

Determining Flammability Limits by Analyzing Diffusive-Thermal Flame Instability. Methane–Air–Diluent Mixture

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Abstract: This paper describes the method for determining flammability limits with the use of equations for diffusive-thermal stability boundaries. The key parameter responsible for the existence of flammability limits is the thermal effect produced by the combustion of gas mixtures. The thermal effect and the equation for diffusive-thermal stability boundaries are used to determine a minimum flame temperature below which combustion is impossible. Flammability limits are significantly affected by the heat capacity of components of the mixture if it is strongly dependent on temperature. For upper and lower flammability limits, a minimum flame temperature is generally different and dependent on the relative concentration and properties of the diluent. The theoretical methods for calculating flammability limits are tested according to the experimental data on the combustion of a methane–air–diluent mixture.

Keywords: flammability limits, diffusive-thermal resistance, thermal effect of gas mixtures, minimum flame temperature.

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INTRODUCTION

The existence of flammability limits still remains an unsolved problem in combustion and explosion physics. At the same time, the experimental data [1–10] and theoretical results [11, 12] accumulated to date allow for reasonable arguments for the explanation of flammability limits.

It is known that the existence of the gases of a slow-burning stationary wave (deflagration) in a combustible mixture requires a strict correlation of three processes [2, 11, 12]: the chemical reactions occurring in relatively narrow space-time intervals, the heat transfer from the chemical reaction zone into the cold region of the mixture, and the substance transfer from the cold region of the mixture into the chemical reaction zone. Any violation of the correlation between these three processes lead to diffusive-thermal instability, which causes

the formation of cellular and more complex structures in the flame [2, 13, 14] or the termination of combustion, for example, in the case of heat removal from the flame [11, 15, 16], and the conversion of the internal energy of combustion products into kinetic energy [17]. This instability may be due to a significant deviation of the equivalence ratio ϕ from unity in rich or lean mixtures and dilution of the mixture with inert gases or inhibitors with relative concentrations r_{in} . However, these causes of instability have something in common that is a change in the flame temperature due to a decrease in the thermal effect of the burning mixture Q [18, 19]. The heat removal from the flame [11, 15, 16] and the conversion of the internal gas energy into kinetic energy [17] can be interpreted as a decrease in the thermal effect.

The occurrence of diffusive-thermal instability does not imply termination of combustion as three-dimensional structures may be formed [13, 14]. But the variation intervals ϕ and r_{in} , where such structures can be observed, are small, and, in the first approximation,

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it is possible to relate the emergence of flammability limits with the occurrence of diffusive-thermal instability. Below it is shown that this approach theoretically makes it possible for the occurrence of the limiting flame temperature $T_{b,\min}$ below which combustion is impossible.

The existence of the limiting temperature is in good agreement with modern ideas where the possibility of reactions in gas mixtures is characterized by an ignition temperature [2, 20]. The phenomenological theory of the flammability limits [21] is based on the assumption of existence of the temperature $T_{f,\min}$ that depends on the mixture composition. Therefore, the temperature is a determining factor in the development of theoretical foundations for the flammability limits.

DIFFUSIVE-THERMAL INSTABILITY

The theoretical results on the diffusive-thermal instability depend on the adopted model of combustion. The complexity of the chemical reactions with a large number of chains and branches [22, 23] complicates the simulation of combustion. The desire to obtain more accurate data on the combustion process leads to the formulation of cumbersome models [3–5, 14, 15] with a large number of physical and chemical parameters. As a result, the analysis of diffusive-thermal instability becomes much more complicated, and it becomes difficult to determine the parametric dependences that define the stable combustion boundary. However, the advantages of the models describing in detail the chemical conversions in a flame lies in the possibility to determine the influence of intermediate products of chemical reactions on the development of instability.

The use of simple combustion models based on the chemical equation $A \rightarrow B$ (A is a combustible mixture and B is a combustion product) allows obtaining the exact solutions of the problem for determination of stability conditions and often leads to simple results in the form of analytical dependences. For example, in [24–26], the stability limit depends on two parameters: the Lewis number Le and the dimensionless activation energy E/RT_b [26] or $E(T_b - T_0)/RT_b^2$ [24, 25]. Here E is the effective activation energy of the chemical reaction $A \rightarrow B$, R is the universal gas constant, and T_b and T_0 are the flame and initial temperatures. The lack of simple models is manifested in the use of the ephemeral parameter E , which is difficult to relate with the real activation energies of elementary chemical reactions involved in combustion. Difficulties increase when there is an extended region in the flame front with small chemical reaction rates or regions with unburned gas [27, 28].

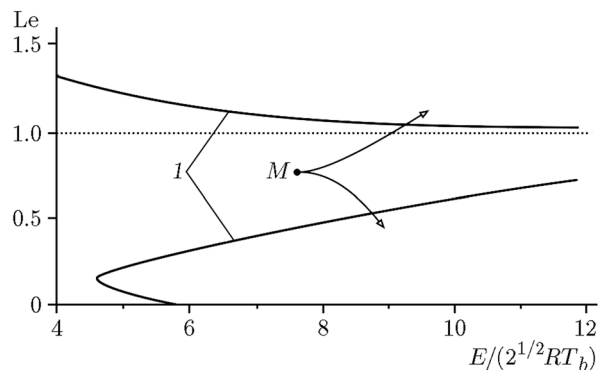


Fig. 1. Stable combustion boundaries (curves I) and possible paths of the representative point M with buckling.

Despite the strong difference of mathematical and physical formulations of combustion equations, the models [3–5, 14, 15, 27, 28] and [24–26, 29] yield largely similar results. The combustion stability in them strongly depends on the Lewis number and flame temperature (or thermal effect) with varying mixture composition.

Figure 1 shows the results of a recent study on diffusion-thermal instability with use of the reaction scheme $A \rightarrow B$ [26, 29]. The stability region is bounded by two boundaries, one of them is in the half-space $Le > 1$ and the other one in $Le < 1$. The initial state of stable combustion under adiabatic conditions is denoted by the point M . Dilution of the mixture changes the Lewis number Le , the effective activation energy E , and the flame temperature $T_b = T_0 + Q/c_p$, where Q is the thermal effect of the reaction, c_p is the heat capacity of the combustion products at constant pressure. The variation of the Le number significantly affects the combustion stability [5, 9, 10, 14, 28]. However, according to the Arrhenius law, the chemical reaction rate depends exponentially on the activation energy and temperature. Therefore, the strongest influence on the combustion stability can be produced by the variation of E and T_b . With a significant deviation of the equivalence ratio ϕ from unity, the energy E and the heat capacity c_p can be considered constant in the first approximation [18, 19]. For a number of mixtures, the equivalence ratios at the lower (ϕ_n) and upper (ϕ_h) limits are subject to the approximated relationship of the symmetry $\phi_n \phi_h \approx 1$, which is a consequence of the dependence of the thermal effect on the equivalence ratio $Q(\phi)$ [18, 19].

