On the velocities of normal and deflagration burning of gaseous mixtures

A A Vasil’ev 1,3) and V A Vasiliev 1,2)

1) Lavrentyev Institute of Hydrodynamics SB RAS, 630090 Novosibirsk, Russia
2) Institute of Laser Physics SB RAS, 630090 Novosibirsk, Russia
3) Novosibirsk State University, 630090 Novosibirsk, Russia

Author’s address: a) gasdet@hydro.nsc.ru , b) vade@laser.nsc.ru

Abstract. In accordance with the classical one-dimensional detonation theory, the lower adiabatic branch of the energy release of the combustible mixture as the geometric locus of the final state points of the system also allows solution for combustion waves whose propagation velocity lies in the range from zero to deflagration speed. The velocity of the normal burning wave falls within this range, but the calculation is traditionally conducted with the help of the thermal theory of combustion (not within the framework of the theory of detonation). In this paper the conservation laws of the detonation theory were used for choice of a point of the final state for a normal flame. The analysis was carried out and estimates were given showing both the degree of compliance of the estimated and experimental values of flame velocities, and the degree of compliance of the qualitative behavior of these dependences on the main parameters of the mixture

1. Introduction

The classical 1-D theory of combustion and detonation is based on the equations of conservation of mass, momentum and energy, written in the following form (in the wavefront system):

\[ \rho_0 D = \rho (D - u) \]
\[ P_0 + \rho_0 D^2 = P + \rho (D - u)^2 \]
\[ I_0 + Q + D^2 / 2 = I + (D - u)^2 / 2 . \]

Here \( \rho \) is the density (kg/m\(^3\)), \( P \) is the pressure (kg/(m\(^2\)s\(^2\))), \( D \) and \( u \) are the wave and mass velocities (m/s), \( I \) is the specific (per unit mass) enthalpy (m\(^2\)/s\(^2\)), \( \alpha \) is the index of the initial state. Traditionally, the specific chemical release of the mixture \( Q \) (J/kg = m\(^2\)/s\(^2\)) is understood as the difference between the total enthalpy of formation of the initial mixture components (index i) and the total enthalpy of formation of chemical products reaction (index j) - taking into account molar or mass ratios:

\[ Q = \sum \alpha_i H_{f_i}^i - \sum \alpha_j H_{f_j}^j , \]

where \( \alpha_{ij} \) are the numerical coefficients for the chemical substances involved in the reaction, the enthalpy of formation of these substances at a standard temperature \( T = 298.15 \) K were used. For gas combustible systems the above equations are supplemented by the equation of state (for mole)

\[ P = \rho RT , \]

then
I = c_p T = γ/(γ - 1) · P/ρ = c_s^2/(γ - 1),

here c_p is the specific heat at constant pressure, T is the temperature, c is the sound speed, γ is the adiabatic exponent, R is the universal gas constant (J/kg K = m^2/s^2 K).

If we introduce the variables y = P/P_0 and x = ρ_0/ρ = v/v_0 (v is the specific volume, m^3/kg), then from the first two equations we get the equation of the Michelson-Rayleigh line

\[ y - 1 = γ_0 M^2 (1 - x), \]

here M = D/c_0 is the Mach number of the stream flowing into the wave front.

The energy equation under the assumption of independence of Q from the pressure and the specific volume Q ≠ f(x, y) – after the transformations is reduced to the form (the Hugoniot adiabat):

\[ y = \left( \frac{γ_0 + 1}{γ_0 - 1} - x + 2γ_0 Q/c_0^2 \right) \left( \frac{γ + 1}{γ - 1} x - 1 \right). \]

The last equation at Q = const represents a hyperbola (y + φ)(x - φ) = η, here φ = (γ - 1)/(γ + 1), η = φ(1/φ_0 - φ + q), q = 2γ_0 Q/c_0^2. From the initial point one can release a set of Michelson-Rayleigh lines, but only lines with a negative slope correspond to the physical sense. Of particular importance are the two Michelson-Rayleigh straight lines released from the point O of the initial state of the combustible mixture with respect to this hyperbola: they determine the minimum supersonic velocity of the detonation wave (DW) – the Chapman-Jouguet velocity D_0 – and the maximum subsonic velocity of deflagration burning D_{def}. It should be specially emphasized that the point F of tangency to the lower branch of the Hugoniot adiabat curve has the property of maximum entropy – \( \partial S/\partial V = 0 \). It is to such a state that the system should move in accordance with the second law of thermodynamics.

2. The thermal model of the normal burning

Although the conservation laws for combustion and detonation waves allow any subsonic propagation velocities of the combustion front 0 ≤ D_t ≤ D_{def} for the lower branch of the Hugoniot adiabat, the velocity of the normal flame S_n ≡ S_un is not derived from the conservation laws, but by the Fourier and Fick laws on the proportionality of the flux density heat and matter (per unit time through a single area) to the gradients of the corresponding parameters. It is believed that the diffusion of active sites from the reaction zone and the thermal conductivity from the heated reaction products are the main mechanisms responsible for propagation of the subsonic combustion front. If chemical reactions take place in the medium, then, in the presence of temperature gradients T ([T] = K) and concentration C ([C] = mol), these equations look as follows:

\[ \frac{∂C}{∂t} = \text{div}(D \text{grad}C) + q', \]

\[ c_p ρ \cdot \frac{∂T}{∂t} = \text{div}(\lambda \text{grad}T) + q''. \]

Here λ is the coefficient of thermal conductivity ([λ] = W/(m·K)), D is the diffusion coefficient ([D] = m^2/s), [q'] = mol/s is the reaction rate, [q''] = W/(m^2·s) is the power density of the energy release.

