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On the nature of an upper concentration limit of flame propagation in an H_2 + air mixture

Nikolai M. Rubtsov* and Boris S. Seplyarskii

Institute for Structural Macrokinetics and Materials Science, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 495 962 8025; e-mail: nmrubtss@mtu-net.ru

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The mechanism of the occurrence of an upper concentration limit of flame propagation at atmospheric pressure taking into account effective heat losses in the termolecular recombination $H + O_2 + M \rightarrow HO_2 + M$ is suggested for the combustion of an H_2 + air mixture.

An approximate analytical method of calculation of velocity and limits of flame propagation (FP) in H_2 + air mixtures at atmospheric pressure in the presence of small chemically active additives (inhibitors) was recently suggested.[1,2] It was shown that the method based on the model of a narrow reaction zone (NRZ)[3] with consideration for termination of active centres of combustion *via* an inhibitor in preheating zone allows one to give the qualitative description of experimental features of FP in hydrogen combustion, among them concentration limits (CLs).

The nature of the CL of combustion of H_2 + air mixtures is under question up to now. It is known that an upper concentration limit of flame propagation (CLFP) in H_2 + air mixture (75% H_2)[4,5] is observed at central initiation when a spherical flame front does not touch reactor walls; *i.e.*, heat losses into the wall are missing. It may be suggested (by analogy with known data[1,2]) that the termination of H atoms in the reaction $H + O_2 + M \rightarrow OH_2 + M$ in preheating zone is the cause of occurrence of CL.

The aim of this work is the approximate analytical determination of upper CLFP of H_2 + air mixture on the basis of NRZ model[1–3] with regard to branched chain mechanism of H_2 oxidation.

Let us consider a simple mechanism of H_2 oxidation including termolecular termination steps with no regard for chain origination.[6] Specific heat of a reaction chain, which includes the following three reactions: $OH + H_2 \rightarrow H_2O + H$ (k_1), $H + O_2 \rightarrow OH + O$ (k_2), $O + H_2 \rightarrow OH + H$ (k_3), is $Q \approx 0$.[6] Steps of recombination of active centres are exothermic ($Q > 0$).[3,6] We assume[3] that heat release occurs in the step $H + H + M \rightarrow H_2 + M$ (k_{11}), M is the third body. As distinct from refs. 1 and 2, the reaction of formation of low chemically active peroxide radicals $H + O_2 + M \rightarrow HO_2 + M$ (k_6) is taken into account. Let us assume[3] $\chi = D_H = D_{O_2}$ (χ is the thermal diffusivity and D is the diffusivity). For rich mixtures, $d(OH)/dt = d(O)/dt = 0$.[6] The process of stationary FP in a system of coordinates incident to the flame front in accordance with the mechanism is given by the set (I) ($\Delta^2 = d^2/dx^2$, $\Delta = d/dx$):

$$\begin{aligned}
&\lambda\Delta^2 T_a(x) - v\rho C_p \Delta T_a(x) + Qk_4 H(x)^2(M) = 0,\\
&D_H\Delta^2 H(x) - v\rho\Delta H(x) + 2k_2 H(x)O_2(x) - \\
&\qquad - k_6 H(x)O_2(x)(M) - k_{11}H(x)^2(M) = 0,\\
&D_{O_2}\Delta^2 O_2(x) - v\rho\Delta O_2(x) - k_2 H(x)O_2(x) - k_6 H(x)O_2(x)(M) = 0,\\
&x = -\infty,\ T = T_0,\ H(x) = 0,\ O_2(x) = O_{20},\\
&x = +\infty,\ T = T_b,\ H(x) = 0,\ O_2(x) = 0.
\end{aligned} \qquad \text{(I)}$$

Here, Q is total specific heat, ρ is density, v is normal flame velocity, λ is thermal conductivity, C_p is heat capacity, $M = 760\times10^{19}T$ cm^{-3}, $H(t)$, $O_2(t)$ are concentrations of atoms H and O_2, respectively, k_6 is the rate constant of the step $H + O_2 + M \rightarrow HO_2 + M$. Set (I) describes the combustion of rich H_2 + air mixtures.[6]

The relation of enthalpy conservation, following from (I), takes the form:[3]

$$\begin{aligned}
&T(x) - T_0 + 2Q/C_p[O_2(x) - O_{20}] + 2Q/C_p H(x) = \text{const};\\
&T_b = T_0 + 2Q/C_p(O_{20})
\end{aligned} \qquad (1)$$

T_b, T_0 are adiabatic combustion and initial temperatures, respectively; O_{20} is initial O_2 concentration.

