# On the Theory of Chain-Thermal Flame Propagation

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## Abstract

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## Physical Chemistry

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# On the Theory of Chain-Thermal Flame Propagation

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Chain-thermal propagation of a thermal flame will be understood as such propagation in which the reaction in the flame develops by a chain mechanism with continuous supply of heat together with active centers from regions with high temperature and a high concentration of active centers. The chain mechanism of the decomposition reaction, including two active centers that react successively with the initial substance and regenerate one another, is represented by a simplified scheme with an active center of one kind ($^1$):

$$\begin{gathered} \mathrm{A} \rightarrow 2\mathrm{P} \quad \text{(initiation)}, \\ \mathrm{P} + \mathrm{A} \rightarrow 2\mathrm{C} + \mathrm{P} \quad \text{(chain)}, \\ \mathrm{P} + \mathrm{P} + \mathrm{M} \rightarrow 2\mathrm{C} + \mathrm{M} \quad \text{(chain termination)}. \end{gathered}$$

Here $A$ is the initial substance, $C$ the final product, $P$ the active center. Assuming that the product of the density $\rho$ by the diffusion coefficient $P_\rho D_p = D$, and that the heat capacity $c$ and the thermal conductivity $\lambda = c\rho D_A$ ($D_A$ is the diffusion coefficient of $A$) do not depend on the temperature $T = T' - T'_0$, we obtain for a stationary laminar flame:

$$\lambda p p' - Bcp + Qn = 0, \tag{1}$$

$$Dp^2 n'' - pn'(B - Dp') + R = 0 \tag{2}$$

with boundary conditions:

$$T = 0, \qquad n = n_0, \qquad p = 0, \qquad pn' = 0; \tag{3}$$

$$T = T_r, \qquad n = n_r, \qquad p = 0, \qquad pn' = 0; \tag{4}$$

where $x$ is the coordinate, $u$ the flow velocity, $n$ the dimensionless concentration of $P$, $n_A$ the dimensionless concentration of $A$, $h$ the thermal effect of the reaction, $K_A(T)$ the reaction-rate constant, $R(T)$ the rate of initiation of $P$, $T_0'$ the initial temperature, $T_r'$ the combustion temperature, determined by the heat release: $h(n_{A_0} - n_{A_r}) = cT_r$, $B = u\rho$, $Q = Q(T) = hK_A(T)n_A(T)$,

$$Q(0) = Q(T_r) = R(0) = R(T_r) = 0, \qquad p = \frac{dT}{dx}, \quad p' = \frac{dp}{dT}, \quad n' = \frac{dn}{dT}.$$

Dividing the region of integration of (1) and (2) into a finite number of intervals $\Delta T_i = T_{i+1} - T_i$ and assuming that within each interval $n' =$ const and $n'' =$ const, we represent the solution of (2) in the form:

$$n = n_0 + bT + eT^2, \tag{5}$$

where $b$ and $e$ are determined so that $n_r = n_0 + bT_r + eT_r^2$, $n' = b + 2eT$, and $n'' = 2e$. Taking this into account, from (2) and (5) we obtain:

$$n = n_0 + (l + zT_r)T - zT^2, \tag{6}$$

where

$$l = \frac{n_r - n_0}{T_r} \quad \text{and} \quad z = \frac{R - lp(B - Dp')}{p(B - Dp')(2T - T_r) - 2Dp^2}. \tag{7}$$

Substituting (6) into (1), we obtain for numerical integration:

$$\lambda pp' - Bcp + \Phi_c = 0, \tag{8}$$

where

$$\Phi_c = \Phi_c(T, p, p'; Dp) = Q\big[(n_0 + lT) - z(T_r - T)T\big].$$

The relationships needed for calculating the flame velocity can be obtained by investigating the dependence of $B$ on the maximum value of the temperature gradient $p_m$. Taking into account that for $T = T_m$, $p'(T_m) = 0$, $p(T_m) = p_m$, and denoting $(n_0 + lT_m) = t$, $(2T_m - T_\Gamma) = s$, $T_m(T_\Gamma - T_m) = r$, from (8) we obtain:

$$-Bcp_m + Q_m(l - z_m r) = 0. \tag{9}$$

If it is assumed that in (5) $b$ and $e$ over the whole region of integration are determined by their values at $T = T_m$, then instead of (6) we obtain the approximate relation

$$n = n_0 + (l - z_{mT_\Gamma})T + z^2_{mT}. \tag{10}$$

Solving (9) and omitting the root that goes to infinity as $\varepsilon = 0$, we find

$$B = \frac{\Phi_m}{cp_m} = \frac{(\alpha p_m^2 + \beta) - \sqrt{(\alpha p_m^2 + \beta)^2 - 4\varepsilon(\gamma p_m^2 + \delta)}}{2\varepsilon p_m}, \tag{11}$$

where

$$\varepsilon = \frac{c}{Q_m}s; \qquad \alpha = 2D_m\frac{c}{Q_m}; \qquad \beta = st + lr; \qquad \gamma = 2D_m t; \qquad \delta = R_m r.$$

