Physical Chemistry

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1961

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Abstract

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ON THE THEORY OF FLAME PROPAGATION IN SYSTEMS WITH UNBRANCHED CHAIN REACTIONS

(Presented by Academician V. N. Kondrat' ev, 20 VII 1960)

In ([1–6]), relations were obtained for determining the flame-propagation velocity for cases in which the diffusion coefficients of the initial substances were equal to the coefficient of thermal diffusivity; in this, the concentrations of the initial substances were regarded as linear functions of temperature. In the present article a solution of the problem is set forth with account taken of the diffusion equation for the initial substance.

The scheme of the model unbranched chain reaction, in which A is the initial substance, P the active center, and C the reaction product, is adopted, in accordance with ([1,3,7]), in the following form:

$$\mathrm{A} \to 2\mathrm{P}, \quad \Phi_R = h_R R = h_R F_R(T')\, n_A; \tag{1}$$

$$\mathrm{P} + \mathrm{A} \to 2\mathrm{C} + \mathrm{P}, \quad \Phi = hK(T')\, n_A n; \tag{2}$$

$$2\mathrm{P} \to \mathrm{A}, \quad \Phi_W = h_W W(T')\, n^2. \tag{3}$$

On the right are written the expressions for the rates of heat release (absorption). Here h_i is the heat effect of the reaction (cal/mol); R is the rate of chain initiation (mol/cm$^3\cdot$sec); K and W are the rate constants of chain propagation and termination (g^2/cm$^3\cdot$mol$\cdot$sec); n_A is the concentration of A (mol/g of mixture); n is the concentration of P (mol/g of mixture), and T' is the temperature (°K).

The system of equations for a laminar plane flame for the given reaction scheme reduces to three equations:

$$\frac{d}{dx}\left(\lambda \frac{dT}{dx}\right) - Bc\frac{dT}{dx} + \Phi_R + \Phi + \Phi_W = 0, \tag{4}$$

$$\frac{d}{dx}\left(D_A \frac{dn_A}{dx}\right) - B\frac{dn_A}{dx} - Kn_A n - 0.5F_R n_A + 0.5Wn^2 = 0, \tag{5}$$

$$\frac{d}{dx}\left(D \frac{dn}{dx}\right) - B\frac{dn}{dx} + F_R n_A - Wn^2 = 0 \tag{6}$$

with boundary conditions:

$$\begin{matrix} T=0, & n=n_0, & n_A=n_{A0}, \\ T=T_{\mathrm{r}}, & n=n_{\mathrm{r}}, & n_A=n_{A\mathrm{r}}, \end{matrix} \qquad \begin{cases} \dfrac{dT}{dx}=\dfrac{dn_A}{dx}=\dfrac{dn}{dx}=0, \end{cases}$$

where $B=u\rho$; $T=T'-T_0'$; $D_A=\rho D_{PA}$; $D=\rho D_P$; x is the coordinate (cm); u is the flow velocity (cm/sec); ρ is the density (g/cm^3); λ is the thermal conductivity of the mixture (cal/cm • sec °C); c is the heat capacity (cal/g °C); D_P and D_{PA} are the diffusion coefficients of P and A, respectively (cm^2/sec). The index 0 refers to the initial state of the fresh mixture ($T'=T_0'$), the index r to the state–

state at the combustion temperature ($T'=T_r'$), while the index m will refer to the state corresponding to the maximum value of the temperature gradient $(dT/dx)_m=p_m\,(T'=T_m)$ (1,3).

If $\lambda=cD_A$, then, as is seen from (4) and (5), n_A will nevertheless not be a function of temperature alone. This means that, when chain reactions proceed in a flame, there can be no strict similarity between the concentration of A and the temperature. It was shown earlier that in many cases (2) one may neglect the quadratic termination of chains near $T=T_m$ (an estimate of the influence of W can always be made from the solution obtained in (2) with allowance for quadratic chain termination). Moreover, one will always have $0.5R_m \ll K_m n_{Am} n_m$, since the activation energy in R is significantly greater than the activation energy of the propagation process (2). For the same reason $|\Phi_{Rm}| \ll |\Phi_m|$, although $h_R > |h|$. Thus, from (4)–(6) we obtain a system of equations similar to that adopted in (1,3,7):

$$\frac{d}{dx}\left(\lambda\frac{dT}{dx}\right)-Bc\frac{dT}{dx}+\Phi=0, \tag{7}$$

$$\frac{d}{dx}\left(D_A\frac{dn_A}{dx}\right)-B\frac{dn_A}{dx}-Kn_An=0, \tag{8}$$

