left(-\dfrac{u}{a}x\right), & \text{for } x \geq 0. \end{cases} \tag{24}$$

The temperature profile can be easily transformed into a concentration profile by using Eqs. 9 and 12:

$$\begin{cases} c = c_0\exp\left[\dfrac{k_0}{u}\exp(-\gamma)x\right], & \text{for} x < 0 \\ c = c_0, & \text{for } x \geq 0. \end{cases} \tag{25}$$

Comparison of analytical and numerical profiles is shown in Figures 5 and 6. It can be seen that the temperature and concentration distributions (Eqs. 24 and 25) take a form corresponding to infinitely narrow reaction zone approximation as $\gamma \rightarrow \infty$.

Conditions for nondegeneration of the combustion wave

We note that Eq. 15 contains some restrictions with respect to physical parameters of the reaction propagation process as well as physico-chemical properties of the reactants; namely, the denominator of Eq. 15 must be positive, that is,

$$\gamma\beta > 1. \tag{26}$$

To find the origin of these conditions and their physical meaning, let us turn to the phase diagram in Figure 1. It is clear that a whole phase manifold for the reactive processes under consideration lies between line 1 corresponding to homogeneous reaction (infinitely large front velocity) and line 3 corresponding to infinitely slow front propagation. To satisfy boundary conditions (4) and avoid the homogeneous reaction regime, it is necessary that the derivative dT/dc at the maximum temperature (see Eq. 9) be greater than the ratio $-\Delta H/c_p$ corresponding to the slope of line 3:

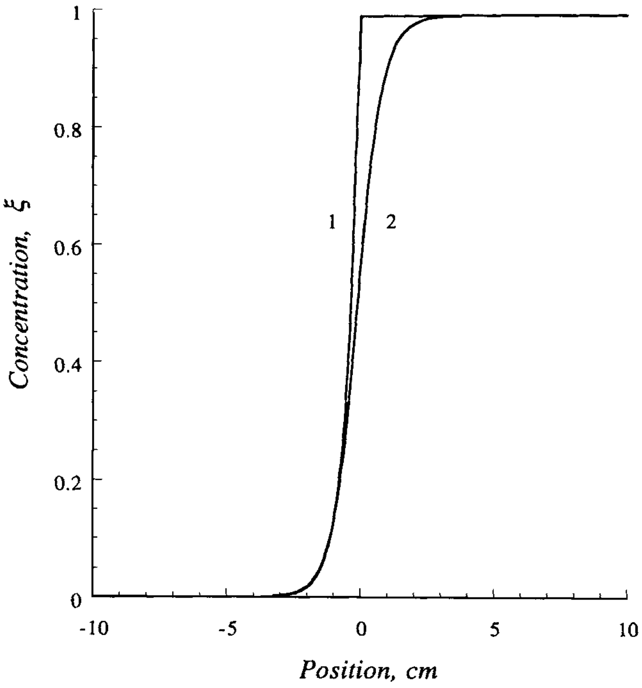

Figure 6. Analytical (1) vs. numerical (2) concentration in propagating reaction wave.

$$\left(\frac{dT}{dc}\right)_{T = T_m,\, c = 0} > -\frac{\Delta H}{c_p}. \tag{27}$$

By taking into account Eqs. 9 and 11 this inequality is easily reduced to Eq. 26 and represents necessary conditions for avoiding thermal runaway.

It is interesting to note that the condition from Eq. 26 is qualitatively the same as those described by Merznanov and Khaikin (1988), in spite of the fact that those conditions were obtained numerically (Aldushin et al., 1978) for the homogeneous combustion systems with the first-order reaction and equal diffusion and heat conductivity coefficients.

A more accurate analytical boundary for the combustion wave nondegeneration can be obtained from Eq. 19 by substituting it into Eq. 9 and using inequality 27 or directly from the denominator of Eq. 19:

$$\beta\gamma + 2\beta > \frac{\pi^2}{6}. \tag{28}$$

Equation 28 can be used for a more detailed study of degeneration boundary.

It should be noted that the necessary nondegeneration conditions were obtained using the stationary approach. In fact, we analyze the conditions when the solution of the stationary problem degenerates. Considerations based on physical sense allowed us to conclude that the nonexistence of a stationary solution corresponds to the necessary conditions for degeneration of the thermal wave.

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Notation

a = thermal diffusivity
c = reactant concentration
c_p = heat capacity
E_a = activation energy
k_0 = frequency factor
R = universal gas constant
t = time
u = front velocity
w = dimensionless front velocity
x = distance

Greek letters

β = dimensionless temperature parameter $[1-T_0/T_m]$
γ = dimensionless activation energy $[E_a/RT_m]$
ϑ = dimensionless temperature $[T/T_m]$

Subscripts

a = value obtained from Eq. 15
E = value cited from Varma et al. (1991)
M = value obtained from Eq. 19
N = value obtained from Eq. 16
0 = initial value

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