THERMAL EFFECT OF THE DILUTED MIXTURE

The total chemical reaction of the formation of CO_2 and H_2 products from the fuel CH_4 and oxidant O_2 are written using the equivalence coefficients $\nu_1 = 1$, $\nu_2 = 2$, $\nu_3 = 2$, and $\nu_4 = 1$:

$$\nu_1 A_1 + \nu_2 A_2 = \nu_3 A_3 + \nu_4 A_4, \quad (1)$$

where A_1 is CH_4 , A_2 is O_2 , A_3 is H_2O , and A_4 is CO_2 . In this reaction, the formation of each molecule of the substance A_3 is accompanied by the release of the energy ε_3 , which means that ε_4 is the energy of the formation of each molecule of the substance A_4 .

The mixture is also characterized by the equivalence ratio

$$\phi = r_1 \nu_2 / (r_2 \nu_1),$$

where r_1 and r_2 are the relative (volume) concentrations of the fuel A_1 and oxidant A_2 .

The mixture contains two diluents with the relative volume concentrations $r_{\text{in}1}$ and $r_{\text{in}2}$, and they can be chemically inert or also possess inhibitory properties. Thus, the original mixture is characterized by the equation $r_1 + r_2 + r_{\text{in}1} + r_{\text{in}2} = 1$.

In case of redundant fuel A_1 ($\phi > 1$) and excluding the impact of the inhibitors, the number of the formed molecules of the products A_3 and A_4 , respectively, is equal to

$$N_3 = \frac{\nu_3}{\nu_2} r_2 N, \quad N_4 = \frac{\nu_4}{\nu_2} r_2 N, \quad (2)$$

where N is the total number of molecules in the mixture. Thus, the energy Σ_1 released in the reaction is calculated according to the equation

$$\Sigma_1 = \varepsilon_3 N_3 + \varepsilon_4 N_4 = \left(\varepsilon_3 \frac{\nu_3}{\nu_2} + \varepsilon_4 \frac{\nu_4}{\nu_2} \right) r_2 N.$$

In the case of redundant oxidant A_2 ($\phi < 1$), we have the similar equations:

$$N_3 = \frac{\nu_3}{\nu_1} r_1 N, \quad N_4 = \frac{\nu_4}{\nu_1} r_1 N, \quad (3)$$

$$\Sigma_2 = \varepsilon_3 N_3 + \varepsilon_4 N_4 = \left(\varepsilon_3 \frac{\nu_3}{\nu_1} + \varepsilon_4 \frac{\nu_4}{\nu_1} \right) r_1 N.$$

The chemical conversion of the fuel with the oxidant mixture into reaction products proceeds according to a chain mechanism [2, 22, 23]. The exact models of such chemical conversion lead to very complex calculations as compared to simple kinetic mechanisms. The use of such models in the analytical theory presented in this paper is difficult.

A simple model of methane combustion [16] consists of 19 elementary chemical reactions, including the

formation of four elementary reactions of the formation of a water molecule of water and a reaction of the formation of a carbon dioxide molecule. The number of chains can be significantly greater. Let $n_{3,1}$ and $n_{3,2}$ be the numbers of destroyed chains of the product formation A_3 under the action of the first and second diluents. The numbers $n_{4,1}$ and $n_{4,2}$ have the same meaning with respect to the product A_4 . The new parameters $n_{3,1}$, $n_{3,2}$, $n_{4,1}$, and $n_{4,2}$ are assumed to be proportional to the number of molecules of diluents in a mixture of $N_{\text{in}1}$ and $N_{\text{in}2}$:

$$n_{3,1} = K_{3,1} N_{\text{in}1}, \quad n_{3,2} = K_{3,2} N_{\text{in}2},$$

$$n_{4,1} = K_{4,1} N_{\text{in}1}, \quad n_{4,2} = K_{4,2} N_{\text{in}2}.$$

The constants $K_{3,1}$ and $K_{4,1}$ have the meaning of average numbers of the molecules of the products A_3 and A_4 , which are not formed by the action of one molecule of the first inhibitor. The other two constants have the same meaning: one molecule of the second inhibitor prevents the synthesis of $K_{3,2}$ and $K_{4,2}$ of the molecules of the substances A_3 and A_4 , respectively.

Accounting for the effect of diluents changes the form of the equations for calculating the synthesized molecules of the products. If there is a redundancy of the fuel, then

$$N_3 = \frac{\nu_3}{\nu_2} r_2 N - n_{3,1} - n_{3,2}$$

$$= \frac{\nu_3}{\nu_2} r_2 N - K_{3,1} N_{\text{in}1} - K_{3,2} N_{\text{in}2},$$

$$N_4 = \frac{\nu_4}{\nu_2} r_2 N - n_{4,1} - n_{4,2}$$

$$= \frac{\nu_4}{\nu_2} r_2 N - K_{4,1} N_{\text{in}1} - K_{4,2} N_{\text{in}2}.$$

Accordingly, the energy Σ_1 changes too:

$$\Sigma_1 = \left(\varepsilon_3 \frac{\nu_3}{\nu_2} + \varepsilon_4 \frac{\nu_4}{\nu_2} \right) r_2 N$$

$$- (\varepsilon_3 K_{3,1} + \varepsilon_4 K_{4,1}) N_{\text{in}1}$$

$$- (\varepsilon_3 K_{3,2} + \varepsilon_4 K_{4,2}) N_{\text{in}2}. \quad (4)$$

If there is a redundancy of the oxidant, then the following equation holds is valid for the released energy Σ_2 :

$$\Sigma_2 = \left(\varepsilon_3 \frac{\nu_3}{\nu_1} + \varepsilon_4 \frac{\nu_4}{\nu_1} \right) r_1 N$$

$$- (\varepsilon_3 K_{3,1} + \varepsilon_4 K_{4,1}) N_{\text{in}1}$$

$$- (\varepsilon_3 K_{3,2} + \varepsilon_4 K_{4,2}) N_{\text{in}2}. \quad (5)$$

The original mixture has the molecular mass μ . Considering 1 mole of the mixture, we assume in Eqs. (4) and (5) that $N = N_A$, where N_A is Avogadro's number. Then, for the specific thermal effects,

in the case of redundancy of the fuel Q_1 and oxidant Q_2 , we have

$$Q_1 = \frac{\Sigma_1}{\mu} = \left(\varepsilon_3 \frac{\nu_3}{\nu_2} + \varepsilon_4 \frac{\nu_4}{\nu_2} \right) r_2 \frac{N_A}{\mu} - \Delta Q,$$

$$Q_2 = \frac{\Sigma_2}{\mu} = \left(\varepsilon_3 \frac{\nu_3}{\nu_1} + \varepsilon_4 \frac{\nu_4}{\nu_1} \right) r_1 \frac{N_A}{\mu} - \Delta Q,$$

$$\begin{aligned} \Delta Q &= (\varepsilon_3 K_{3,1} + \varepsilon_4 K_{4,1}) r_{in1} \frac{N_A}{\mu} \\ &+ (\varepsilon_3 K_{3,2} + \varepsilon_4 K_{4,2}) r_{in2} \frac{N_A}{\mu}. \end{aligned}$$