Determining the derivative of $B$ (11) with respect to $p_m$ and setting its numerator equal to zero, we obtain the equation

$$a_1y^3 + a_2y^2 + a_3y + a_4 = 0, \tag{12}$$

where

$$y = p_m^2; \qquad a_1 = \alpha^2\gamma; \qquad a_2 = -\alpha(2\beta\gamma - 3\alpha\delta);$$
$$a_3 = \beta(\beta\gamma - 2\alpha\delta); \qquad a_4 = -\delta(\beta^2 - 4\varepsilon\delta).$$

The form of the dependence of $B$ according to (11), for a negative discriminant of equation (12), is shown in Fig. 1. The dashed line marks that part of the dependence for which the integral curves issuing from the point $p = 0$, $T = T_\Gamma$ do not satisfy condition (3). If, in the problem of flame propagation, diffusion of the active center were not taken into account, then the chain reaction at similar temperatures would develop only through initiation—as in self-ignition. In this case, solving the system of kinetic equations together with the heat-balance equation, one can find the dependence of the concentration $P$ on temperature, $n_c = n_c(T)$, and, substituting it into (1), obtain a single equation in which the rate of heat release is a function only of temperature, $\Phi_c = Q(T)n_c(T) = \Phi_c(T)$. Thus, for the dependence of $B$ on $p_m$ in the absence of diffusion of $P$, one obtains:

$$B' = \frac{\Phi_{cm}}{cp_m}. \tag{13}$$

The form of (13) is shown in Fig. 1. The dependences $n_c(T)$ and $\Phi_c(T)$ for the decomposition of hydrazine were determined in (1) (Figs. 2 and 3). Owing to the absence of grounds for selecting a unique value of the flame velocity from the spectrum $B' \geq B_c$, a self-ignition temperature $T > T_0 = 0$ is introduced into the theory, up to which no chemical reaction occurs. With the aid of this

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

assumption, a certain unique $B$ is obtained, whose numerical value is very close to $B_c$ if $T > 0$ is close to $T_0 = 0$. The dependence $B$ according to (11) has a fundamentally different form, since $\Phi$ is a function of the temperature gradient and increases as $p_m$ increases, i.e., as the width of the reaction zone decreases, which leads to an increase of the diffusion flux of $P$ into the region of low and intermediate temperatures. The limiting $(p_m)$ is the greatest possible $p_m$ for which the integral curves satisfying (4) still reach the point $p = 0$, $T = 0$. It corresponds to the greatest possible rate of heat release $(\Phi\ ) = Qn_s \simeq Qn$ and to the limiting value of the parameter $B = B$. The dependences $n_s$ and $(\Phi\ )$ for the flame of hydrazine decomposition were determined in (1) by numerical integration of (1) and (2) and are given in Figs. 2 and 3. In contrast to (13), the dependence (11)

gives the limiting $B_\mathrm{p}$, corresponding to the state at point $P$, which will be stable under stationary propagation if the flame has an inherent

**Fig. 1.** Dependence of the mass velocity $B$ on the maximum temperature gradient $p_m$. $B$—for chain-thermal propagation; $B'$—without taking into account diffusion of active centers

**Fig. 2.** Dependence of the concentration of active center $P$ on temperature during decomposition of hydrazine: $n_s$—in the flame (1), $n_\mathrm{p}$—in the flame according to relation (10), $n_c$—during self-ignition or in a flame without taking into account diffusion of active centers (1)

tendency to pass to states with increased velocity. If, conversely, the flame tends to propagate with the lowest possible velocity, then the state $K$ according to (11), as well as the state $C$ according to (13), will be stable. The dependence of $B$ on $p_m$ according to (11) provides, in chain-thermal propagation, a stable state for all possible tendencies. The presence of a minimum according to (11) would physically mean that, within the limits from $B_\mathrm{min}$ to $B_\mathrm{p}$, two sharply different states correspond to each flame velocity. Since spontaneous (natural) processes proceed with the maximum increase in entropy, the part of the curve to the left of $K$ will be physically unreal from $B_\mathrm{min}$ to $B_\mathrm{p}$, in comparison with its segment to the right of $K$, which corresponds to a greater degree of deviation of the process from the equilibrium course. The principle of determining the flame velocity from the state $P$ makes it possible to explain the limits of propagation (existence) of the flame, since as the combustion temperature decreases the point $P$ shifts to the left and approaches point $K$, and then passes into a position to the left of $K$.

