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Abstract

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CALCULATION OF THE VELOCITY OF NORMAL FLAME PROPAGATION IN MIXTURES OF HYDROGEN WITH CHLORINE

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The theory of the velocity of normal flame propagation has recently been generalized by Ya. B. Zel' dovich to flames in which the chemical reaction proceeds by a chain mechanism (1). The basic assumption of the new theory is that all elementary reactions, including radical reactions, have a sufficiently large activation energy ($E \gg RT_r$, where T_r is the combustion temperature). By specifying the distribution of temperature and concentrations in the form of the Michelson profile, it was possible to obtain expressions for the velocity of flame propagation both for unbranched and for branched chain reactions.

More exact relations can be obtained if the temperature and concentration profiles are found by approximate integration of the heat-conduction and diffusion equations. This possibility was pointed out by Ya. B. Zel' dovich. Namely, if it is assumed that the concentration of active centers in the reaction zone is constant, $[\mathrm{B}] \simeq [\mathrm{B}]_m = \text{const}$, then, neglecting the convective term in the heat-conduction equation in the same way as is done in the theory of thermal flame propagation (2), one obtains the temperature profile near the combustion temperature

$$\frac{dx}{dT} = \lambda \left[2 \int_T^{T_r} \lambda q \Phi(T, [\mathrm{B}]_m)\, dT \right]^{-1/2}, \tag{1}$$

where λ is the coefficient of thermal conductivity, q is the heat effect of the reaction, Φ is the rate of heat release, and T is the temperature. Using this temperature profile instead of the Michelson one and applying the expansion of D. A. Frank-Kamenetskii, we obtain, analogously to the way it was done in (1), the flame-propagation velocities and the concentrations of active centers in the reaction zone. We shall assume, as usual, that the process is isobaric and neglect thermal diffusion, mutual diffusion, and heat losses. For example, when the reaction proceeds according to the scheme

$$\mathrm{A} + \mathrm{X} \to 2\mathrm{B} + \mathrm{X}, \quad w_{\mathrm{B}} = 2[\mathrm{A}][\mathrm{X}]\, k_1 \exp(-E_1/RT);$$
$$\mathrm{A} + \mathrm{B} \to \mathrm{C} + \mathrm{B}, \quad w_{\mathrm{A}} = -[\mathrm{A}][\mathrm{B}]\, k_2 \exp(-E_2/RT),$$

we have

$$(\rho_0 u_0)^4 = 4 f_1\left(\frac{E_2}{E_1}\right)\left(\frac{RT_r}{E_2}\right)^4\left(\frac{\lambda_r}{c_{pr}}\right)^2\left(\frac{c_{pr}T_r}{q[\mathrm{A}_0]}\right)^4 \frac{\chi_1^2}{D_{\mathrm{A}r}^2}[\mathrm{A}]_0[\mathrm{X}]\, k_{1r}k_{2r} \exp\left(-\frac{E_1+E_2}{RT_r}\right), \tag{2}$$

$$[\mathrm{B}]_m^2 = f_1(E_2/E_1)[\mathrm{A}_0][\mathrm{X}](k_{1r}/k_{2r}) \exp[-(E_1 - E_2)/RT_r]\,. \tag{3}$$

Here $w_{\mathrm{A}}, w_{\mathrm{B}}$ are the rates of reaction of the initial substance A and the active center B; c_p is the heat capacity; the subscript r refers to the combustion temperature, the subscript 0 to the initial mixture. The function

$$f_1(E_2/E_1) = \int_0^\infty \xi \exp(-\xi E_1/E_2)\,[1 - (1+\xi)\exp(-\xi)]^{-1/2}\, d\xi$$

can be approximately represented in the form

$$f_1(E_2/E_1) \approx \sqrt{2E_2/E_1}.$$

In formula (2) and in what follows, the diff—

difference between the diffusion coefficients D_A and the thermal diffusivity coefficient $\varkappa$. Under the condition $\dot{E} \gg RT_r$, as is known from $^{(3)}$, the concentration of the initial substance in the reaction zone is smaller by a factor $\varkappa/D_A$ than for $\varkappa = D_A$. When the Michelson profile is used, in the formula for $(\rho_0 u_0)^4$ one should put $\frac{1}{2} f_1(E_2/E_1)$, while in the formula for $[B]_m$ one should put $2(E_2/E_1)^2$.

