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Abstract

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

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In the work of Giddings and Hirschfelder (^1) a system of differential equations describing the process of propagation of a laminar flame during the course of a branched chain reaction was integrated numerically; this reaction was represented by a model reaction with one active center and included two processes: $2P \rightarrow A$ (quadratic chain termination) and $P + A \rightarrow C + 2P$ (the process of chain propagation and branching).

A general solution of the flame-propagation problem for the case of a one-center model reaction was outlined in (^2), where relatively simple formulas for determining the flame-propagation velocity, taking into account the influence of branching and quadratic chain termination, were derived for reactions of the degenerate-branched type. From the data of (^2) one can obtain an approximate formula corresponding to the reaction scheme adopted in (^1), and determine the deviation in the magnitude of the flame-propagation velocity given by this formula in comparison with the results obtained by numerical integration (^1), as was done for cases with unbranched reactions ([3-5]).

The reaction scheme, in which A is the initial substance, P is the active center, and C is the reaction product, will be written, in accordance with (^2), in the form

$$
\begin{array}{ll}
A \rightarrow 2P \quad \text{(initiation)}, & \\
P + A \rightarrow 2C + P \quad \text{(propagation)}, & Q_R = h_R R(T'), \\
P + A \rightarrow C + 2P \quad \text{(branching)}, & Q_n = hFn = hK(T')\, n_A n, \\
(P \rightarrow \text{linear termination}); & Q_V n = hVn = hK_V(T')\, n_A n, \\
2P \rightarrow A \quad \text{(quadratic termination)}. & Q_W n^2 = h_W W(T')\, n^2 *;
\end{array}
$$

On the right are written the expressions for the rates of heat liberation (absorption). Here h_i is the thermal effect of the reaction (cal/mole); K_i and W are the rate constants of the reactions ($g^2/cm^3 \cdot mole \cdot sec$); R is the rate of chain initiation ($mole/cm^3 \cdot sec$); n is the concentration of P (mole/g of mixture); n_A

is the concentration of A (mole/g of mixture); T' is the temperature (°K). It is assumed, in accordance with (^{2}-5), that $R = R(T')$ and $F = F(T')$.

The flame-propagation velocity u_0, on the basis of (‸2), will be determined by the relation

$$u_0 = \frac{1}{\rho_0}\eta p_*, \tag{1}$$

where p_* is found from the equation

$$p_*^6\eta A_1 - p_*^4(\eta^2 A_2 + \eta A_3 + A_5) - p_*^2(\eta A_4 - A_6 - \eta A_7 + A_8) + A_9 = 0, \tag{2}$$

* W is the rate constant for consumption of P.

the coefficients of which are calculated from the formulas:

$$A_1 = 4cD_m^2 hw, \tag{3}$$

$$A_2 = (c + lhw)^2 r^2 W_m, \tag{4}$$

$$A_3 = 2D_{mr}[(c - lhw)Q_{\Sigma m} + 2cV_{mhw} - t(c + lhw)Q_{Wm}], \tag{5}$$

$$A_4 = r^2[lQ_{\Sigma m}^2 - V_m(c - lhw)Q_{\Sigma m} - cV_{mhw}], \tag{6}$$

$$A_5 = 4D_m^2(t^2 Q_{Wm} + Q_{Rm} + tQ_{\Sigma m})hw, \tag{7}$$

$$A_6 = 2D_{mtr}(Q_{\Sigma m} + V_{mhw})Q_{\Sigma m}, \tag{8}$$

$$A_7 = 2r^2(c + lhw)(R_{mhw} + Q_{Rm})W_m, \tag{9}$$

$$A_8 = 2D_{mr}[(R_{mhw} - Q_{Rm})Q_{\Sigma m} + 2t(R_{mhw} + Q_{Rm})Q_{Wm} - 2V_m hwQ_{Rm}], \tag{10}$$

$$\begin{aligned} A_9 = r^2[&(Q_{\Sigma m}R_m + V_m hwR_m - V_m Q_{Rm})Q_{\Sigma m} - Q_{Rm}^2 W_m \\ &- (V_m^2 Q_{Rm} + 2W_m R_m Q_{Rm} + Q_{Wm}R_m^2)hw]. \end{aligned} \tag{11}$$

In (1)–(11) the following notation has been adopted: ρ is the density (g/cm^3); c is the heat capacity (cal/g $\cdot$ °C); D_P is the diffusion coefficient of the active center P (cm^2/sec); λ is the thermal conductivity of the mixture (cal/cm $\cdot$ sec $\cdot$ °C); $D = \rho D_P$; $T = T' - T'_0$; $r = T_m(T_\Gamma - T_m)$; $T_m = 0.5T_\Gamma$; $Q_\Sigma = Q + Q_V$; $l = \dfrac{n_\Gamma - n_0}{T_\Gamma}$; $t = n_0 + lT_m$ and $\eta = \dfrac{4\lambda_0}{c_0 T_m}$. The index 0 refers to the initial state of the fresh mixture ($T' = T'_0$), the index Γ to the state at the combustion temperature ($T' = T'_\Gamma$), and the index m to the state corresponding to the maximum value of the temperature gradient ($T' = T'_m$).

