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AD-A286 611

JPRS: 9239

9 May 1961

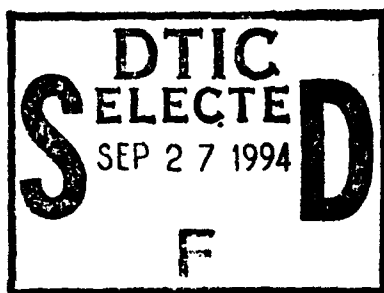


THEORY OF CHAIN-THERMAL FLAME PROPAGATION

REPORT 2

TWO ACTIVE CENTERS WITH DIFFERENT DIFFUSION COEFFICIENTS

By L. A. Lovachev



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FOREWORD

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JPRS: 9239

CSO: 5977-A/2

THEORY OF CHAIN-THERMAL FLAME PROPAGATION.

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TWO ACTIVE CENTERS WITH DIFFERENT DIFFUSION
COEFFICIENTS

[Following is the translation of an article by
L. A. Lovachev entitled "Teoriya Tsepochechno-
Teplogo Rasprostraneniya Plameni. Soobshcheniye
2. Dva Aktivnykh Tsentra S Razlichnymi Koeffitsi-
yentami Diffuzii" (English version above) in Iz-
vestiya Akademii Nauk SSSR - Otdeleniye Khimiches-
kikh Nauk (Bulletin of the Academy of Sciences of the
USSR - Chemistry Section), Moscow, No. 7, 1960,
pages 1191 - 1199.]

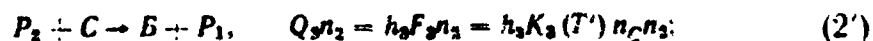
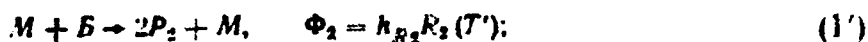
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In the foregoing article¹ the relationships for the determination of the velocity of flame propagation in a system with two active centers having identical diffusion coefficients were obtained. This problem for two active centers with identical diffusion coefficients was solved by reducing it to a problem with a simplified system of chain reaction and active centers of the same kind, considered in the first article² which was devoted to the theory of chain-thermal propagation of laminar flame in a homogeneous gaseous mixture. In a series of works there were considered: the dependence of the flame propagation velocity on pressure and temperature^{3, 2, 1}, the influence of the heat conductivity of the hot mixture and of the diffusion coefficients of the active centers on the velocity of flame propagation^{5, 4}, and the role of branching and rupture of chains in chain reactions having relatively low speeds of the branching processes⁴.

In this article a relationship is developed according to which the flame propagation velocity and the distribution of the concentration of active centers in dependence on temperature change in a non-branched reaction system which includes two kinds of active centers having different

diffusion coefficients can be calculated.

The system of the reaction and the system of the equations. The system of the reaction in which A and B represent the starting materials, C - the end product of the reaction and P_1 and P_2 - the active centers is set up in the following form:



On the right are written the expressions for the rates of heat liberation (or absorption). Here h_i is the heat effect of the reaction in cal/mole; n_1 and n_2 - concentrations of the active centers P_1 and P_2 in mole/g of mixture; n_A , n_B and n_C - the concentrations of the materials A, B, and C in mole/g of mixture; K_1 and W_1 - constants for the reaction rates in $\text{g}^2/\text{cm}^3 \cdot \text{mole} \cdot \text{sec}$; R_1 - the rate of chain generation mole/ $\text{cm}^3 \cdot \text{sec}$; T' - temperature in $^\circ\text{K}$. It is

assumed that the diffusion coefficients of the starting materials D_A and D_E and the product D_C are equal to the coefficient of temperature conductivity ($\lambda = c\rho D_A = c\rho D_E = c\rho D_C$), and therefore the rates of chain generation (1) and (1') and also the expression for F_1 are written as functions of temperature only.