Let us test the theory on the example of the reaction of combination of hydrogen with chlorine. At the combustion temperature of the mixture H_2—Cl_2 (approximately 2500° K), HCl, and even more so H_2, dissociate only slightly, whereas chlorine dissociates almost completely. Therefore, as the chain-initiation reaction we shall consider only the dissociation of chlorine

$$\mathrm{Cl}_2 + X \to 2\mathrm{Cl} + X, \qquad w_{\mathrm{Cl}} = 2[\mathrm{Cl}_2][X]\, k_1 \exp(-E_1/RT),$$

where X is any molecule. Chain propagation in this reaction is determined by the stage

$$\mathrm{Cl} + \mathrm{H}_2 \to \mathrm{HCl} + \mathrm{H}, \qquad w_{\mathrm{H2}} = -[\mathrm{Cl}][\mathrm{H}_2]\, k_2 \exp(-E_2/RT).$$

The concentration of hydrogen atoms may be regarded as quasi-stationary (the usual condition of quasi-stationarity under flame conditions must be replaced by the condition $D_H[\mathrm{H}] < D_{\mathrm{Cl}}[\mathrm{Cl}]$).

If there is an excess of chlorine in the mixture, then after the hydrogen has burned out, the chlorine remaining in the reaction products will continue to dissociate and supply active centers. Two limiting cases are possible here:

1) The equilibrium concentration $[\mathrm{Cl}]_p$ is already attained in the reaction zone.

2) The equilibrium concentration $[\mathrm{Cl}]_p$ is formed only very far beyond the reaction zone. The concentration $[\mathrm{Cl}]_m$ in the zone itself is small, much smaller than the equilibrium value, and is determined by the rate of diffusion of active centers from the reaction products into the combustion zone. In this case the temperature immediately beyond the reaction zone will be higher than the equilibrium theoretical combustion temperature. To a first approximation it can be calculated without taking dissociation into account at all. The temperature will fall to the equilibrium value only far beyond the reaction zone. Ya. B. Zel' dovich and S. B. Ratner (4) first drew attention to this possibility.

We shall assume that the second case occurs. This assumption can be checked by finding the concentration $[\mathrm{Cl}]_m$ in the reaction zone and comparing it with $[\mathrm{Cl}]_p$ (see Table 1). The formulas for the case of excess chlorine in the mixture have the following form:

$$(\rho_0 u_0)^4 = 4\left(\frac{RT_r}{E_2}\right)^2 \left(\frac{\lambda}{c_{pr}}\right)^2 \left(\frac{c_{pr}T_r}{q[\mathrm{H}_2]_0}\right)^2 \frac{D_{\mathrm{Cl\,r}}}{D_{\mathrm{H2\,r}}}[\mathrm{Cl}_2]_r[X]\,k_{1\mathrm{r}}k_{2\mathrm{r}}\exp\left(-\frac{E_1+E_2}{RT_r}\right); \tag{4}$$

$$[\mathrm{Cl}]_m = 2u_r^{-2}D_{\mathrm{Cl\,r}}[\mathrm{Cl}_2]_r[X]\,k_{1\mathrm{r}}\exp[-E_1/RT_r]. \tag{5}$$