In (2) for the rate of quadratic chain termination the expression $W'(n^2 - n_t^2)$ was used, which at $T' = T'_\Gamma$ became zero. This was necessary because there, on the basis of the scheme adopted earlier ([3]), it was assumed that $R(T'_\Gamma) = 0$. Here it is assumed that $R(T'_\Gamma) = W(T'_\Gamma)n_\Gamma^2$, and therefore there is no need for the indicated form of writing the rate of quadratic chain termination.

For systems with branched reactions, relations (1)–(11) can be simplified if it is assumed that the initial and final concentrations of the active center are equal to zero ($n_0 \simeq n_\Gamma \simeq 0$, i.e. $l \simeq t \simeq 0$). However, even in this form the expressions for A_i remain complicated. It was previously shown ([3–5]) that at ordinary rates of chain initiation their influence on the magnitude of the flame-propagation velocity is small. The same conclusion can also be drawn on the basis of the relations obtained in ([2,6]). Thus, taking $R_m \simeq 0$ (and then also $Q_{Rm} \simeq 0$), we obtain, instead of (2)–(11), new formulas ($A'_5 = A'_6 = A'_7 = A'_8 = A'_9 = 0$):

$$p_*^4 A'_1 - p_*^2(\eta A'_2 + A'_3) - A'_4 = 0, \tag{2'}$$

where

$$A'_1 = 4D_m^2 hw,$$

$$A'_2 = cr^2 W_m,$$

$$A'_3 = 2D_{mr}(Q_{\Sigma m} + 2V_{mhw}),$$

$$A'_4 = -r^2(Q_{\Sigma m} + V_{mhw})V_m.$$

From (2′) we obtain the relation for determining p_*:

$$p_*^2 = \frac{(\eta A'_2 + A'_3)}{2A'_1}\left[1 - \sqrt{1 + \frac{4A'_1 A'_4}{(\eta A'_2 + A'_3)^2}}\right]. \tag{12}$$

The fraction under the radical in (12) is always less than unity (this condition is also satisfied when $W_m = 0$). Expanding the radical in (12) into a series and retaining only the first two terms, we find an approximate value of p_*, after substitution of which into (1) we obtain a relation for determining the flame-propagation velocity under the condition that $n_0 = n_r = R_m = 0$:

$$u_0 = \eta \frac{1}{\rho_0} \sqrt{\frac{r\left(Q_{\Sigma m} + V_m h_W\right) V_m}{\eta c_m r W_m + 2 D_m \left(Q_{\Sigma m} + 2 V_m h_W\right)}}. \tag{13}$$

If in (13) we put $F_m = 0$, i.e., assume that a purely branched reaction takes place, then we obtain the relation

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0} \sqrt{\frac{c_0 \left(h_V + h_W\right) V_m^2}{2\lambda_0 c_m T_r W_m + 2 c_0 D_m \left(h_V + 2 h_W\right) V_m}}, \tag{14}$$

to which there corresponds the simplified reaction scheme adopted in ([1]), consisting of only two processes: $2P \to A$ and $P + A \to C + 2P$.

Table 1

Flame-propagation velocities (cm/sec)

	$\chi = c_0\rho_0 D_P/\lambda_0$	$\chi = c_0\rho_0 D_P/\lambda_0$	$\chi = c_0\rho_0 D_P/\lambda_0$
	1	2	0
Numerical integration ([1])	55.1	54.8	58.3
According to relation (14)	59.7	58.5	60.9

According to relation (14), the values of the flame-propagation velocities were calculated for three cases for which in ([1]) the values of u_0 had been determined by numerical integration of the corresponding system of equations. In carrying out the calculations, all initial data were taken from ([1]). The results of the calculations are given in Table 1.