The system of equations describing the process of the stationary propagation of the horizontal laminar flame for the reduced reaction system and the assumed conditions is brought down to three equations

$$\lambda\rho\frac{dT}{dx} - Bcp + Q_1n_1 + Q_2n_2 + Q_3n_3 + Q_4n_4 + \sum X_i n_i^2 + \Phi = 0, \quad (5)$$

$$D_1\frac{dn_1}{dx^2} - B\frac{dn_1}{dx} + F_2n_2 + F_3n_3 - F_1n_1 - F_4n_4 + R_1 - W_1n_1^2 = 0, \quad (6)$$

$$D_2\frac{dn_2}{dx^2} - B\frac{dn_2}{dx} + F_1n_1 + F_4n_4 - F_2n_2 - F_3n_3 + R_2 - W_2n_2^2 = 0, \quad (7)$$

where $B = u\rho$, $D_1 = \rho D_{P_1}$, $D_2 = \rho D_{P_2}$, $T[x] = T' - T^0$, $\Phi = \Phi_1 + \Phi_2$, $\sum X_i n_i^2 = X_1 n_1^2 + X_2 n_2^2$ and $p = \frac{dT}{dx}$; x - the coordinate on the axis of the normal flame surface in cm; u - the flow rate directed along the x - axis in cm/sec; ρ - density in g/cm³; λ - heat conductivity in cal/cm · sec · degree; c - heat capacity at constant pressure in cal/g · degree; D_{P_1} and D_{P_2} - the diffusion coefficients of the active

centers P_1 and P_2 in $\text{cm}^2/\text{sec.}$.

The index "0" will refer to the initial state of the fresh mixture ($T' = T'_0$), index "r" to the state at combustion temperature ($T' = T'_r$), but index "m" to the state corresponding to the maximal value of the temperature gradient ($T' = T'_m$).

The sum of the functions of the heat liberation rates in (5) and the sums of the functions of the reaction rates in (6) and in (7) are equal to zero at $T' = T'_0$ and $T' = T'_r$. The limiting conditions for equations (5), (6), and (7) are:

$$T' = T'_0, n_1 = n_{10}, n_2 = n_{20}, \frac{dT}{dx} = \frac{dn_1}{dx} = \frac{dn_2}{dx} = 0; \quad (8)$$

$$T' = T'_r, n_1 = n_{1r}, n_2 = n_{2r}, \frac{dT}{dx} = \frac{dn_1}{dx} = \frac{dn_2}{dx} = 0. \quad (9)$$

Similar conditions are true for flames without heat loss into the surrounding medium and were accepted on the strength of the foregoing consideration^{1,2}.

Determination of the velocity of flame propagation.

The calculation of the quadratic rupture of the chains which considerably complicates the end results does not lead to a marked change in the value of the theoretical velocity of flame propagation⁴. Therefore, in

the beginning it will be assumed that $W_1 = W_2 = 0$. Further it will be shown how to figure the velocity of flame propagation by taking into consideration the velocities of the quadratic chain rupture and utilizing the approximate relationships obtained in [4] (figures in brackets refer to references in the bibliography, transl.).

The method of solution of this problem based on the idea of solution of equations of type (6) and (7) with conditions (8) and (9) in the form of polynomials of the second degree was considered in detail and proved in [2]. In agreement with [2] and on basis of (5), (6), and (7) the concentrations of active centers at temperature $T = T_m$ corresponding to the maximal value of the temperature gradient $\frac{P = P_m}{\text{gradient}}$ can be written as follows:

$$n_{1m} = t_1 + (R_{1m} + G_{2m}n_{2m} - G_{1m}n_{1m} - Bl_1\rho_m) N_1, \quad (10)$$

$$n_{2m} = t_2 + (R_{2m} + G_{1m}n_{1m} - G_{2m}n_{2m} - Bl_2\rho_m) N_2, \quad (11)$$

$$\text{where } l_1 = \frac{n_{1r} - n_{10}}{T_r}, \quad l_2 = \frac{n_{2r} - n_{20}}{T_r},$$

$$N_1 = \frac{r}{2D_{1m}\rho_m^2}, \quad N_2 = \frac{r}{2D_{2m}\rho_m^2},$$

$$t_1 = n_{10} + l_1 T_m, \quad t_2 = n_{20} + l_2 T_m.$$

$$r = T_m(T_r - T_m), \quad G_1 = F_1 + F_4,$$

$$G_2 = F_3 + F_5 \approx T_m = 0.5T_r.$$

Solving (10) and (11) we find after rearrangement

$$n_{1m} = \frac{l_1 + (R_{1m} - B l_1 p_m) N_1 + [(l_1 N_2 + l_2 N_1) + (R_m - B l_1 p_m) N_1 N_2] G_{1m}}{1 + G_{1m} N_1 + G_{2m} N_2}, \quad (12)$$

$$n_{2m} = \frac{l_2 + (R_{2m} - B l_2 p_m) N_2 + [(l_1 N_2 + l_2 N_1) + (R_m - B l_2 p_m) N_1 N_2] G_{2m}}{1 + G_{1m} N_1 + G_{2m} N_2}, \quad (13)$$

where $l = l_1 + l_2$ and $R = R_1 + R_2$.