Let us specify the distribution of O_2.[3] O_2 completely consumes in NBZ in the branching (k_2) and termolecular (k_6) reactions. Since the branching step has substantial activation energy E it occurs in NBZ. Let us place the zone at the origin of the coordinates. Then outside NBZ:

$$O_2(x) = O_{20}[1 - \exp(ux/D_{O_2})],\ x < 0,\ O_2(x) = 0,\ x > 0 \qquad (2)$$

H atoms consume only in termolecular recombination (k_{11}) outside of NBZ. The temperature in NBZ is lower than T_b because zones of branching and heat release are separated (Figure 1). Since the branching zone is narrow, the balance of O_2 gives: $v\rho O_{20} = \int[k_2 H(x)O_2(x) + k_6 H(x)O_2(x)(M)]$.[3] Note that in branching zone in rich mixtures at 1 atm both the step $H + O_2 + M \rightarrow HO_2 + M$ (k_6) and steps including HO_2 reactions are of minor importance.[7,8] With the known data[6,9] on $k_2 = 0.30\times10^{-9}\exp(-16760/RT)$ cm^3 molec^{-2} s^{-1} and $k_6 \sim 10^{-32}$ cm^6 molec^{-2} s^{-1}, we obtain that at $T > 1500$ K $k_6M/k_2 << 1$.

Therefore, both according to ref. 3 and aforesaid in NBZ approximation $v\rho O_{20}\delta(x) = k_2 H(x)O_2(x)$, where $\delta(x)$ is the Dirac delta function. Let H_m be maximal concentration of $H(x)$. It is achieved at $x = 0$.

We consider recombination in the vicinity of $x = 0$, where $H(x) \approx H_m$, then let $k_{11}H(x)^2(M) \approx k_{11}H(x)H_m(M)$. The equation for $H(x)$ takes the form:[3]

$$D_H\Delta^2 H(x) - v\rho H(x) + 2v\rho O_{20}\delta(x) - k_{11}H(x)H_m(M) = 0. \qquad (3)$$

At $x \neq 0$ (but in the vicinity of $x = 0$) $\delta(x) = 0$ and we have homogeneous linear equation; its solution is sought in the form:

$$H(x) = H_m\exp(sx). \qquad (4)$$

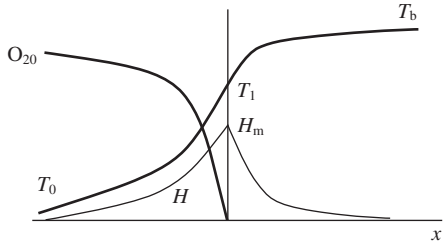

Figure 1 Distributions of temperature and concentrations in the vicinity of narrow reaction zone.[3]

The characteristic equation is $D_H s^2 - v\rho s - k_{11}H_m(M) = 0$, its solutions are:

$$s_{1,2} = v\rho \pm \sqrt{[(v\rho)^2 + 4D_H k_{11}H_m(M)]/2D_H}. \quad (5)$$

In equation (5) s_1 is taken at $x < 0$, s_2 – at $x > 0$. The first condition of joining solutions of equation (5) at $x = 0$ is the equality of concentrations provided by equation (4). The second condition implies that the sum of fluxes of H atoms to both directions from $x = 0$ must be equal to the amount of H atoms which form in the branching step.[3] To calculate the sum, equation (3) is integrated near NBZ:

$$[D_H \Delta H(x)]_{x<0} - [D_H \Delta H(x)]_{x>0} = v\rho O_{20}. \quad (6)$$

Substitution of equation (5) in equation (6) gives:

$$v\rho O_{20} = H_m\sqrt{(v\rho)^2 + 4D_H k_{11}H_m(M)}. \quad (7)$$

We specify $T(x = 0) = T_1$ (Figure 1), $n = (T_b - T_0)/O_{20}$, then we have $T_1 = T_b - 2nH_m$ and values of $dT(x)/dx$ to the left and to the right of the point $x = 0$ identically equal to each other:

$$[\Delta T(x)]_{x=0} = 2O_{20}v\rho/D_H - 2nH_m s_1 = -2nH_m s_2.$$

We add these values taking into account that $s_1 + s_2 = v\rho/D_H$, $n = (T_b - T_0)/O_{20}$, $T_1 = T_b - 2nH_m$:

$$T(x) = T_0 + \exp(v\rho x/2D_H)(T_1 - T_0), \qquad -D_H/v\rho < x < 0. \quad (8)$$