In Q_1 and Q_2 , we turn from the dependences on r_1 and r_2 to the dependence on the equivalence ratio. After eliminating the variable r_2 from the equations

$$r_1 + r_2 + r_{in1} + r_{in2} = 1, \quad \phi = r_1 \nu_2 / (r_2 \nu_1), \quad (6)$$

we have

$$r_1 = \frac{(1 - r_{in1} - r_{in2})\phi}{\phi + \nu_2/\nu_1}. \quad (7)$$

Using this expression in the first equation of system (6), we find

$$r_2 = \frac{1 - r_{in1} - r_{in2}}{\phi \nu_1 / \nu_2 + 1}. \quad (8)$$

After substituting r_1 and r_2 from Eqs. (7) and (8) in the expressions for Q_1 and Q_2 and introducing the common denotation Q for the thermal effect, we have the final result:

$$Q = \begin{cases} Q_* \left[\frac{(\nu_1 + \nu_2)\phi}{\phi \nu_1 + \nu_2} - \psi \right], & \phi \leq 1, \\ Q_* \left[\frac{\nu_1 + \nu_2}{\phi \nu_1 + \nu_2} - \psi \right], & \phi \geq 1, \end{cases} \quad (9)$$

where

$$Q_* = \frac{\varepsilon_3 \nu_3 + \varepsilon_4 \nu_4}{\nu_1 + \nu_2} \frac{N_A}{\mu} (1 - r_{in1} - r_{in2}),$$

$$\mu = r_1 \mu_1 + r_2 \mu_2 + r_{in1} \mu_{in1} + r_{in2} \mu_{in2},$$

$$\psi = \frac{\Delta Q}{Q_*} = (\nu_1 + \nu_2)$$

$$\times \frac{(\nu_3 K_{3,1} + \nu_4 K_{4,1}) r_{in1} + (\nu_3 K_{3,2} + \nu_4 K_{4,2}) r_{in2}}{(\varepsilon_3 \nu_3 + \varepsilon_4 \nu_4)(1 - r_{in1} - r_{in2})}.$$

Here μ_1 and μ_2 are the molecular masses of the fuel A_1 and oxidant A_2 ; μ_{in1} and μ_{in2} are the molecular masses of the first and second diluents.

EQUATIONS FOR CALCULATING THE FLAMMABILITY LIMITS

The boundaries [26, 29] for the steady combustion (see Fig. 1) for larger values of the Zeldovich number $Ze = E/(\sqrt{2}RT_b) > 7$ can be approximated by the expressions

$$\text{Le} > 1: \text{Le} = 1 + \frac{1}{Ze}, \quad \text{Le} < 1: \text{Le} = 1 - \frac{4.5}{Ze}.$$

We consider the case where $\text{Le} < 1$. The combustible mixture has an original temperature T_0 . During the combustion of the undiluted mixture, the flame temperature $T_b = T_0 + Q/c_p$ is reached with the thermal effect Q (under adiabatic conditions).

In the case of dilution of the mixture with chemically inert substances or inhibitors or deviation of the mixture from the equivalence composition at the stability boundary, the thermal effect Q adopts the smallest possible value of Q_{\min} , at which the flame can still exist. This means that the flame temperature reaches a minimum value too: $T_b = T_{b,\min}$. Then the equation for the stable combustion boundary with account for the determination of the Zeldovich number can be written in the form

$$T_{b,\min} = T_0 + Q_{\min}/c_p, \quad (10)$$

where

$$T_{b,\min} = \frac{(1 - \text{Le})E}{4.5\sqrt{2}R}.$$

In the absence of precise data about Le and E , it is possible that the temperature $T_{b,\min}$, which, in contrast to Le and E , can be found by relatively easy measurements, is taken as an experimentally determined parameter.

The stability conditions [26, 29] are found on the basis of the simplest combustion models, in which the composition of the mixture is not specified. In the experiments themselves, the mixtures have a complex composition and may be enriched or depleted by a combustible component and can be diluted with a chemical inert gas or inhibitor. This may lead to a noticeable change in Le and E . Consequently, $T_{b,\min}$ may change too. Therefore, finding the upper and lower flammability limits requires the use of the two temperatures $T_{b,\min 1}$ and $T_{b,\min 2}$ for the lower and upper limits, respectively.

Let us find the equations for calculating the lower flammability limit ϕ_n and fuel concentration r_{1n} . To do that, in Eq. (10), we use an expression for the thermal effect [Eq. (9)] with $\phi \leq 1$:

$$T_{b,\min 1} = T_0 + \frac{Q_*}{c_p} \left[\frac{(\nu_1 + \nu_2)\phi_n}{\phi_n \nu_1 + \nu_2} - \psi \right].$$

Therefore,

$$\phi_n = \frac{\nu_2}{\nu_1} \times \frac{c_p(T_{b,\min 1} - T_0)/Q_* + \psi}{1 + \nu_2/\nu_1 - [c_p(T_{b,\min 1} - T_0)/Q_* + \psi]}. \quad (11)$$

The fuel concentration at the lower limit r_{1n} is found from expression (7):

$$r_{1n} = \frac{(1 - r_{in1} - r_{in2})\phi_n}{\phi_n + \nu_2/\nu_1}. \quad (12)$$

The equations for calculating the upper flammability limit ϕ_h and the fuel concentration in it r_{1h} are found from the basic equations (10) and (9), where the representation of the thermal effect with $\phi \geq 1$ is used:

$$T_{b,\min 2} = T_0 + \frac{Q_*}{c_p} \left(\frac{\nu_1 + \nu_2}{\phi_h \nu_1 + \nu_2} - \psi \right).$$

Therefore,

$$\phi_h = \frac{1 + \nu_2/\nu_1}{c_p(T_{b,\min 2} - T_0)/Q_* + \psi} - \frac{\nu_2}{\nu_1}. \quad (13)$$

For the fuel concentration on the upper limit r_{1h} , we find

$$r_{1h} = \frac{(1 - r_{in1} - r_{in2})\phi_h}{\phi_h + \nu_2/\nu_1}. \quad (14)$$

Equations (11)–(14) are essential for calculating the flammability limits. They do not take into account the possibility of the formation of free carbon and carbon monoxide at a low flame temperature. The incomplete combustion of methane can be accounted for if Eq. (1) is replaced with a more exact equation. Therefore, Eqs. (11)–(14) can be taken as the first approximation.

The most complete experimental data on the flammability limits of the mixtures based on hydrocarbon fuels are given in [1]. Therefore, below the equations are given in a form suitable for comparing the theoretical results with the experimental data [1].