With excess hydrogen, the reaction proceeds owing to active centers formed in the reaction zone itself. Their concentration may turn out to be greater or smaller than the equilibrium concentration in the reaction products. In the first case, recombination of Cl atoms will occur beyond the reaction zone. In the second case, equilibrium is attained by dissociation of HCl. Calculations using the formulas (6), (7) given below show that the second case occurs. To estimate the flux of chlorine atoms caused by dissociation of HCl, one may use formula (5), substituting in it, instead of the rate of chlorine dissociation, the rate of HCl dissociation. It turns out that this flux can give a [Cl] concentration in the reaction zone at least three orders of magnitude smaller than that formed in the zone itself from Cl_2, and it may be neglected. (This is due to the low rate of HCl dissociation.) The flux of Cl atoms due to dissociating Cl_2, which is present in the equilibrium reaction products, has an even smaller effect on the concentration $[\mathrm{Cl}]_m$. The temperature immediately beyond the reaction zone is higher than the theoretical combustion temperature; however, in a first approximation the difference may be neglected, and if necessary the temperature may be corrected, knowing from the first approximation the concentration of active centers. The formulas for the case of excess H_2 in the mixture ···

have the form

$$(\rho_0 u_0)^4 = 4 f_2 \left(\frac{E_2}{E_1}\right) \left(\frac{RT_r}{E_2}\right)^3 \left(\frac{c_{\mathrm{pr}} T_r}{q[\mathrm{Cl}_2]_0}\right)^3 \frac{\mu_{\mathrm{Cl2}}}{\mu_{\mathrm{H2}}} \left(\frac{\lambda_r}{c_{\mathrm{pr}}}\right)^2 [\mathrm{H}_2]_r [\mathrm{X}] k_{1\mathrm{r}} k_{2\mathrm{r}} \exp\left(-\frac{E_1+E_2}{RT_r}\right) \tag{6}$$

(μ is the molecular weight),

$$[\mathrm{Cl}]_m^2 = f_2 \left(\frac{E_2}{E_1}\right) \frac{RT_r}{E_2} \frac{c_{\mathrm{pr}} T_r}{q[\mathrm{H}_2]_r} \frac{\mu_{\mathrm{H2}}}{\mu_{\mathrm{Cl2}}} [\mathrm{Cl}_2]_0 [\mathrm{X}] \frac{k_{2\mathrm{r}}}{k_{1\mathrm{r}}} \exp\left(-\frac{E_1-E_2}{RT_r}\right), \tag{7}$$

where

$$f_2(E_2/E_1) = \int_0^\infty \xi \exp(-\xi E_1/E_2)[1-\exp(-\xi)]^{-1/2}\, d\xi \simeq (\sqrt{\pi}/2)(E_2/E_1)^{3/2}.$$

The case of a stoichiometric mixture differs from the case of a mixture with excess hydrogen only in that the hydrogen concentration in the reaction zone falls to zero (without taking dissociation into account in the first approximation)

$$(\rho_0 u_0)^4 = 4 f_1 \left(\frac{E_2}{E_1}\right) \left(\frac{RT_r}{E_2}\right)^4 \left(\frac{\lambda_r}{c_{\mathrm{pr}}}\right)^2 \frac{\chi_r^2}{D_{\mathrm{H2r}} D_{\mathrm{Cl2r}}} \left(\frac{c_{\mathrm{pr}} T_r}{q[\mathrm{Cl}_2]_0}\right)^4 \times$$

$$\times [\mathrm{Cl}_2]_0 [\mathrm{X}] k_{1\mathrm{r}} k_{2\mathrm{r}} \exp\left(-\frac{E_1+E_2}{RT_r}\right); \tag{8}$$

$$[\mathrm{Cl}]_m^2 = f_1 \left(\frac{E_2}{E_1}\right) \frac{D_{\mathrm{H2r}}}{D_{\mathrm{Cl2r}}} [\mathrm{Cl}_2]_0 [\mathrm{X}] \frac{k_{1\mathrm{r}}}{u_{2\mathrm{r}}} \exp\left(-\frac{E_1-E_2}{RT_r}\right). \tag{9}$$