Substituting (12) and (13) into (5) and considering that at $T = T_m$, $p = p_m$ and $(dp/dT)_m = 0$, and also using the relationship obtained earlier $B = \eta p_m = \eta p_m [2]$ in which $\eta = 4\lambda_0/cT_m$ we obtain by introducing these symbols in (10) and (11):

$$A_1 p_m^3 + A_2 p_m^2 + A_3 p_m + A_4 = 0, \quad (14)$$

where $A_1 = 4c\eta D_{1m} D_{2m}$.

$$A_2 = 2c\eta (G_{1m} D_{2m} + G_{2m} D_{1m}) + 2\eta (S_{1m} l_1 D_{2m} + S_{2m} l_2 D_{1m}) -$$

$$- 4D_{1m} D_{2m} (S_{1m} l_1 + S_{2m} l_2) - 4E_{1m} D_{2m} \Phi_m,$$

$$A_3 = \eta l (S_{1m} G_{2m} + S_{2m} G_{1m}) r^2 - 2r (l_1 D_{1m} + l_2 D_{2m}) (S_{1m} G_{2m} + S_{2m} G_{1m}) -$$

$$- 2r \Phi_m (G_{1m} D_{2m} + G_{2m} D_{1m}) - 2r (S_{1m} R_{2m} D_{2m} + S_{2m} R_{1m} D_{1m}),$$

$$A_4 = -R_m r^2 (S_{1m} G_{2m} + S_{2m} G_{1m}),$$

$$S_1 = Q_1 + Q_3 = h_1 F_1 + h_3 F_3,$$

$$S_2 = Q_2 + Q_3 = h_2 F_2 + h_3 F_3.$$

The calculation of the chain generation rates does not substantially influence the theoretical value of the flame propagation velocity with the exception of special cases when into the hot mixture a material is introduced which is easily decomposed with the formation of active centers. Therefore, disregarding the rates of chain generation, i.e. assuming that $R_1 = R_2 = R = \phi = 0$, we obtain from (14)

$$A_1 p_*^4 + A_2 p_*^2 + A_3 = 0, \quad (15)$$

where A_2' and A_3' are A_2 and A_3 at $R_1 = R_2 = \phi = 0$.

The velocity of flame propagation will be determined using relationships which are found from the relationship $B = \eta p_*$ placing these values into (5), (6), and (7):

$$u_0 = \frac{1}{p_*} \eta p_*. \quad (16)$$

where p_* is determined from equation (14) or from the approximate equation (15).

From relationship (16) and equation (15) for the determination of the velocity of flame propagation simpler approximate relationships can be obtained which are similar to those which were derived in foregoing works^{1,2,5}. Assuming that in (15) $A_1 \approx 0$ and also taking into conside-

ration that $A_2 \approx 2c\eta r(G_{1m}D_{2m} + G_{2m}D_{1m})$ we find

$$p_*^2 = \frac{(t_1 D_{1m} + t_2 D_{2m})(S_{1m}G_{2m} + S_{2m}G_{1m})}{c\eta(G_{1m}D_{2m} + G_{2m}D_{1m})} \left(1 - \frac{2q}{\alpha}\right), \quad (17)$$

where $\frac{2q}{\alpha} = \frac{2q_1 q_2 (t_1 + t_2)}{(t_1 x_1 q_1 + t_2 x_2 q_2)}$,

$$x_1 = \frac{cD_{10}}{\lambda_0}, \quad x_2 = \frac{cD_{20}}{\lambda_0}, \quad D_{10} = D_{1m}q_1,$$

$$D_{20} = D_{2m}q_2, \quad q_1 = \frac{\mu_0}{\mu_m} \left(\frac{T'_0}{T'_m}\right)^{a_1-1}$$

$$\text{at } D_{P1} \sim (T')^{a_1}, \quad q_2 = \frac{\mu_0}{\mu_m} \left(\frac{T'_0}{T'_m}\right)^{a_2-1}$$