We make up a balance equation of O_2 according to distributions of $O_2(x)$ (2) and $T(x)$ (8), then use Frank–Kamenetsky transform.[10] The following equation is obtained:

$$v\rho O_{20} = \int k_2 H(x)O_2(x)dx = 4D_H H_m k_2^0 \exp(-E/RT_1)\alpha^2/(v\rho),$$
$$\alpha = RT_1^2/E(T_1 - T_0) \quad (9)$$

As a consequence we have three equations (7), (9) and $T_1 = T_b - 2nH_m$ and three unknowns H_m, T_1 and v. One can obtain from equations (7) and (9):

$$M = -(H_m^2 - O_{20}^2)k_2^0 \exp(-E/RT_1)\alpha^2/k_{11}H_m^2 =$$
$$= k_2^0 \exp(-E/RT_1)\alpha^2 \frac{(T_b - T_0)^2 - (T_b - T_1)^2}{(T_b - T_1)^2}. \quad (10)$$

Let T_1 be close to T_b: $T_b - T_1 = \theta << T_b - T_0$. This is called[3] the case of strong recombination. Then we have from equation (10):

$$M = k_2^0 \exp(-E/RT_b)R^2T_b^4/k_{11}T_0^2E^2\theta^2, \text{ and } \theta = \pm\frac{\sqrt{k_{11}Mk_2^0\exp(-E/RT_b)}\,T_b^2R}{k_{11}ME}.$$

For positive θ value, which is only meaningful, we obtain the flame velocity v:

$$v^2\rho^2 = 4D_H k_2^0 \exp(-E/RT_b)\frac{\sqrt{k_4(M)k_2^0\exp(-E/RT_b)}\,T_f^6R^3}{k_4(M)E^3(T_b - T_0)^3}. \quad (11)$$

Note that equation (11) is coincident with equation (70) from ref. 3.

Mathematical analogy between heat losses into walls[10–12] and effective heat losses due termolecular termination in the step (k_6) will be shown below, so we consider the propagation of planar stationary combustion wave with heat losses using NBZ model.[12] The system of equations takes the form:

$$x < 0: \ \lambda\Delta^2T_a(x) - v_f\rho C_p\Delta T_a(x) - \delta_a[T_a(x) - T_o] = 0,$$
$$x > 0: \ \lambda\Delta^2T_c(x) - v_f\rho C_p\Delta T_c(x) - \delta_c[T_c(x) - T_o] = 0,$$
$$x = \pm\infty, T = T_0, x = 0, T_a = T_c, T_c = T_f \quad (II)$$
$$\lambda\Delta T_a(x) - \lambda\Delta T_c(x) = Q[O_2]_0 v_f\rho.$$

Indexes 'a' and 'c' specify quantities relating to preheating zone and to products. Index 'f' specifies values of temperature and flame velocity in the presence of heat losses. The last equation expresses heat balance on the reaction surface.[12] Set (II) is closed by the equation, which accounts for exponential dependence of combustion rate on temperature[12] according to equation (11):

$$v_f^2/v^2 = \exp[3/2E(T_f - T_b)/RT_fT_b]. \quad (12)$$

Taking a logarithm of (12), in view of $T_f/T_b \approx 1$ we obtain:

$$T_f - T_b = \frac{2RT_b^2\ln(v_f^2/v^2)}{3E}. \quad (13)$$

On the other hand, one can get the following expression for T_f from the solution of set (II):[12]

$$T_f - T_b = -\lambda(T_b - T_0)(\delta_a + \delta_c)/C_p^2v_f^2\rho^2 \quad (14)$$

Setting equal right hand sides of equations (13) and (14), changing $v_f^2/v^2 = \zeta$ we have:

$$F(\zeta) = \zeta\exp(\beta/\zeta) = 1,$$
$$\text{where } \beta = 3E/2RT_b^2\lambda(T_b - T_0)(\delta_a + \delta_c)/C_p^2v_f^2\rho^2. \quad (15)$$

It follows from the analysis of equation (15) that the CL in the presence of heat losses occurs with decreasing temperature by a characteristic interval.