Figure 3

Figure 3: Figure 3

**Fig. 3.** Dependence of the heat-release rate on temperature during decomposition of hydrazine (1): $\Phi_c$—during self-ignition, $(\Phi_{\mathrm{c}})_{\mathrm{p}}$—the greatest possible rate in chain-thermal propagation

Exact determination of the limiting values and dependences for $P$ requires numerical integration of (1) and (2). However, it turns out that relations (11) and (10) give results so close to the exact ones that numerical integration may be avoided. From the roots of (12) we find the approximate value of the gradient at point $P$ as the mean:

$$p_{\mathrm{p}}^2 \simeq y_{\mathrm{av}} = \frac{y_2 + y_3}{2} \simeq \frac{\beta}{\alpha}. \tag{14}$$

Expanding the radical in (11) in a series and taking (14) into account, we obtain for the linear

flame velocity:

$$u_0 = \frac{1}{\rho_0} \sqrt{\frac{n_r Q_m \rho_m D p_m}{2cT_r}}. \tag{15}$$

To find the quantities entering into (15), one may approximately take $T_m = 0.5T_r$ (see Table 1). Using for the boundary of the spectrum the approximate relation $B_* = \eta p_*$, where $\eta = \dfrac{4\lambda_0}{cT_m}$, we find from (9):

$$p_*^4(\alpha - \varepsilon\eta)\eta - p_*^2(\gamma - \beta\eta) - \delta = 0. \tag{16}$$

Equating $p_*$ from (16) and $p_p$ from (14), we determine $T = T_m$.

To check the approximate relations obtained, numerical calculations were performed for the example of the flame of hydrazine decomposition, for which in (1) all the necessary values and dependences had been obtained by numerical integration. For an initial composition with $T_0' = 300^\circ$K and $T_r' = 1950^\circ$K, all the initial data were taken from (1). The discriminant (12) was calculated, and it was established that, for this particular case, the dependence (11) has the form shown in Fig. 1. It was found that $T_m = 875^\circ$ and $(p_m)_p = 1.72 \cdot 10^5$ deg/cm. The experimentally measured flame velocity for this composition, cited in (1), is $u_0 = 185$ cm/sec.

**Table 1**

Calculated values of the flame velocity $u_0$
(cm/sec)

| Numerical integration according to ([1]) | By formula (11) $T_m = 875°$ | By formula (15) $T_m = 875°$ | By formula (15) $T_m = \frac{1}{2}T_r = 825°$ |
|---:|---:|---:|---:|
| 160 | 155 | 148 | 147 |

By relation (10) the dependence of $n$ on $T$ was calculated at the limiting state (point $P$ in Fig. 1). This dependence $n_p$ is given in Fig. 2, where, for comparison, the same dependence obtained by numerical integration (1) is plotted. As can be seen, the agreement in all the results is quite satisfactory.

In (1), numerical integration gave the flame velocity $u_0 = 11$ cm/sec for an initial composition with $T_0' = 300°\mathrm{K}$ and $T_r' = 1280°\mathrm{K}$. The measured flame velocity is $u_0 = 10$ cm/sec. Calculation by formula (15) gives, with the same initial data, $u_0 = 8.6$ cm/sec.

It follows from formula (15) that the flame velocity is inversely proportional to the fourth root of the pressure. Formula (15) makes it possible to find the true activation energy of the second reaction from the experimental dependence of the square of the flame velocity on the reciprocal temperature, if $\lambda_r$ is expressed through the equilibrium constant, which includes the heat effect of the reaction forming $P$. The slope of this experimental dependence in chain-thermal propagation depends both on the activation energy and on the heat effect.

In the present calculations, and in (1), chain termination was not taken into account. If the termination rate is taken into account, the dependence $n_p$ shown in Fig. 2 would be lower. If one assumes that the second reaction is branched ($P + A \rightarrow 2C + (i+1)P$), then, knowing $n_p$, one can find such an $i$ as is necessary in order to compensate for the chain termination that actually occurs by branching, so that all the previously calculated values and dependences remain unchanged. It was found that $i = 0.008$. This calculation simultaneously confirms the validity of the assumption of neglecting chain termination in solving the original system of equations.

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## CITED LITERATURE

[1] D. B. Spalding, Phil. Trans. Roy. Soc. London., **149**, A, No. 957, 1 (1956).

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