$$\text{at } D_{P2} \sim (T')^{a_2}, \quad \tau = 4D_m q \frac{1}{\alpha T'_m}$$

$$\text{and } D_m = \frac{t_1 D_{1m} + t_2 D_{2m}}{t_1 + t_2}.$$

Placing p_* from (17) into (16) and placing these values into (10) and (11) we obtain an approximate relationship for the determination of the velocity of flame propagation

$$u_0 = \varphi \varphi_D \frac{1}{\rho_0} \sqrt{\frac{(n_{1r}D_{1m} + n_{2r}D_{2m})(S_{1m}G_{2m} + S_{2m}G_{1m})}{2cT_r(G_{1m} + G_{2m})}}, \quad (18)$$

where

$$\varphi = 2\sqrt{\frac{2q}{\alpha} \left(1 - \frac{2q}{\alpha}\right)}. \quad (19)$$

$$\varphi_D = \sqrt{\frac{(n_{1r}D_{1m} + n_{2r}D_{2m})(G_{1m} + G_{2m})}{(n_{1r} + n_{2r})(G_{1m}D_{2m} + G_{2m}D_{1m})}} \quad (20)$$

The relationship (18) can be represented in a form which conforms with the form of the relationships obtained in foregoing works^{1,2,5} for simpler cases if the effective total concentration of the active center of one type n_r , the effective diffusion coefficient D_{pm} , and the effective value Q_m are introduced. After simple rearrangements we obtain from (18) and (20)

$$u_0 = \varphi \frac{1}{\varphi_0} \sqrt{\frac{n_r Q_m \tau_n D_{pm}}{2\epsilon T_r}} \quad (21)$$

where

$$n_r = (n_{1r} + n_{2r}) \frac{(n_{1r}D_{1m} + n_{2r}D_{2m})}{(n_{1r} + n_{2r})} \frac{(G_{1m} + G_{2m})}{(G_{1m}D_{2m} + G_{2m}D_{1m})} \quad (22)$$

$$D_{pm} = \frac{n_{1r}D_{p1m} + n_{2r}D_{p2m}}{n_{1r} + n_{2r}} \quad (23)$$

$$Q_m = \frac{S_{1m}G_{2m} + S_{2m}G_{1m}}{G_{1m} + G_{2m}} \quad (24)$$

Previously, when the disintegrating flame was considered² the mechanism of the gradual (non-branched) chain reaction was represented by a simplified system with one kind of active centers. The simplified system was introduced to facilitate the solution of the flame propagation

problem in a system reacting according to the chain mechanism. The relationships (21) to (24) verify the substantiality of the simplified system of the chain reaction assumed earlier^{2,4} and give an opportunity to determine for this simplified system the effective concentration of one kind of active center at combustion temperature (22), the effective diffusion coefficient (23) and the effective constant of the rate of the chain continuation process which in conformity with (24) is equal to $2Q_m/cT_r$. All of the effective values indicated are determined from the data of the reaction system with two active centers and different coefficients of their diffusion.

Relationships (18) or (21) do not take into consideration the influence of the rates of the generation and the quadratic rupture of the chains. Using the approximate relationships obtained in [4] and adduced to also in [1] we find from (21) the final relationship for the determination of the velocity of flame propagation u_0 taking into consideration all of the processes according to (1), (1'), (2), (3), (2'), (3'), (4), and (4'):

$$u_0 = \varphi \psi \frac{1}{\rho_0} \sqrt{\frac{n_r Q_m \rho_m D_{pm}}{2cT_r}}, \quad (25)$$

where n_r , D_{pm} and Q_m are found from relationships (22), (23) and (24), but the coefficients of the rate, ξ and ψ , taking into consideration the influence of the generation rates and the rates of the quadratic chain rupture, are calculated from the relationships:

$$\xi = \sqrt{\frac{1}{2} \left(1 + \sqrt{1 + \frac{16q\alpha T_r R_m}{(x - 2q)^2 n_r^2 Q_m}} \right)}. \quad (26)$$

$$\psi = \left(1 + \frac{q\alpha T_r W_m}{x Q_m} \right)^{-\frac{1}{2}}, \quad (27)$$

where $R_m \approx R_{1m} + R_{2m}$ and $W_m \approx W_{1m} + W_{2m}$, but q/x is found from a relationship corresponding to (17). Such a representation of the total effective rates of the generation and the quadratic rupture of chains in the form of sums of the rates for unlike active centers having differing diffusion coefficients is not entirely as strict as in the cases when the diffusion coefficients are equal.¹ However, with ξ and ψ being little different from unity one can successfully use the relationships (26) and (27), which often takes place in real cases.