As indicated above upper CLFP occurs when heat losses into reactor wall are missing.[4,5] It can be assumed that the CL is caused by the loss of active centres in the reaction of chain break involved in the kinetic mechanism of hydrogen oxidation, namely, $H + O_2 + M \rightarrow HO_2 + M$.

In preheating zone (as distinct from flame zone) the reaction plays marked role because its rate slightly depends on temperature due to low activation energy.[13,14] The reaction of H atom drawn from reaction zone by diffusion with O_2 makes up slightly active HO_2 radical and 44 kcal mol^{-1}.[15] It means that the break of H atom in the step (k_6) approximately corresponds to energy loss $q = (Q - 44)$ kcal mol^{-1}, which would be released if the step H + H + M occurred. As known,[1,2] the process qualitatively comprises heat losses discussed above. In accordance with our assumptions heat losses due to termolecular termination are equal to $qk_6H(x)(O_2)_0(M)$. Based on equation (1) it can be shown that in preheating zone $H(x) \approx 2O_{20}[T(x) - T_0]/(T_b - T_0)$. Then the set (I) if only losses due to chain termination in the step (k_6) are allowed for takes the form:

$$x < 0: \ \lambda\Delta^2T_a(x) - v_f\rho C_p\Delta T_a(x) - 2qk_6O_{20}^2(M)[T_a(x) - T_o]/N(T_b - T_0) = 0,$$
$$x > 0: \ \lambda\Delta^2T_c(x) - v_f\rho C_p\Delta T_c(x) = 0, \quad (III)$$
$$x = -\infty, T = T_0; x = +\infty, T = T_f; x = 0, T_a = T_c, T_c = T_f;$$
$$\lambda\Delta T_a(x) = Q[O_2]_0 v_f\rho, \ \lambda\Delta T_c(x) = 0.$$

Here, N is the Avogadro number. Evidently, the first equations of sets (II) and (III) will coincide with each other if we take $2qk_6O_{20}^2(M)/N(T_b - T_0) = \delta_a$, $\delta_c = 0$. With allowance made for this, the solutions will coincide too. Then the solution of set (III) gives the relation similar to equation (14):

$$T_f - T_b = -2\lambda(T_b - T_0)qk_5O_{20}^2(M)/N(T_b - T_0)/C_p^2v_f^2. \quad (16)$$

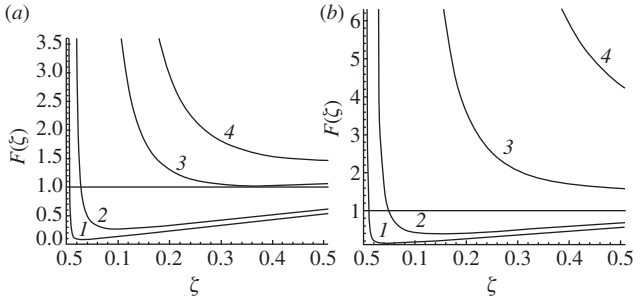

Figure 2 Dependences of $F(\zeta)$ on ζ by equation (15) for different content of (*a*) air in flammable mixture (*1*) 0.25, (*2*) 0.22, (*3*) 0.2 and (*4*) 0.15; (*b*) O_2 in flammable mixture (*1*) 0.052, (*2*) 0.048, (*3*) 0.042 and (*4*) 0.035.

Setting equal right hand sides of equations (14) and (16), changing $v_f^2/v^2 = \zeta$ we have the equation, coincident with equation (15) in which the value of β is:

$$\beta = \frac{3\lambda q k_6 O_{20}^2(M)E}{NC_p^2 v^2 \rho^2 R T_b^2}. \quad (17)$$

Note that as the amount of H_2 in the mixture increases when both the amount of O_2 and the value of T_b defined by equation (1) decrease.