$$\frac{d}{dx}\left(D\frac{dn}{dx}\right)-B\frac{dn}{dx}+F_Rn_A=0. \tag{9}$$

On the basis of the previously developed method for the approximate solution of diffusion equations (1–3), the concentrations of A and P at the temperature $T=T_m$ may be written in the following form:

$$n_{Am}=t_A\omega_A-K_mN_An_{Am}n_m, \tag{10}$$

$$n_m=t\omega+F_{Rm}Nn_{Am}, \tag{11}$$

where $t=n_0+lT_m$; $t_A=n_{A0}+l_AT_m$, $l=(n_r-n_0)/T_r$, $l_A=(n_{Ar}-n_{A0})/T_r$, $\omega=1-2q/\varkappa$, $\omega_A=1+2q_A/\varkappa_A$, $\varkappa=c_0D_0/\lambda_0$, $\varkappa_A=c_0D_{A0}/\lambda_0$, $D_0=D_mq$,

$$D_{A0} = D_{Am} q_A, \quad q = \frac{\mu_0}{\mu_m}\left(\frac{T_0}{T'_m}\right)^{a-1} \quad \text{for} \quad D_P \sim (T')^a, \quad q_A = \frac{\mu_0}{\mu_m}\left(\frac{T_0}{T'_m}\right)^{a_A-1} \quad \text{for}$$

$$D_{PA} \sim (T')^{a_A}, \quad N = r/2D_m p_m^2, \quad N_A = r/2D_{Am} p_m^2, \quad r = T_m(T_r - T_m) \text{ and } T_m = 0.5\,T_r.$$

Solving (10) and (11), we find the expression

$$n_{Am} = \frac{(1 + t\omega K_m N_A)}{2F_{Rm} K_m N N_A}\left[\sqrt{1 + \frac{4t_A \omega_A F_{Rm} K_m N N_A}{(1 + t\omega K_m N_A)^2}} - 1\right], \tag{12}$$

after substitution of which into (11) we determine n_m.

It can be shown, on the basis of previous results ([2,8]), that the expression $t\omega K_m N_A \cong 2q_A/\xi\varkappa_A$, where ξ is a coefficient taking into account the influence of the rate of chain initiation ([8]). For $\lambda = cD_A$ and $t_A h = c_m T_m$ the equality will be exact. Since this equality is needed only for a rough estimate, it may also be used when $\lambda \neq cD_A$. Assuming that the fraction under the radical in (12) is less than unity, and using the equality given, we obtain

$$\frac{4t_A \omega_A D_{Am}(2q_A)^2}{(t\omega)^2 D_m(\varkappa_A + 2q_A)^2}\frac{F_{Rm}}{K_m} < 1. \tag{13}$$

If inequality (13) is satisfied, then the radical in (12) may be expanded in a series, and for n_{Am} one obtains the simple relation:

$$n_{Am} = \frac{t_A \omega_A}{(1 + t\omega K_m N_A)}. \tag{14}$$

Substituting (14) into (11), we find

$$n_m = t\omega\left[1 + \frac{t_A \omega_A F_{Rm} N}{t\omega(1 + t\omega K_m N_A)}\right]. \tag{15}$$

The fraction in square brackets in (15) is of the same order as the fraction under the radical in (12), but in (15) the fraction is added to unity, and therefore the requirement that it be small must be more stringent. If the fraction is equal to unity, then, assuming that $F_{Rm} \cong 0$, the error in n_{Am} according to (14) will be 18%, while the error in n_m according to (15) will reach 50% under the same conditions.

Substituting (14) and (15) into (7) and taking $F_{Rm} = 0$, after transformations we find, for $T = T_m$,

$$p_m^2 = \frac{1}{c_m \eta} t\omega K_m \left[ht_A + \frac{2q_A}{\chi_A} (ht_A - c_m T_m) \right]. \tag{16}$$

Substituting (14) and (15) into (7) at $T = T_m$, but with $F_{Rm} \neq 0$, we obtain

$$c_m \eta p_m^4 - t\omega (ht_A \omega_A - 2c_m \eta \delta_A) p_m^2 - hK_m (t_A \omega_A)^2 \delta F_{Rm} - K_m^2 (t\omega)^2 \delta_A (ht_A \omega_A - c_m \eta \delta_A) = 0, \tag{17}$$

where $\eta = 4\lambda_0 / c_0 T_m$, $\delta_A = r/2D_{Am}$, and $\delta = r/2D_m$.

The flame-propagation velocity is determined by the relation [1,3]

$$u_0 = \frac{1}{\rho_0} \eta p_m, \tag{18}$$

where p_m is found from (16) or (17). If, instead of relation (14), it is necessary to use relation (12), then (12) and (11) should be substituted into (7) at $T = T_m$. From the resulting equation one can determine p_m for (18).