RELATIVE CONCENTRATIONS IN COMBUSTION PRODUCTS

We consider the case of redundancy of the fuel in the mixture ($\phi > 1$). The number of molecules of the products A_3 and A_4 for any $\phi > 1$ is given by Eqs. (2). The number of the molecules of the fuel A_1 in the combustion products

$$N_1'' = \left(1 - \frac{1}{\phi}\right) r_1 N.$$

Considering this value and Eqs. (2), the total number of molecules in the combustion products is determined by the expression

$$N_{pr} = N_{in1} + N_{in2} + \left(1 - \frac{1}{\phi}\right) r_1 N + \frac{\nu_3 + \nu_4}{\nu_2} r_2 N.$$

The relative concentrations are $r_{in1} = N_{in1}/N$ and $r_{in2} = N_{in2}/N$, so we can write

$$N_{pr} = N \left[r_{in1} + r_{in2} + \left(1 - \frac{1}{\phi}\right) r_1 + \frac{\nu_3 + \nu_4}{\nu_2} r_2 \right].$$

Making a replacement according to the equality $r_2 = \nu_2 r_1 / (\nu_1 \phi)$, we have

$$N_{pr} = N R_{bur},$$

$$R_{bur} = r_{in1} + r_{in2} + \left(1 - \frac{1}{\phi} + \frac{\nu_3 + \nu_4}{\nu_1 \phi}\right) r_1. \quad (15)$$

The relative concentrations of the first and second diluents (if they do not undergo a chemical conversion) are now determined in the combustion products by the following equations:

$$r'_{in1} = \frac{N_{in1}}{N_{pr}} = \frac{r_{in1}}{R_{bur}}, \quad r'_{in2} = \frac{N_{in2}}{N_{pr}} = \frac{r_{in2}}{R_{bur}}. \quad (16)$$

The concentration r'_1 of the fuel residue in the combustion products and the concentrations r_3 and r_4 of the substances A_3 and A_4 are calculated in the equations

$$\begin{aligned} r'_1 &= \frac{N_1''}{N_{pr}} = \frac{(1 - 1/\phi)r_1}{R_{bur}}, \\ r_3 &= \frac{N_3}{N_{pr}} = \frac{\nu_3}{\nu_1 \phi} \frac{r_1}{R_{bur}}, \\ r_4 &= \frac{N_4}{N_{pr}} = \frac{\nu_4}{\nu_1 \phi} \frac{r_1}{R_{bur}}. \end{aligned} \quad (17)$$

Equations (16) and (17) are used to calculate the upper flammability limit. Therefore, the following replacements should be made in them and in the determination of R_{bur} (15): $\phi \rightarrow \phi_h$ and $r_1 \rightarrow r_{1h}$.

We find the equation for calculating the concentrations of the components of the combustion products in the redundancy of oxidant in the mixture ($\phi < 1$). In this case, the number of the molecules of the products A_3 and A_4 for any $\phi < 1$ is calculated by Eqs. (3). The residue of the number of the molecules of the oxidant A_2 in the combustion products

$$N_2'' = (1 - \phi)r_2 N = \left(\frac{1}{\phi} - 1\right) \frac{\nu_2}{\nu_1} r_1 N.$$

Then it is not difficult to find that

$$\begin{aligned} N_{pr} &= N R_{ox}, \\ R_{ox} &= r_{in1} + r_{in2} \\ &+ \left(\frac{1}{\phi} - 1\right) \frac{\nu_2}{\nu_1} r_1 + \frac{\nu_3 + \nu_4}{\nu_1} r_1. \end{aligned} \quad (18)$$

As a result, we have the following equations for the concentrations of the components:

$$r'_{\text{in1}} = \frac{N_{\text{in1}}}{N_{\text{pr}}} = \frac{r_{\text{in1}}}{R_{\text{ox}}}, \quad r'_{\text{in2}} = \frac{N_{\text{in2}}}{N_{\text{pr}}} = \frac{r_{\text{in2}}}{R_{\text{ox}}}, \quad (19)$$

$$r'_2 = \frac{\nu_2}{\nu_1} \left(\frac{1}{\phi} - 1 \right) \frac{r_1}{R_{\text{ox}}}, \quad r_3 = \frac{\nu_3}{\nu_1} \frac{r_1}{R_{\text{ox}}}, \quad (20)$$

$$r_4 = \frac{\nu_4}{\nu_1} \frac{r_1}{R_{\text{ox}}}.$$

Equations (19) and (20) are used to calculate the lower flammability limit. Therefore, the following replacements should be made in them and in the determination of R_{ox} (18): $\phi \rightarrow \phi_n$ and $r_1 \rightarrow r_{1n}$.

CALCULATION OF THE FLAMMABILITY LIMITS

The heat capacity of the combustion products c_p in Eqs. (11) and (13) takes different values in the search for the upper and lower flammability limits. To calculate c_p , the known thermodynamics equations [30] are used. In particular, the composition of the combustion products on the upper limit is characterized by the concentrations r'_{in1} , r'_{in2} , r'_1 , r_3 , and r_4 . Then, the heat capacity is found from the equation

$$c_p = g_1 c_{p1} + g'_{\text{in1}} c_{p,\text{in1}} + g'_{\text{in2}} c_{p,\text{in2}} + g_3 c_{p3} + g_4 c_{p4}, \quad (21)$$

where $c_{p,\text{in1}}$, and $c_{p,\text{in2}}$ are the heat capacities at a constant pressure of the first and second diluents; c_{p1} , c_{p3} , and c_{p4} denote the heat capacities of the fuel A_1 and the substances A_3 (water) and A_4 (carbon dioxide). The relative mass concentrations of the fuel g_1 and the diluents g'_{in1} and g'_{in2} in the combustion and reaction products g_3 and g_4 are calculated according to the expressions

$$g_1 = \frac{\mu_1}{\mu_{\text{pr}}} r'_1, \quad g'_{\text{in1}} = \frac{\mu_{\text{in1}}}{\mu_{\text{pr}}} r'_{\text{in1}}, \quad (22)$$

$$g'_{\text{in2}} = \frac{\mu_{\text{in2}}}{\mu_{\text{pr}}} r'_{\text{in2}}, \quad g_3 = \frac{\mu_3}{\mu_{\text{pr}}} r_3, \quad g_4 = \frac{\mu_4}{\mu_{\text{pr}}} r_4.$$

The molecular mass of the combustion products is

$$\mu_{\text{pr}} = \mu_1 r'_1 + \mu_{\text{in1}} r'_{\text{in1}} + \mu_{\text{in2}} r'_{\text{in2}} + \mu_3 r_3 + \mu_4 r_4. \quad (23)$$

On the lower limit, the composition of the combustion products is characterized by the concentrations r'_{in1} , r'_{in2} , r'_2 , r_3 , and r_4 . Accordingly, the heat capacity is found from the equation

$$c_p = g_2 c_{p2} + g'_{\text{in1}} c_{p,\text{in1}} + g'_{\text{in2}} c_{p,\text{in2}} + g_3 c_{p3} + g_4 c_{p4}. \quad (24)$$

The relative mass concentrations of the oxidant g_2 and the diluents g'_{in1} and g'_{in2} in the combustion and reaction products g_3 and g_4 are calculated according to the expressions

$$g_2 = \frac{\mu_2}{\mu_{\text{pr}}} r'_2, \quad g'_{\text{in1}} = \frac{\mu_{\text{in1}}}{\mu_{\text{pr}}} r'_{\text{in1}}, \quad g'_{\text{in2}} = \frac{\mu_{\text{in2}}}{\mu_{\text{pr}}} r'_{\text{in2}}, \quad (25)$$

$$g_3 = \frac{\mu_3}{\mu_{\text{pr}}} r_3, \quad g_4 = \frac{\mu_4}{\mu_{\text{pr}}} r_4;$$

$$\mu_{\text{pr}} = \mu_2 r'_2 + \mu_{\text{in1}} r'_{\text{in1}} + \mu_{\text{in2}} r'_{\text{in2}} + \mu_3 r_3 + \mu_4 r_4.$$

The experimental data [1] on the flammability limits are given with the parameters r_{air} , r_1 , and r_{dil} are the relative (volume) concentrations of air, fuel, and one of the diluents (He, H₂O, CO₂, N₂, et al.)

$$r_{\text{air}} + r_1 + r_{\text{dil}} = 1. \quad (26)$$

The nitrogen concentration in air is $r_{\text{N}_2} \approx 0.79$, and the oxygen concentration is $r_{\text{O}_2} \approx 0.21$. In this case, the concentrations r_2 , r_{in1} , and r_{in2} should be defined as the functions of the variables r_{air} , r_1 , r_{dil} , r_{N_2} , and r_{O_2} .