The data of Table 1 illustrate good agreement between the values of the flame-propagation velocities calculated from the approximate relation (14) and the values obtained by numerical integration ([1]). This confirms the correctness of relation (14) and substantiates the possibility of using it to determine experimental values of the rate constants of elementary processes for branched reactions from the dependences of the flame-propagation velocity on temperature.

In [6] an approximate relation was obtained for determining the flame-propagation velocity in the combustion of hydrogen according to a branched-chain-reaction scheme including three types of active centers:

$$u_0 = \frac{4\lambda_0}{\rho_0 c_0}\sqrt{\frac{K^0_{2m} n_{Bm} \rho_m}{D_{P2m}}}, \tag{15}$$

where K_2^0 (cm^3/mole·sec) is the rate constant of the process $H + O_2 \rightarrow OH + O$; n_B (mole/g of mixture) is the concentration of O_2, and D_{P2} (cm^2/sec) is the diffusion coefficient of hydrogen atoms.

If in (14) we put $W_m \cong 0$ and $h_W \cong 0$, then we obtain the relation corresponding to (15), which in [6] was obtained under the condition that $W_m = 0$. Having the solution (14) for the model reaction scheme, but with allowance for quadratic chain termination, one can estimate the influence of the rate of quadratic chain termination when using (15).

It was noted in [2] that relation (15) had not been checked by comparison with data obtained by numerical integration. The data of Table 1 provide such a check and substantiate the use of (15) for determining the experimental value of K_2^0 given in [2].

In [1] it was established (Table 1) that a significant change in the diffusion coefficient of the active center, all other conditions being equal, does not

leads to an appreciable change in the flame-propagation velocity, the latter decreasing as D_p increases. Relation (14) makes it possible to explain this change in u_0. In the numerical integration in [1] a rather high value was adopted for the rate constant of quadratic chain termination, at which the first term in the denominator of relation (14) is approximately 10-20 times greater than the second. Therefore the calculated value of u_0 depends almost not at all on D_p.

In [2], on the basis of the data of [7], the experimental ratio of flame-propagation velocities was given for two mixtures ($0.21H_2 + 0.11O_2$), one of which contained 0.68A, and the other 0.68He. This ratio $(u_0)_{He}/(u_0)_A = 2.40$. The same ratio, calculated with the aid of relation (15), proved to be 2.85. It follows from (14) that if the first term in the denominator under the radical is considerably greater than the second, then u_0 is proportional to the square root of the thermal conductivity $u_0 \sim \sqrt{\lambda_0}$ and is practically independent of the magnitude of D_{pm}. In that case, on replacing argon by helium one would have $(u_0)_{He}/(u_0)_A = \sqrt{\lambda_{He}/\lambda_A} = 1.94$. The experimental ratio lies within the limits between 1.94 and 2.85. From this it apparently follows that quadratic chain termination plays a certain role in the case under consideration, and one can solve the inverse problem—to determine the experimental value of the rate constant of quadratic chain termination from the ratio 2.40. If the denominator under the radical in (14) is represented in the form $(C_1\lambda_0 + C_2 D_{pm})$, where C_1 and C_2 do not depend on λ_0 and D_{pm} and are identical in magnitude for

the mixture with argon and the mixture with helium, then, at $\lambda_{He}/\lambda_A = 3.76$, $(D_p)_{He}/(D_p)_A = 1.74$, and $(u_0)_{He}/(u_0)_A = 2.40$ ([7]), the ratio calculated with the aid of relation (14) for the mixture with argon is $(C_1\lambda_0/C_2D_{pm})_A = 0.52$. This also shows that the influence of quadratic chain termination is appreciable.

In order to find C_1 and C_2, and to calculate the rate constant of quadratic chain termination in triple collisions $K_{Wm} = W_m\mu_m/\rho_m^3$, it is necessary to know all the quantities entering into (14). However, at $(C_1\lambda_0/C_2D_{pm})_A = 0.52$, the calculation of K_{Wm} can only be a rough estimate. At $C_1\lambda_0 > C_2D_{pm}$, such a calculation would be much more accurate, but for this it would be necessary to determine $(u_0)_{He}/(u_0)_A$ at lower temperatures, at which the influence of quadratic chain termination should be considerably more appreciable than at temperatures of $2200 \div 2400°K$.

Since the estimate of the magnitude K_{Wm} is rough, in calculating K_{Wm} for the above-mentioned mixtures the combustion temperature and all the other parameters were not calculated. All the quantities necessary for the calculation were taken from the data given in ([6]) for a mixture containing $0.43H_2 + 0.57$ air. It was found that $K_{Wm} \simeq 10^{17}$ cm^6/mole$^2 \cdot$ sec.

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