Assuming, as it was done in [2], that the distribution of the concentrations of the active centers P_1 and P_2 is determined by the values of the quantities at $T = T_m$

(the admissibility of such an assumption was proven in [2]) we obtain in conformity with (12) and (13) and by placing the values in (10) and (11) the dependence of the concentration of the active centers on the temperature:

$$n_1(T) = \frac{(4D_{1m}D_{2m}p_m^4 l_1)T + [G_{2m}A_n + 2D_{2m}p_m^3 (R_{1m} - \eta l_1 p_m^2)]T(T_r - T)}{4D_{1m}D_{2m}p_m^4 + 2p_m^3 (G_{1m}D_{2m} + G_{2m}D_{1m})T(T_r - T)}, \quad (28)$$

$$n_2(T) = \frac{(4D_{1m}D_{2m}p_m^4 l_2)T + [G_{1m}A_n + 2D_{1m}p_m^3 (R_{2m} - \eta l_2 p_m^2)]T(T_r - T)}{4D_{1m}D_{2m}p_m^4 + 2p_m^3 (G_{1m}D_{2m} + G_{2m}D_{1m})T(T_r - T)}, \quad (29)$$

where $A_n = 2p_m^2(l_1D_{1m} + l_2D_{2m})T + (R_m - \eta l p_m^2)T(T_r - T)$, but $p_m = p_*$ is found from the solution of (14) or (15) or from the approximate relationship (17).

In contrast to the functions $n_1(T)$ and $n_2(T)$ obtained in [2] for the case when the diffusion coefficients of both active centers are equal, the dependences (functions) (28) and (29) are derived taking into consideration the rates of chain generation.

DISCUSSION OF THE RESULTS OBTAINED

Let us consider some of the consequences resulting from the relationship (21) or (25). Having assumed in (24) for the sake of simplicity that $F_{3m} = 0$ and $F_{4m} = 0$

we obtain for the quantity Q_m a simpler relationship $Q_m = (h_1 + h_2)F_{1m}F_{2m}/(F_{1m} + F_{2m})$. The quantity Q_m on which the rate of heat liberation in (25) depends and, consequently, also the velocity of flame propagation are determined in the same way as in [1], namely, from the smallest of the values F_{1m} or F_{2m} . When $F_{1m} = F_{2m}$ the quantity $Q_m = (h_1 + h_2) F_{1m}/2 = (h_1 + h_2) F_{2m}/2$. The quantity Q_m does not depend on n_{1r} and n_{2r} and on individual heat effects, but is determined by the algebraic sum of the heat effects of two consecutive chain continuation processes. The rate of heat liberation depends also on the product $n_r D_{Pm}$ [relationships (22) and (23)], the value of which will be basically determined by that of the products $n_{1r} D_{P1m}$ or $n_{2r} D_{P2m}$ which turns out to be the highest under the given conditions. The active center with the greatest product $n_{1r} D_{P1m}$ will be the determining (leading) active center. For the case considered in [1] with equal diffusion coefficients the leading active center was the one which had the greatest concentration value at the combustion temperature.

The product of the two fractions on the right side of the relationship (22), i.e. the quantity $n_r/(n_{1r} + n_{2r})$, will always be within the limits between the two extreme

possible values D_{1m}/D_{2m} and D_{2m}/D_{1m} . Let us also consider the product $n_r D_{Pm}$ of the relationships (22) and (23) at $F_{3m} = F_{4m} = 0$ (this means that in the relationship (22) instead of G_{1m} and G_{2m} there will be F_{1m} and F_{2m} , respectively). It is obvious that this product to a considerable degree is determined by the diffusion flow of the active centers or the leading active center having the maximal product $n_{1r} D_{P1m}$. However, the diffusion flow of the leading active center also depends on the ratio of the rates of the consecutive processes (2) and (3), i.e. on the ratio of the quantities F_{1m} and F_{2m} , since the diffusion flow depends not only on n_{1r} and n_{2r} , but also on the concentration of the leading active center at $T = T_m$ which in turn depends on the rate of consumption and formation of the leading active center. Let us assume, for example, that $n_{1r} D_{1m} > n_{2r} D_{2m}$, then the quantity n_r according to relationship (22) will essentially depend on the size of the quantities $F_{1m} D_{2m}$ and $F_{2m} D_{1m}$. Moreover, if $F_{1m} D_{2m} > F_{2m} D_{1m}$, then the concentration P_1 at $T = T_m$ will to a high degree depend on the rate of consumption P_1 according to process (2). This is explained by the high rate of consumption P_1 . If, however, $F_{1m} D_{2m} < F_{2m} D_{1m}$, then the concentration P_1 in the reaction zone will to a