Obviously, $r_{\text{in2}} = r_{\text{dil}}$. The nitrogen contained in the air is assumed to be the first diluent. The total number of molecules in the mixture N , of which the number of air molecules is $N_{\text{air}} = N_{\text{N}_2} + N_{\text{O}_2}$, where N_{N_2} and N_{O_2} are the numbers of nitrogen and oxygen molecules. Then,

$$r_{\text{air}} = \frac{N_{\text{air}}}{N} = \frac{N_{\text{O}_2}}{N} + \frac{N_{\text{N}_2}}{N}$$

$$= \frac{N_{\text{O}_2}}{N_{\text{air}}} \frac{N_{\text{air}}}{N} + \frac{N_{\text{N}_2}}{N_{\text{air}}} \frac{N_{\text{air}}}{N} = r_{\text{O}_2} r_{\text{air}} + r_{\text{N}_2} r_{\text{air}}.$$

Given this equation, Eq. (26) takes the form

$$r_{\text{O}_2} r_{\text{air}} + r_{\text{N}_2} r_{\text{air}} + r_1 + r_{\text{dil}} = 1.$$

It can be seen here and from the first equation in system (6) that the desired functions are

$$r_2 = r_{\text{O}_2} r_{\text{air}}, \quad r_{\text{in1}} = r_{\text{N}_2} r_{\text{air}}, \quad r_{\text{in2}} = r_{\text{dil}}. \quad (27)$$

Here are the final equations: the calculation of the lower flammability limit r_{1n} is carried out according to Eqs. (11), (12), and (18)–(20). They are supplemented with Eqs. (24) and (25) to calculate the product of the heat capacity of the combustion products and with Eq. (27) to determine the input parameters of r_2 , r_{in1} , and r_{in2} .

The calculation of the upper flammability limit of r_{1h} is carried out with the use of Eqs. (13)–(17) supplemented with expressions (21)–(23) and (27).

All algebraic equations for the lower and upper flammability limits are nonlinear with regard to the unknowns r_{1n} and r_{1h} . They are solved by the method of simple iterations [31].

Approximated expressions for calculating the dependence of the heat capacity of the gas on temperature (the pressure is $p = 1$ bar) and the range of their applicability

Gas	Approximated expression for c_p , kJ/(kg·K)	Temperature, K	Maximum relative error, %
O ₂	$c_p = 1.0697 + 0.9 \cdot 10^{-4}(T - 873)$	873–2873	1.6
N ₂	$c_p = 1.1401 + 1.1 \cdot 10^{-4}(T - 873)$	873–2873	3.0
CH ₄	$c_p = 2.2526 + 0.8 \cdot 10^{-2}(T - 298)^{0.8}$	298–2073	2.4
CO ₂	$c_p = 0.8274 + 0.7 \cdot 10^{-2}(T - 273)^{0.6}$	273–1873	2.7

The heat capacities of helium and water are weakly dependent on temperature [32, 33], and here they are assumed to be equal to $c_p(\text{He}) = 5.192$ kJ/(kg·K) and $c_p(\text{H}_2\text{O}) = 2.34$ kJ/(kg·K). The experimental data [32, 33] on the remaining gases are approximated by the expressions (see the table). These expressions do not guarantee the best approximation from all possible options, but allow estimating the effect of the heat capacity of flammability limits.

The enthalpy of the formation of water in the form of gas and carbon dioxide are $\Delta H(\text{H}_2\text{O}) = -242$ kJ/mol and $\Delta H(\text{CO}_2) = -393.5$ kJ/mol, respectively [16]. Hence, we conclude that $\varepsilon_3 = -\Delta H(\text{H}_2\text{O})/N_A = 4.02 \cdot 10^{-19}$ J and $\varepsilon_4 = -\Delta H(\text{CO}_2)/N_A = 6.54 \cdot 10^{-19}$ J.

Given the dissociation, the values of ε_3 and ε_4 should be taken as too low [2, 11, 34]. Therefore, they are reduced by 1.36 times: $\varepsilon_3 = 2.96 \cdot 10^{-19}$ J and $\varepsilon_4 = 4.81 \cdot 10^{-19}$ J. Then, for the mixture of methane and air of equivalence composition ($\phi = 1$) not diluted with helium, we have the flame temperature of 1978 K, which is in good agreement with the experimental data [35], where the maximum temperature is indicated as 2000 K.

The minimum flame temperatures on the upper and lower limits are given in the form of

$$\begin{aligned} T_{b,\min 1} &= T_{\text{lim}1}(1 - a_1 r_{\text{in}2}), \\ T_{b,\min 2} &= T_{\text{lim}2}(1 - b_1 r_{\text{in}2} - b_2 r_{\text{in}2}^2), \end{aligned} \quad (28)$$

where the coefficients a_1 , b_1 , and b_2 are chosen for agreement of the theoretical results with the experimental data, and the temperatures $T_{\text{lim}1}$ and $T_{\text{lim}2}$ are assumed to be known from these experiments on the combustion of an undiluted mixture. In particular, for the methane–air mixture, $T_{\text{lim}1} = 1160$ K and $T_{\text{lim}2} = 1753$ K. This choice of temperature for the upper and lower flammability limits yields $r_{1h} \approx 0.15$ and $r_{1n} \approx 0.05$ [1].

The heat capacities of the gases O₂, N₂, CH₄, and CO₂ are calculated by the expressions in the table, where $T = T_{b,\min 1}$ on the lower limit and $T = T_{b,\min 2}$ on the upper limit.

For the methane–air–helium mixture, $a_1 = 0.4$, $b_1 = 0.64$, and $b_2 = 0.602$. The constants $K_{3,1} =$

$K_{3,2} = K_{4,1} = 0$ and $K_{4,2} = 0.0886$, i.e., the weak inhibition of the CO₂ formation with helium is permitted. The theoretical results and experimental data for this mixture are shown in Fig. 2a. At the right boundary ($r_{\text{in}2} = r_{\text{lim}}$), we have $T_{b,\min 1} = T_{b,\min 2} = 926$ K. Another solution for $K_{4,2} = 0$ is obtained with the coefficients $a_1 = -0.34$, $b_1 = 0.452$, and $b_2 = 0$. They result in a high limiting temperature equal to 1354 K, and the calculated flammability limits differ significantly from the experimental data. Clearly, on the right boundary of the variation $r_{\text{in}2} = r_{\text{lim}} = 0.5$ (Fig. 2a) and $r_{\text{in}2} = r_{\text{lim}} = 0.3$ (Fig. 2b), the equality $T_{b,\min 1} = T_{b,\min 2}$ should be valid. Therefore, one of the coefficients a_1 , b_1 , and b_2 is expressed in terms of the other ones, for example,

$$\begin{aligned} b_2 &= -\frac{1}{r_{\text{lim}}^2} \\ &\times \left[\frac{T_{b,\min 1}}{T_{b,\min 2}} (1 - a_1 r_{\text{lim}}) + b_1 r_{\text{lim}} - 1 \right]. \end{aligned} \quad (29)$$

The greatest deviation between the theoretical results and experimental data occurs near the extreme right point $r_{\text{in}2} = r_{\text{lim}}$, where $r_{1n} = r_{1h}$. This is observed in all cases of the dilution of the methane–air mixture.