Equation (15) was solved graphically (Figure 2). If the curve of $F(\zeta)$ crosses a horizontal straight line with an ordinate equal to 1 then equation (15) has two solutions and CL occurs. If the curve of $F(\zeta)$ is tangent to the line with an ordinate equal to 1 then CL is attained [Figure 2(*a*)]. The values of amount of air at CLFP were calculated using the following parameters:

$k_{11} = 0.1\times10^{-31}(T_b/T_0)^{-0.4}$ cm^6 molec^{-2} s^{-1},[16]
$M = 760\times10^{19}/T_b$, $\rho = 10^{-3}$ g cm^{-3},[17]
$C_p = 2$ cal g^{-1} K^{-1},[17] $\lambda = 800\times10^{-6}$ cal cm^{-1} s^{-1} K^{-1},[17]
$k_2 = 0.30\times10^{-9}\exp(-16760/RT)$ cm^3 molec^{-1} s^{-1},[19]
$T_0 = 300$ K, $R = 2$ cal mol^{-1} K^{-1},
$O_{20} = 0.21(1 - f_{H_2})760\times10^{19}/T_b$,

where f_{H_2} is a fraction of H_2 in the mixture, $q = 20$ kcal mol^{-1}, $N = 6\times10^{23}$ molec mol^{-1}, D_H is the mean diffusivity in H_2 + air mixture for $f_{H_2} = 0.75$ (1 cm^2 s^{-1}).[17] The values of v without losses in equation (17) were calculated by equation (11) for each T_b cited below and inserted in equation (17). The values of T_b were calculated independently using the published algorithm;[20] the corresponding values of T_b and v made up for

$f_{H_2} = 0.85$ – 974 K – 40 cm s^{-1}, $f_{H_2} = 0.8$ – 1170 K – 54 cm s^{-1},
$f_{H_2} = 0.78$ – 1280 K – 92 cm s^{-1}, $f_{H_2} = 0.75$ – 1380 K – 155 cm s^{-1}.

Dependences of $F(\zeta)$ on ζ by equation (15) at given β, calculated by equation (17) for different amounts of H_2 in the mixture are shown in Figure 2(*a*). Notice that β increases with increase in the amount of H_2 in the mixture providing the occurrence of CL.[12] Calculated value of $v_f = 54$ cm s^{-1} correlates with experimental one ~50 cm s^{-1}.[21] The amount of air at CL makes up 20% in qualitative agreement with experimental one of 25%.

To verify the approach suggested the concentration of O_2 at CLFP of $H_2 + O_2$ mixture was estimated (experimental value of O_2 at CLFP makes up 5%[4,5,21]). In this case the following values of parameters were used to calculate β: $\rho = 9\times10^{-4}$ g cm^{-3},[17] $\lambda = 1000\times10^{-6}$ cal cm^{-1} s^{-1} K^{-1},[17,18] $O_{20} = (1 - f_{H_2})750\times10^{19}/T_b$, D_H is the mean diffusivity in $H_2 + O_2$ mixture for $f_{H_2} = 0.95$ (1.2 cm^2 s^{-1}).[17] This takes into account the increase in amount of H_2 in the mixture $H_2 + O_2$ as compared with the mixture H_2 + air near upper CLFP. The values of other parameters were similar to above. The values of v and T_b were calculated in the same way as those for H_2 + air mixtures by equation (11); the values of T_b and the corresponding v values made up for

$f_{H_2} = 0.965$ – 1071 K – 45 cm s^{-1}, $f_{H_2} = 0.958$ – 1168 K – 59 cm s^{-1},
$f_{H_2} = 0.952$ – 1275 K – 107 cm s^{-1}, $f_{H_2} = 0.948$ – 1385 K – 169 cm s^{-1}.

Dependences of $F(\zeta)$ on ζ by equation (15) at given β, calculated by equation (17) for different amounts of H_2 in the mixture are shown in Figure 2(*b*). As is seen in Figure 2(*b*) the amount of O_2 at CL is ~4.5% in agreement with experimental value 5%.[4,5,21]

On the basis of the calculations performed, the following hypothesis may be set up for the flames caused by chain branched reactions. One of the possible reasons of occurrence of CFPL is a feature of the only kinetic mechanism of the chain branched reaction providing positive feedback between temperature and velocity of the flame front rather than heat losses.

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