If the source terms q' and q'' are chosen proportional to the Arrhenius dependence of the reaction rate w, then for the Lewis number Le = D/ζ = Dp_c_ρ/λ ≈ 1 (ζ is the temperature conductivity coefficient) and certain boundary and initial conditions, the equations for the propagation of heat and diffusion can be made identical. The method of solving these equations and the assumptions used are described in sufficient detail in many textbooks (for example, [1-4]).

We note that the thermal nature of the process of flame propagation has been studied in more detail. The result of the research was the calculation of the normal propagation velocities of the flame S_n = S_un for first-order reactions – formula.
\[ S_{n1}^2 = \frac{2\zeta kT_0}{(T_f - T_0)^2 T_f} \left( \frac{RT^2}{E} \right)^2 e^{-E/RT_f}, \]

and for second-order reactions – formula
\[ S_{n2}^2 = \frac{4\zeta kC_0 T_0^2}{(T_f - T_0)^2 T_f^2} \left( \frac{RT^2}{E} \right)^3 e^{-E/RT_f}. \]

We note that the solution of the "identical" equation exists if the velocity has its own value – the velocity of propagation of the laminar flame \( S_{\text{lam}} = \sqrt{\zeta/\tau} \), where \( \tau = [A \exp(-E/RT)]^{-1} \) is the characteristic reaction time. From pressure and temperature the laminar velocity depends as \( v_{\text{lam}} \approx P^{n/2-1} \exp(-E/2RT_0) \).

It is well known that in most cases the conversion of the initial mixture into reaction products occurs through a variety of elementary reactions - a detailed scheme for the combustion of heavy hydrocarbons already has more than 2000 elementary reactions. Only in limited cases the generalized kinetics behaves like a whole (first or second) order, in most cases the order of the generalized reaction turns out to be fractional. Especially it should be emphasized that such an order is unknown in advance and, moreover, can change with varying parameters of the mixture (pressure, temperature, component ratio, ...). Even such a system repeatedly studied as hydrogen-oxygen continues to "present surprises" to this day, when the calculated and experimental parameters are not confused with each other. The number of "surprises" increases significantly for heavy hydrocarbons, for example, an unconventional (inclined N-shaped profile), the behavior of the ignition delays as the \( T \)–changes - the existence of a "negative temperature coefficient" (or the same delay at three different temperatures).

3. Experimental and calculated data about velocities of normal and deflagration burning

The report analyzes the ratio of the velocities of normal and deflagration burning of typical gas mixtures. If the deflagration velocity is determined by the condition of tangency, then the considerations as to which condition the slope of the Michelson-Rayleigh line should be determined the state behind the wave of normal burning, is absent in scientific literature. In given paper not only the values of the parameters are analyzed, but also their functional dependence on the parameters of the mixture. In addition, the speed of a "purely diffusion wave" is considered.

Figure 1 presents experimental data on the flame velocity for a number of hydrocarbon mixtures [4]. For most hydrocarbons, the numerical values for gas mixtures are about 40-60 cm/s, somewhat higher values are fixed for ethylene (80 cm/s) and acetylene (160 cm/s). The record holder for flame speed is hydrogen, whose flame velocities are almost an order of magnitude higher in comparison with hydrocarbons – (3–10) m/s. We note at once that the normal flame velocity for most gas mixtures is of the order of 1 m/s, while the deflagration velocity is almost two orders of magnitude larger and amounts to several tens of m/s.

![Fig.1. Data on the normal flame velocity in various hydrocarbon mixtures.](image-url)
A Mach number $M_n = S_n / c_0 \approx 10 / 540 \approx 1.85 \cdot 10^{-2}$ corresponds to a hydrogen-oxygen mixture of velocity $S_n \approx 10$ m/s. For hydrocarbon mixtures $M_n = S_n / c_0 \approx 0.5 / 300 \approx 1.667 \cdot 10^{-3}$. With such low Mach number, the slope of the Rayleigh-Michelson line is practically invisible and the final state of the combustion products differs little from the state obtained during combustion in the $P = \text{const}$ mode. In turn, the point of tangency of the Rayleigh-Michelson straight line to the lower branch of the adiabatic energy release of the mixture is characterized by the fact that the entropy of the system reaches its maximum, which is the basic requirement of the thermodynamics of thermal processes. At the point corresponding to the normal combustion rate ($P = \text{const}$), the maximum entropy condition is not satisfied. That is why the laminar flames easily pass to the regime of turbulent combustion, the velocities of which are higher and correspond more to the deflagration point. The velocities of deflagration burning for stoichiometric mixtures of hydrogen with oxygen and air are equal $D_{df} = 83.6$ and $D_{df} = 71.3$ m/s, respectively.