We consider the case of dilution of the methane–air mixture with water vapors and assume that $\mu_{\text{in}2} = 0.018$ kg/mol. The water is a strong catalyst for a chemical reaction between an intermediate CO product and oxygen [2]. Therefore, the inhibition of the CO₂ formation chains with water molecules is unlikely, and here it is accepted that $K_{3,1} = K_{3,2} = K_{4,1} = K_{4,2} = 0$. But the presence of the excess amount of water molecules may contribute to the occurrence of the diffusion-thermal instability and lead to termination of combustion. The results presented in Fig. 2b are obtained with the following constants $a_1 = -0.7$, $b_1 = 0.69$, and $b_2 = 0$. On the right boundary $r_{\text{in}2} = 0.3$, we have $T_{b,\min 1} = T_{b,\min 2} = 1404$ K. The weak inhibition with molecules H₂O and carbon dioxide CO₂ can be permitted by assuming that the constants of the destruction of the chains $K_{3,1}$, $K_{3,2}$, $K_{4,1}$, and $K_{4,2}$ are different from zero (of the order of 10^{-2} to 10^{-3}). But

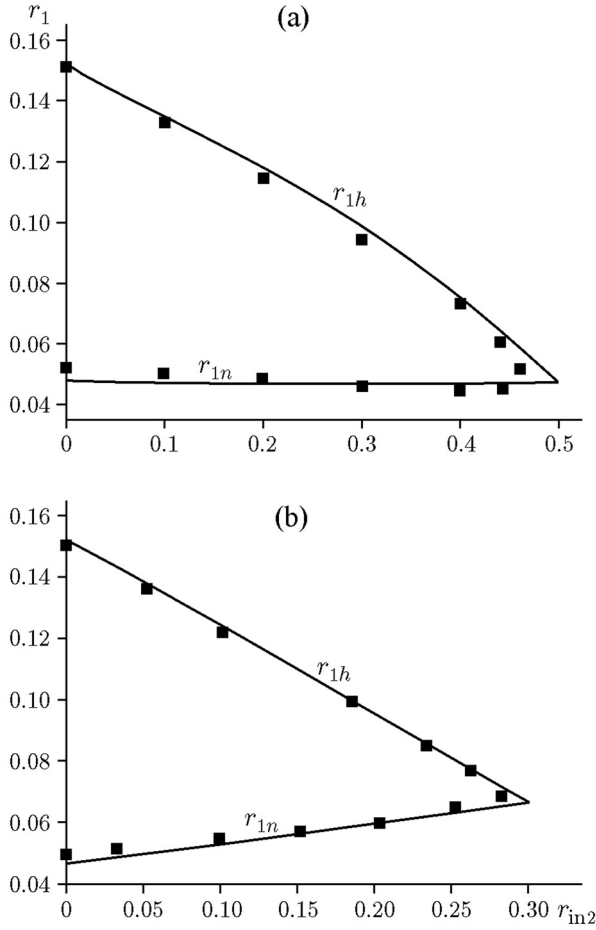


Fig. 2. Flammability limits for the methane-air mixture when diluted with helium (a) and water vapors (b) (points refer to the experimental data [1]).

then, the agreement between the theoretical and experimental results requires accepting other numerical data in the functions $T_{b,min1}(r_{in2})$ and $T_{b,min2}(r_{in2})$.

We consider the case of dilution of the methane-air mixture with the inhibitors C_2F_5H (Fig. 3a) and CHF_3 (Fig. 3b). The temperature is $T_{lim2} = 1772$ K (then, $r_{1h} \approx 0.14$ for $r_{in2} = 0$ [6]). Due to lack of data, the heat capacities of these inhibitors were assumed to be equal to $c_p(C_2F_5H) = 1340$ and $c_p(CHF_3) = 1122$ J/(kg·K) (these heat capacities have freons [32]).

Upon dilution with the inhibitor C_2F_5H , the coefficients are $a_1 = 0.5$, $b_1 = 3.35$, and $b_2 = -2.815$; the constants are $K_{3,1} = K_{4,1} = K_{3,2} = 0$ and $K_{4,2} = 0.35$. The temperatures at the right boundary $r_{in2} = 0.13$ are equal to $T_{b,min1} = T_{b,min2} = 1080$ K. Accordingly, upon dilution with the inhibitor CHF_3 , $a_1 = -0.2$, $b_1 = 1.6$, and $b_2 = -0.963$; $K_{3,1} = K_{4,1} = K_{3,2} = 0$, $K_{4,2} = 0.046$. The minimum temperature for $r_{in2} = 0.25$ are equal to $T_{b,min1} = T_{b,min2} = 1219$ K. It is seen from the results

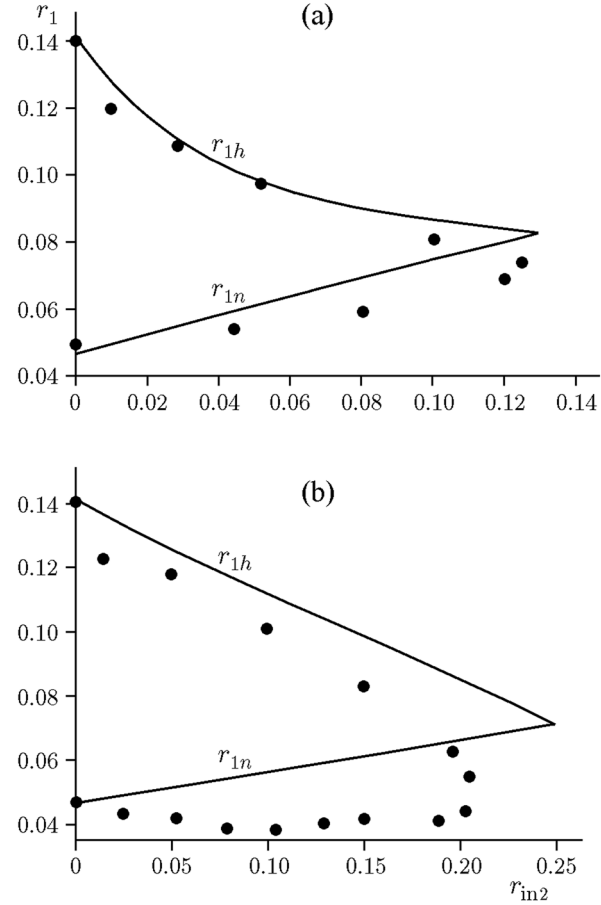


Fig. 3. Flammability limits for the methane-air mixture when diluted with C_2F_5H (a) and CHF_3 (b) (points refer to the experimental data [6]).

in Fig. 3 that the values of the numerical coefficients a_1 , b_1 , and b_2 are strongly affected by the molecular mass and heat capacity of the diluent. The inhibitor C_2F_5H with the constant of destruction 7.22 times greater is more effective than CHF_3 .