Calculations were carried out for the rates of flame propagation for various compositions of the initial mixture at $T_0 = 291^\circ\mathrm{K}$ and $P_0 = 1$ atm. Theoretical combustion temperatures and heat capacities were calculated according to $^{(5-7)}$. In the case of excess H_2, the equilibrium composition was calculated from the equilibrium $\mathrm{HCl} \rightleftarrows \frac{1}{2}\mathrm{H}_2 + \mathrm{Cl}$. For mixtures with excess chlorine, in the calculations

Table 1

$[Cl_2]_0$, atm.	0.3	0.4	0.5	0.6	0.7	0.8
T_r, °K	2045	2440	2520	2495	1930	1375
$[H_2]_r$, atm.	0.4	0.2	0.044	0	0	0
$[Cl_2]_r$, atm.	0	0	0	0.2	0.4	0.6
$[Cl]_r$, atm.	0.002	0.025	0.089	0	0	0
$[Cl]_p$, atm.	0.002	0.025	0.089	0.213	0.077	0.016
$[Cl]_m$, atm.	$2.7 \cdot 10^{-5}$	$6.1 \cdot 10^{-4}$	$2.3 \cdot 10^{-2}$	$4.3 \cdot 10^{-6}$	$3.4 \cdot 10^{-6}$	$4.5 \cdot 10^{-8}$
c_{pr}, cal/g• deg	0.360	0.283	0.237	0.199	0.170	0.152
$\rho_r \cdot 10^4$, g/cm^3	1.350	1.475	1.978	2.120	3.165	5.060
$\lambda_r \cdot 10^4$, cal/cm• sec • deg	4.960	3.230	2.820	2.280	1.678	1.134
$\chi_r^2/D_{H_2}D_{Cl2}$	–	–	0.209	–	–	–
D_{Cl}/D_{H_2}	–	–	–	0.206	0.223	0.259
$k_{1r} \cdot 10^{-8}$, gCl/g mixture • sec	2.28	1.85	1.96	0.409	0.836	0.126
$k_{2r} \cdot 10^{-5}$, gH$_2$/g mixture • sec	0.407	0.484	0.872	1.013	2.240	5.730
E_1/RT_r	14.1	11.86	11.5	11.0	15.0	21.1
E_2/RT_r	1.67	1.42	1.36	1.37	1.78	2.49

	$[Cl_2]_0$, atm.	0.3	0.4	0.5	0.6	0.7	0.8
u_0, cm · sec		171	237	263	224	106	27.9

dissociation was not taken into account in the thermodynamic quantities. The coefficients of thermal conductivity and diffusion were calculated according to (8,9). The thermal conductivity of the mixture in the case of excess chlorine, when the combustion products contain components differing little in molecular weight, was taken equal to the mean molar value; in the case of excess hydrogen and for the stoichiometric mixture it was calculated from the formula $\lg\lambda = \sum_i c_i \lg\lambda_i$, where c_i is the mole fraction of the i-th component. For the chlorine dissociation reaction, the activation energy is $E_1 = 57\,500$ cal/mol. The pre-exponential factor was calculated in accordance with the work of E. E. Nikitina (10) by the formula

$$k_1 = 3.3 \cdot 10^{-2} Z_0 (E_1/RT)^{3/2} \sqrt{1 + 71/\mu_r}\ \text{cm}^3/\text{s},$$

where Z_0 is the number of gas-kinetic collisions, and μ_r is the mean molecular weight of the mixture. The kinetic constants of the chain-propagation reaction, calculated according to (11), are

$$E_2 = 6800\ \text{cal/mol}; \qquad k_2 = 1.32 \cdot 10^{-10}\ \text{cm}^3/\text{s}.$$

Table 1 gives the results of calculating a number of quantities entering into the formulas. The concentrations are given in partial pressures; the subscript r refers to quantities at the rear boundary of the reaction zone, which, for cases of excess chlorine in the initial mixture, corresponds to nonequilibrium reaction products.