Figure 2 shows experimental data on flame velocities in hydrogen mixtures [5], and Fig. 3 – data on the temperature of the combustion products of the same mixtures. There is a good correlation
between the flame speed and product temperature for hydrogen-oxygen mixtures with a change in the hydrogen concentration – with maxima near the stoichiometric composition \( c_{\text{H}_2} = 0.667 \). At the same time for hydrogen-air mixtures the correlation is worse, it is clear that the maximum of the flame speed \( c_{\text{H}_2} \approx 0.45 \) does not coincide with the maximum temperature and is shifted away from the stoichiometric ratio \( c_{\text{H}_2} = 0.296 \).

It can be seen from Fig. 3 that the general patterns of the behavior of the product temperature are almost similar under deflagration burning and burning modes in the regime of \( P = \text{const} \), although the temperature values themselves exhibit a certain difference: under deflagration burning \( T \) is lower, since part of the chemical energy is then converted into kinetic energy of products.

Figure 4 presents data on the specific energy release of hydrogen mixtures. Comparison of the profiles of the flame velocity in Fig. 2 and the energy release profile in Fig. 4 indicates a weak correlation of the profiles of these parameters.

4. The diffusion influence on normal burning

Analysis of the main elements fixed in the combustion products shows that as the concentration of hydrogen in the mixture increases, a gradual decrease in oxygen is observed, water is seen as the final product of the reaction with the maximum yield at a stoichiometric ratio. Along with them, the active atoms of hydrogen and oxygen, as well as the OH radical, appear in appreciable quantities in the products. Such particles can play a certain role in their diffusion from the product zone to the initial fuel mixture due to their significantly greater activity due to the significantly higher temperature and the thermal velocity of the products (for example, by initiating the replication reaction of the \( \text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O} \) chain). Let us make some estimates of the diffusion activity of hydrogen mixtures.

The diffusion coefficient of the initial mixture of gases A and B (H2 and O2) was determined through the molar concentrations of the mixture components and their individual self-diffusion coefficients according to the formula

\[
1 / D_{AB} = c_A / D_A + c_B / D_B
\]

[6]. The diffusion coefficient of the initial mixture increases monotonically from \( D_{\text{O}_2} = 0.18 \text{ cm}^2/\text{s} \) to \( D_{\text{H}_2} = 1.28 \text{ cm}^2/\text{s} \). Since hydrogen has the maximum diffusion coefficient, it plays a decisive role in the propagation of the flame among the remaining combustion products, especially as the concentration of hydrogen in the mixture increases. The value of the diffusion coefficient of combustion products was recalculated to the temperature by the formula

\[
D_{\text{diff}}^\text{f} = D_{\text{diff}}^0 (T / 273)^{1/5}
\]

[6].

For pure diffusion, the problem is determined by three parameters, the coordinate \( ([r] = \text{m}) \), the time \( ([t] = \text{s}) \), and the diffusion coefficient \( ([D] = \text{m}^2/\text{s}) \) From the dimensions of the determining
parameters, the obvious relationship for the coordinate \( r^2 = Dt \) and diffusion rate \( S_{\text{diff}} = 0.5\sqrt{D/t} \) follows. Using the data on the temperature of the products combustion (Fig. 4) and the last formula the "purely diffusion velocity" (PDV) was calculated – the results are presented in Fig. 5 (the dimension of diffusion velocity \([S] = \text{cm/s}\)).

The comparison shows that the dependence profile of diffusion velocities is similar to the profile of the specific energy release of hydrogen mixtures, presented in Fig. 4. The values of the \( S_{\text{diff}} \) were found to be two orders of magnitude smaller than those of the experimental \( S_n \) ones. The difference is significantly reduced if the average geometric velocity between the diffusion velocity and the deflagration velocity is taken as the flame velocity \(-S \approx \sqrt{S_{\text{diff}} \cdot S_{\text{def}}}\).

References

[1] Shchelkin K I, Troshin Ya K 1963 *Gas dynamics of combustion* (Moscow, Academy of Sciences of the USSR)

[2] Mikhelson V A 1893 On the normal rate of ignition of explosive gas mixtures *Uchenye zapiski Imperatorskogo Moskovskogo Universiteta. Department of Physics and Mathematics. The tenth start-up* (Moscow, University Printing House)

[3] Zeldovich Ya B, Frank-Kamenetsky D A 1981 Theory of thermal flame propagation *Theory of combustion and explosion* (Moscow, Science)

[4] Varnatts Yu, Maas U, Dubl R 2003 *Combustion. Physical and chemical aspects, modeling, experiments, formation of pollutants* (Moscow, Fizmatlit)

[5] Gelfand B E, Popov O E, Chyvanov B V 2008 *Hydrogen: Parameters of Combustion and Explosion* (Moscow, Fizmatlit)

[6] Kikoin I K 1976 Tables of physical quantities (reference book) (Moscow, Atomizdat)