The flame temperature with the equivalence composition $T_{b,st}$ for $\phi = 1$ was also calculated. The dependences of the temperatures $T_{b,st}$, $T_{b,min1}$, and $T_{b,min2}$ on the concentration of the diluent r_{in2} for the methane-air- CHF_3 are shown in Fig. 4.

A similar situation occurs for all of the compositions discussed above. The theoretical results in Fig. 3 differ from the experimental data. It was found that it is possible to achieve “very good agreement” between the theory and experiment if we do not to impose the condition $T_{b,min1} = T_{b,min2}$ at the right extreme point of definition of $r_{in2} = r_{lim}$. But these results have no physical meaning.

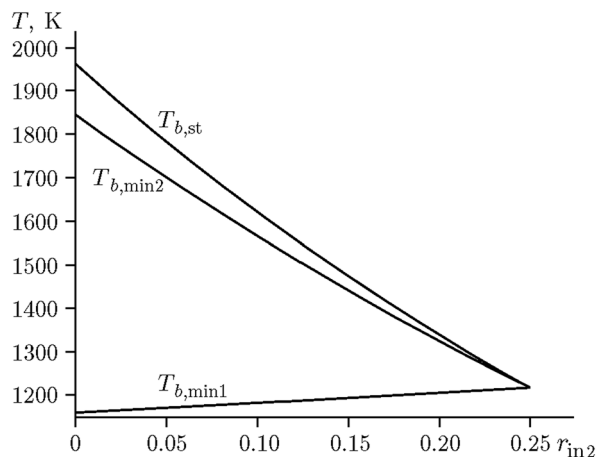


Fig. 4. The functions $T_{b,st}(r_{in2})$, $T_{b,min1}(r_{in2})$ and $T_{b,min2}(r_{in2})$ for the methane–air– CHF_3 mixture.

The calculations with the constants of the heat capacities of the gases O_2 , N_2 , CH_4 , and CO_2 has almost no effect on the flammability limits with the dilution of He and H_2O . At the same time, the values of the coefficients a_1 , b_1 , and b_2 and the constant $K_{4,2}$. But the flammability limits are practically the same as in Fig. 2. Noticeably worse results are obtained for the cases of dilution with the inhibitors $\text{C}_2\text{F}_5\text{H}$ and CHF_3 . The parameters a_1 , b_1 , b_2 , and $K_{4,2}$ are changing too. If the agreement between the theoretical and experimental results can be obtained in the assumption of constant heat capacities with the maximum relative error equal to 20–25%, then, with account for the variability of the heat capacities, the error increases up to 50–60%. This is not necessarily due to a lack of the calculation method. Perhaps, the inhibitors allow for the formation of intermediate products of the reaction between C and CO, but prevent the synthesis of CO_2 . Then, Eq. (1) and the calculated equations obtained above on its basis cannot be applied.

CONCLUSIONS

Previously, there were different views on the nature of flammability limits [2, 6–8, 11, 12, 16, 19, 22, 23]. To date, there are two basic views, which are thermal and kinetic mechanisms. The thermal mechanism [2, 11, 12, 16, 19] relates the occurrence of flammability limits with heat losses from the flame zone, and the kinetic mechanism [6–8, 22, 23] relates it with rupture in the chemical reaction chains. In the theory described above, these two mechanisms are combined in a common physical picture. The fluorine-containing $\text{C}_2\text{F}_5\text{H}$ and CHF_3

and other bromine-based inhibitors are highly toxic substances. The strong influence of the heat capacity of the mixture on the flammability limits indicates that the role of inhibitors can possibly be played by chemically resistant and nontoxic substances with a high heat capacity, especially at high temperatures.

The well-known Le Chatelier equation [35] and its improved forms [27, 28] allow calculating the flammability limits of mixtures with the use of preliminarily known (from experiments) limits of each fuel component. However, finding the upper and lower flammability limits of mixtures containing only one substance with an oxidant remains uncertain.

The method described above makes it possible to find the limits of such mixtures approximately, including the cases with the content of inhibitors in the mixture. The terms for the loss of the diffusive-thermal flame stability, which were adopted as conditions for achieving the flammability limit, lead to the concept of a minimum flame temperature below which combustion is impossible. This temperature is different for the upper and lower limits and may depend on the concentration of the diluent in the mixture and its nature. But the problem that remains unresolved is finding the theoretical dependences $T_{b,min1}(r_{in2})$ and $T_{b,min2}(r_{in2})$ and their rigorous explanations based on the modern ideas of the kinetics of chemical reactions in a combustion wave.

Hence, it is clear that the analysis of combustion of complex mixtures on the basis of the simple kinetics of chemical reactions provides many opportunities to build simple schemes and methods for determining the flammability limits.

The practical application of the above-given equations occurs with a complexity of establishing the dependences $T_{b,min1}(r_{in2})$ and $T_{b,min2}(r_{in2})$. These temperatures are the input parameters in calculating the flammability limits and should be known preliminarily. In [1, 6], there are no data on the flame temperature. Therefore, they were selected above for the agreement of the theoretical results with the experimental data.

Let us consider the practical application of the obtained results to mixtures with unknown flammability limits. The reaction equation of the form (1), the constants $K_{3,1}$, $K_{4,1}$, $K_{3,2}$, and $K_{4,2}$, and the energies ε_3 and ε_4 are assumed to be known.

For a broad class of compounds, it is sufficient to have the functions of the form (28), which contain six unknowns: T_{lim1} , T_{lim2} , a_1 , b_1 , b_2 , and r_{lim} . Therefore, the practical application of the described method of calculation of the flammability limits only requires determining the temperatures $T_{b,min1}$ and $T_{b,min2}$ at 3 to 4 points, where two of them, T_{lim1} and T_{lim2} , are

determined at $r_{in2} = 0$. One measurement should be carried out for $r_{in2} = r_{lim}$. This allows determining the values of r_{lim} and a_1 and a relationship between the coefficients b_1 and b_2 . This relationship is equivalent to Eq. (29). One of the coefficients b_1 and b_2 remains unknown. Another experimental measurement at the inner point of the interval $[0; r_{lim}]$ and on the upper flammability limit ($r_1 = r_{1h}$) helps finding the remaining coefficient b_1 (or b_2). After that, the flammability limits all the inner points of the interval $[0; r_{lim}]$ can be calculated.

The calculation results are sensitive to changes in the temperature $T_{b,min1}$ and $T_{b,min2}$, so their measurement (and determination of coefficients in them) should be carried out with high precision, with a relative error of not greater than 2–3%.