Substituting (16) into (18), we obtain the final relation for determining the flame-propagation velocity

$$u_0 = \varphi \frac{1}{\rho_0} \sqrt{\frac{n_r Q'_m \rho_m D_{Pm}}{2c_m T_r}}, \tag{19}$$

where

$$\varphi = 2\sqrt{\frac{2q}{\chi}\left(1 - \frac{2q}{\chi}\right)}; \qquad Q'_m = Q_m \left[1 + \frac{2q_A}{\chi_A}\left(1 - \frac{c_m T_m}{ht_A}\right)\right]; \qquad Q_m = hK_m t_A;$$

for $n_{Ar} = 0$, $t_A = n_{A0}/2$. This relation, for $c_m T_m = ht_A$, will coincide with those relations which in [1–3] were obtained under the condition that $n_{Am} = t_A$.

The distribution of concentrations as a function of temperature, in accordance with (14) and (15), according to [1,3], will be determined by

$$n_A(T) = \frac{(n_{A0} + l_A T) - \dfrac{\eta l_A}{2D_{Am}}(T_r - T)T}{1 + \dfrac{K_m}{2D_{Am} p_m^2}\left[(n_0 + lT) - \dfrac{\eta l}{2D_m}(T_r - T)T\right](T_r - T)T}, \tag{20}$$

$$n(T) = (n_0 + lT) - \frac{\eta l}{2D_m}(T_r - T)T + F_{Rm} \frac{(T_r - T)T}{2D_m p_m^2} n_A(T), \tag{21}$$

where p_m is found from (16) or (17).

If the influence of R on u_0 is negligibly small, then $\xi = 1$, and for $c_m T_m = ht_A$, $t\omega K_m N_A = 2q_A/\chi_A$. In this case, since $\omega_A = 1 + 2q_A/\chi_A$, from (14) we obtain that $n_{Am} = t_A$. This means that, independently of the value of the diffusion coefficient of the initial substance A, its concentration at the temperature T_m is equal to the concentration that is obtained for $\lambda = cD_A$. A change in the value of D_A will manifest itself only in a certain deformation of the dependence $n_A(T)$ in comparison with the case when $\lambda = cD_A$, and therefore will have a very small effect on the magnitude of the flame-propagation velocity.

To illustrate this circumstance, numerical calculations were carried out for the example of the flame of hydrazine decomposition, which was studied in ([1,3,7]). All initial data for a flame with combustion temperature $T_r' = 1950$°K were taken from ([7]) and are also given in ([3]).

Fig. 1 gives the dependences of the concentration of the initial substance A on temperature. The initial concentration is $n_{A0} = 0.972$ g/g of mixture, and the concentration at the combustion temperature is $n_{Ar} = 0$. Dependence 1 corresponds to the case $\lambda = cD_A$ and is an exact solution. Dependence 2 also corresponds to $\lambda = cD_A$, but is calculated from the approximate solution (20), obtained as a result of solving the system of equations (7)–(9). Comparison of dependences 1 and 2 shows that the approximate solution (20) gives $n_A(T)$ practically coinciding with the exact dependence. This means that in systems with unbranched chain reactions, when solving problems on flame propagation, one may approximately assume that the concentrations of the initial substances are linear functions of temperature, without thereby introducing any noticeable errors into the final results. Such an assumption, which was used in previous works ([1–6,8]), considerably simplifies the solution of the indicated problem.

Fig. 1. Dependence of the concentration n_A of the initial substance A (in g/g of mixture) on temperature in a hydrazine-decomposition flame: 1–exact solution for $\lambda = c(D_A)_1$; 2–by the approximate solution (20) for $\lambda = c(D_A)_2 = c(D_A)_1$; 3–by relation (20) for $(D_A)_3 = (D_A)_1/1.5$; 4–by relation (20) for $(D_A)_4 = 1.5(D_A)_1$.

Fig. 1. Dependence of the concentration n_A of the initial substance A (in g/g of mixture) on temperature in a hydrazine-decomposition flame:
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Comparison of dependences 3 and 4 with dependence 2 (Fig. 1) makes it possible to conclude that the value of the diffusion coefficient of the initial substance under ordinary conditions does not exert any appreciable influence on the value of the flame-propagation velocity in systems with unbranched chain reactions. At $T = T_m$, the dependences $n_A(T)$ for all D_A converge to one point. However, strictly speaking, this convergence, as is evident from relations (16) and (14), will occur only when $c_m T_m = ht_A$, i.e., in those cases where dissociation of the combustion products does not lead to a practically appreciable decrease in the combustion temperature. With appreciable dissociation, even for $\lambda = cD_A$, there can strictly be no similarity between the temperature and the concentration of the initial substance.

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Received
18 VII 1960

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Note: Figure translations are in progress. See original paper for figures.