low degree depend on the diffusion flow, because the rate of formation P_1 according to the process (3) is comparatively high. However, as a whole, as it follows from inspection of the product $n_r D_{pm}$, the velocity of flame propagation is determined to a more significant degree by diffusion flow of the active centers in a system of unbranched chain reactions, which is quite evident physically. In cases when there will be a highly branched reaction or an unbranched reaction with a relatively high rate of generation of active centers (this can happen upon addition of small quantities of ozone or any other substance to the hot mixture, which (the substance) would rapidly decompose with a formation of active centers at temperatures below that of combustion) the leading role of the diffusion of the active centers in the flame propagation will be eliminated as a consequence of the high rate of generation of active centers in the reaction zone due to the branching or generation of chains.

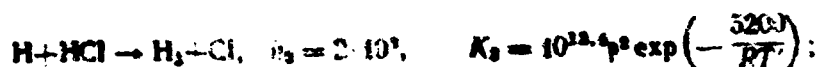
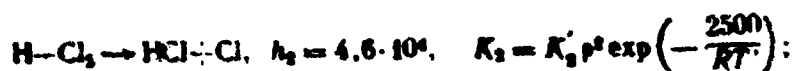
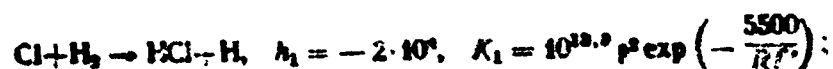
The leading active center will basically determine the character of the dependencies of the flame propagation rate on pressure and combustion temperature. The concentrations of the various active centers can by themselves depend on the pressure and temperature of combustion of

a mixture of a given initial composition^{1,3,5}. Upon changing the initial composition of the mixture the rapidity of the change in the concentration of the given active center changes with a change in pressure and temperature.³ Therefore when the pressure is changed the leading role may pass from one active center to another and will depend on the composition of the mixture. Therefore, also the effective activation energy determined by formulas obtained without taking into consideration the diffusion of the active centers will depend on the initial composition of the hot mixture^{1,3}.

Relationship (25) enables to determine the true constants and energies of activation of elementary processes from the experimental dependencies of the rate of flame propagation on pressure and temperature of combustion¹. Relationships (16) and (14) allow to determine the experimental values of the constants and activation energies with a great accuracy.

Numerical calculations. The relationships obtained enable to carry out calculations of absolute theoretical values of the flame propagation velocities for real cases when the values found experimentally (not dependant on the flame by purely kinetic methods) and necessary for the

calculation of the rate constants and activation energies of elementary processes are assumed. The system shown in the beginning of the article is true for the combustion of halogen-hydrogen mixtures. As an example combustible chlorine-hydrogen mixtures were selected whose kinetics are well known and can be represented by the following system of chain reactions:



where two values for the coefficient K_2' were assumed: $K_2' = 10^{13.7}$ and $K_2' = 10^{13.4}$. The dependencies of the rate constants of the reactions shown were taken from the data of Trotman-Dickenson⁶ and Schumacher⁷.

Data for two mixtures obtained on the basis of thermodynamic calculations are shown in table 1, where μ is the molecular weight of the mixture.

For both mixtures the diffusion coefficients of the active centers and the heatconductivity were taken from the work of Hellwig and Anderson⁸: $D_{\text{P}10} = 0.19$ (chlorine

atom) and $D_{P20} = 1.04$ (hydrogen atom) at $\alpha_1 = \alpha_2 = 1.9$ and $\lambda_0 = 8.6 \cdot 10^{-5}$.