REFERENCES

1. M. G. Zabetakis, *Flammability Characteristics of Combustible Gases and Vapors* (Bureau of Mines, Washington, 1965).
2. B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Academic Press, New York, 1987).
3. A. L. Sanshez and F. A. Williams, "Recent Advances in Understanding of Flammability Characteristics of Hydrogen (Review)," *Prog. Energ. Combust. Sci.* **41**, 1–55 (2014).
4. U. J. Pfahe, M. C. Ross, J. E. Shepperd, K. O. Pasamehetoglu, and C. Unal, "Flammability Limits, Ignition Energy, and Flame Speeds in H_2 - CH_4 - NH_3 - N_2O - O_2 - N_2 Mixtures," *Combust. Flame* **13** (1–2), 140–158 (2000).
5. Li Qiao, W. J. A. Dahm, M. F. Gerard, and S. O. Elane, "Burning Velocities and Flammability Limits of Premixed Methane/Air/Diluents Flames in Microgravity," in *46th AIAA Aerospace Sciences Meeting and Exhibit, Reno, Nevada, January 7–10, 2008*.
6. V. V. Azatyan, Yu. N. Shebeko, I. A. Bolod'yan, and V. Yu. Navtsenya, "Effect of Diluents of Various Chemical Nature on the Flammability Limits of Gas Mixtures," *Fiz. Goreniya Vzryva* **42** (6), 96–102 (2006) [*Combust., Expl., Shock Waves* **42** (6), 708–714 (2006)].
7. V. V. Azatyan, I. A. Bolod'yan, V. Yu. Navtsenya, and Yu. N. Shebeko, "The Dominant Role of the Competition of Branching and Termination of Reaction Chains in the Formation of the Flammability Limits of Flame Propagation," *Zh. Tekh. Fiz.* **76** (5), 775–784 (2002).
8. V. V. Azatyan, I. A. Bolod'yan, S. N. Kopylov, N. M. Rubtsov, and Yu. N. Shebeko, "Kinetic Regimes of Developed Chain Combustion," *Fiz. Goreniya Vzryva* **39** (3), 127–137 (2003) [*Combust., Expl., Shock Waves* **39** (3), 354–363 (2003)].
9. T. T. Aung and S. Kadowaki, "The Effects of Unburned-Gas Temperature and Heat Loss on the Diffusive-Thermal Instability of Premixed Flames," *J. Therm. Sci. Technol.* **8** (1), 323–335 (2013).
10. S. Kadowaki, M. Yahata, and H. Kobayashi, "Effects of the Unburned-Gas Temperature and Lewis Number on the Intrinsic Instability of High-Temperature Premixed Flames," *J. Therm. Sci. Technol.* **6** (3), 376–390 (2011).
11. Ya. B. Zel'dovich, G. I. Barenblatt, V. B. Librovich, and G. M. Makhviladze, *The Mathematical Theory of Combustion and Explosion* (Nauka, Moscow, 1980) [in Russian].
12. F. A. Williams, *Combustion Theory* (The Benjamin/Cummings, San Francisco, 1985).
13. O. Zik and E. Moses, "Fingering Instability in Combustion: An Extended View," *Phys. Rev. E* **60** (1), 518–531 (1999).
14. C. Kaiser, J.-B. Liu, and P. D. Ronney, "Diffusive-Thermal Instability of Counter Flow Flames at Low Lewis Number," in *38th Aerospace Sciences Meeting and Exhibit, Reno, Nevada, January 10–13, 2000*.
15. E. Hu, J. Fu, L. Pan, X. Jiang, Z. Huang, and Y. Zhang, "Experimental and Numerical Study on the Effect of Composition on Laminar Burning Velocities of $H_2/CO/N_2/CO_2$ /Air Mixtures," *Int. J. Hydrogen Energ.* **37**, 18509–18519 (2012).
16. D. B. Spalding, *Combustion and Mass Transfer* (Pergamon Press, Oxford–New York, 1979).
17. K. O. Sabdenov and M. Erzada, "Mechanism of the Negative Erosion Effect," *Fiz. Goreniya Vzryva* **49** (3), 22–33 (2013) [*Combust., Expl., Shock Waves* **49** (3), 273–282 (2013)].
18. K. O. Sabdenov, "The Nature of Flammability Limits," *Izv. Tomsk. Politekh. Univ.*, No. 4, 41–40 (2007).
19. K. O. Sabdenov and T. M. Baitasov, "The Thermal Nature of Flammability Limits," *Inzh. Fiz. Zh.* **88** (3), 716–721 (2015).
20. M. Vidal, W. J. Rogers, J. C. Holste, and M. S. Mannan, "A Review of Estimation Methods for Flash Points and Flammability Limits," *Process Saf. Prog.* **23** (1), 47–55 (2004).
21. A. N. Lopanov and E. A. Fanina, "Simulation of Flame Distribution Under Adiabatic Conditions," *Tekhnol. Tekhnosfer. Bezopasnosti* **1** (47), 1–4 (2013); <http://ipb.mos.ru.ttb>.
22. N. N. Semenov, *Chain Reactions* (Nauka, Moscow, 1986).
23. N. M. Emanuel and D. G. Knorre, *Chemical Kinetics Course* (Vysshaya Shkola, Moscow, 1984) [in Russian].
24. G. I. Barenblatt, Ya. B. Zeldovich, and A. T. Istratov, "On the Theory of Thermal-Diffusive Instability of Laminar Flame," *Prikl. Mekh. Tekh. Fiz.* **4**, 21–26 (1962).
25. A. P. Aldushin and S. G. Kasparyan, "On the Thermal-Diffusive Instability of the Combustion Front," *Dokl. Akad. Nauk SSSR* **244** (1), 67–70 (1979).

26. K. O. Sabdenov, "On the Thermal-Diffusive Instability of the Laminar Flame," *Inzh.-Fiz. Zh.* **75** (4), 73–79 (2002).
27. Sh. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, and A. Sekiya, "A Study on flammability limits of Fuel Mixtures," *J. Hazard. Mater.* **155** (3), 440–448 (2008).
28. Sh. Kondo, K. Takizawa, A. Takahashi, K. Tokuhashi, and A. Sekiya, "Flammability Limits of Five Selected Compounds Each Mixed with HFC-125," *Fire Saf. J.* **44** (2), 192–197 (2009).
29. E. R. Shrager, I. M. Vasenin, and K. O. Sabdenov, "Comparative Analysis of the Results of Solving the Problem of the Diffusion-Thermal Flame Instability," *Math. Tom. Polytechnic. Univ.* **308** (6), 28–33 (2005).
30. V. A. Kudinov, *Engineering Thermodynamics* (Vysshaya Shkola, Moscow, 2000) [in Russian].
31. N. N. Kalitkin, *Numerical Methods* (Nauka, Moscow, 1978) [in Russian].
32. N. B. Vargaftik, *Guide on the Thermophysical Properties of Liquids and Gases* (Nauka, Moscow, 1972).
33. *Chemist's Handbook*, Ed. by B. P. Nikolskii (Khimiya, Moscow, 1982) [in Russian].
34. W. E. Baker, P. A. Cox, P. S. Westine, J. J. Kulesz, and R. A. Strehlow, *Explosion Hazards and Evaluation* (Elsevier, Amsterdam–Oxford–New York, 1983).
35. P. G. Demidov, V. A. Shandyba, and V. A. Shcheglov, *The Combustion and Properties of Flammable Substances* (Khimiya, Moscow, 1981) [in Russian].