Comparison of the calculated flame-propagation velocities with the experimental data of A. I. Rozlovskii (12) is given in Fig. 1. Such agreement between the approximate theory and experiment is surprising, since the activation energy of chain propagation is by no means large ($E_2/RT_r \approx 1.5$). One may try to explain this fact as follows. The zone of generation of active centers is narrow ($E_1/RT_r \approx 10 \div 20$). Outside this zone the concentration of Cl atoms is as if they simply diffuse out of the generation zone, since in the reaction the chlorine atom is regenerated. Therefore, outside the generation zone,

$$[\text{Cl}] = [\text{Cl}]_m \exp(-ux/D_{\text{Cl}}).$$

(Near the generation zone the Cl concentration will become greater than the equilibrium concentration because of the temperature drop; recombination will

Fig. 1. Dependence of flame-propagation velocity on mixture composition: a—calculated points, b—experimental data of A. I. Rozlovskii

Figure 1: Fig. 1. Dependence of flame-propagation velocity on mixture composition: a—calculated points, b—experimental data of A. I. Rozlovskii

begin to prevail, and the decrease in [Cl] will be even steeper.) The rate of the chain-propagation reaction responsible for heat release is

$$w_{\mathrm{H}_2} = -k_2[\mathrm{Cl}]_m[\mathrm{H}_2] \times \exp(-ux/D_{\mathrm{Cl}}) \exp(-E_2/RT).$$

The factor $\exp(-ux/D_{\mathrm{Cl}})$ is equivalent to increasing the effective activation energy by the amount

$$\Delta E = -\frac{d \ln w_{\mathrm{H}_2}}{d(1/RT)} - E_2 \approx$$

$$\approx -\frac{u}{D_{\mathrm{Cl}}} RT^2 \frac{dx}{dT} > 0.$$

Find dx/dT from formula (1) at the temperature $T \approx T_r - RT_r^2/E_1$. For the most unfavorable case of a stoichiometric mixture, $\Delta E/RT_r \approx 2.5$, i.e. the decrease in the Cl concentration before the generation zone is equivalent to increasing the activation energy by approximately 20000 cal/mol.

Fig. 1. Dependence of flame-propagation velocity on mixture composition: *a* —calculated points, *b*—experimental data of A. I. Rozlovskii.

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CITED LITERATURE

1. Ya. B. Zel' dovich, *Kinetika i kataliz*, **2**, issue 3, 305 (1961).
2. Ya. B. Zel' dovich, D. A. Frank-Kamenetskii, *ZhFKh*, **12**, issue 1, 100 (1938).
3. Ya. B. Zel' dovich, *ZhFKh*, **22**, issue 1, 27 (1948).
4. Ya. B. Zel' dovich, S. B. Ratner, *ZhETF*, **11**, 170 (1941).

5. Ya. B. Zel' dovich, A. I. Leipunskii, *Calculations of Heat Processes at High Temperature*, Moscow, Publishing House of the Bureau of New Technology, 1947.

6. A. P. Vanichev, *Thermodynamic Calculation of Combustion and Efflux in the Region of High Temperatures*, Moscow, Publishing House of the Bureau of New Technology, 1947.

7. D. Kay, T. Laby, *Handbook of Physics for the Experimental Physicist*, Foreign Literature Publishing House, 1949.

8. J. O. Hirschfelder, R. B. Bird, E. L. Spotz, *J. Chem. Phys.*, **16**, No. 10, 968 (1948).

9. J. O. Hirschfelder, R. B. Bird, E. L. Spotz, *Chem. Rev.*, **44**, No. 1, 205 (1949).

10. E. E. Nikitin, *DAN*, **119**, No. 3, 526 (1958).

11. A. M. Markevich, *ZhFKh*, **22**, issue 8, 941 (1948).

12. A. I. Rozlovskii, *ZhFKh*, **30**, issue 11, 2489 (1956).

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