The results of calculations according to relationship (25) are given in table 2, where the data for corresponding mixtures obtained by Bartolome⁹ are also given. In view of some confusion in regard to the value of the coefficient of process (3) the calculations were carried out with the two values of K_2 indicated above. In both cases $\xi = 1.00$ and $\psi = 1.00$, although an extremely high value, $K_{R1} = 10^{16} \rho^2 \exp\left(-\frac{57\,000}{RT}\right)$ was taken for the rate constant of the generation of chlorine atoms. For the rate constant of the quadratic rupture of the chains the value taken was $2 \cdot 10^{-32} \text{ cm}^6/\text{molecule}^2 \cdot \text{sec}$. The results of the calculations show that when the rate of the quadratic chain rupture is taken into account there is practically no influence on the calculated value of the flame propagation velocity (for $\psi = 1.00$).

The comparison of the experimental values of the velocities of flame propagation with the theoretical ones, calculated using relationship (25) and given in table 2, indicates their satisfactory agreement. In the first article, which was devoted to the study of the flame propa-

Table 1

The Data of the Thermodynamical
Calculation

1) Величина	T°	n _B (H ₂)	n _A (Cl ₂)	n _{HCl} (HCl)	A _i (d _i)	B _i (h _i)	C
2) Размерности	°K	3) M/10 см ³					4) $\frac{H_{HCl}}{g/M}$
0,5 H ₂ + +0,5 Cl ₂	T ₀ = 293	1,37 · 10 ⁻³	1,37 · 10 ⁻³	0	0	0	36,5 0,208
	T _m = 1389	7,36 · 10 ⁻³	6,85 · 10 ⁻³	1,26 · 10 ⁻³	—	—	35,8 0,225
	T _r = 2485	1,01 · 10 ⁻³	1,65 · 10 ⁻³	2,51 · 10 ⁻³	2,25 · 10 ⁻³	1,26 · 10 ⁻³	35,1 0,241
0,6 H ₂ + +0,4 Cl ₂	T ₀ = 293	2,03 · 10 ⁻³	1,35 · 10 ⁻³	0	0	0	29,6 0,258
	T _m = 1337	1,36 · 10 ⁻³	6,75 · 10 ⁻³	1,32 · 10 ⁻³	—	—	29,5 0,275
	T _r = 2389	6,97 · 10 ⁻³	1,67 · 10 ⁻³	2,84 · 10 ⁻³	3,63 · 10 ⁻³	2,23 · 10 ⁻³	29,3 0,283

1. Quantity

2. Dimension

3. Moles/gram of mixture

4. g/mole

5. cal/g · degree

Table 2

Experimental and Theoretical Values of Flame
Propagation Velocities (cm/sec) for Chlorine-
hydrogen Mixtures

① Состав смеси	$0.6\text{H}_2 + 0.4\text{Cl}_2$	$0.5\text{H}_2 + 0.5\text{Cl}_2$
② Опытные данные Бартоломе [9]	405	350
③ По соотношению (25) при $K_2' = 10^{13.7}$	347	368
④ По соотношению (25) при $K_2' = 10^{13.4}$	252	278

1. Composition of mixture
2. Experimental data of Bartolome⁹
3. From relationship (25) at $K_2' = 10^{13.7}$
4. From relationship (25) at $K_2' = 10^{13.4}$

gation process in a system with a simplified scheme of the chain reaction and which included active centers of one kind, comparison of results obtained by theoretical calculation according to a relationship of the type of (25) with results obtained by numerical integration of the equation of the initial system was given. The difference in the numerical values of the flame propagation velocities in these two cases was a few percent. Taking this circumstance into consideration, and also the data on the comparison of experimental and theoretical values given in table 2 a conclusion must be made that the theoretical consideration of the system with the unbranched chain reaction correctly describes the real process of flame propagation.

The results obtained (table 2) substantiate the possibility to determine the true constants and the activation energies of chain continuation processes from the experimental dependencies of the flame propagation velocity on the combustion temperature.

The author expresses his deep appreciation to V. N. Kondrat'yev for his valuable advice and help in this work.

CONCLUSIONS

1. For the scheme of an unbranched chain reaction with two active centers relationships were obtained for the determination of the flame propagation velocity which take into consideration the diffusion of both of the active centers that have differing diffusion coefficients and which also take into consideration the rate of generation and the rate of the quadratic rupture of the chains.

2. For two cases of combustion of chlorine-hydrogen mixtures the theoretical values of the flame propagation velocities were calculated, which are in a satisfactory agreement with experimental data.

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Submitted
on
2 December 1958

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