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Enthalpy profile in a flat laminar flame front

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The enthalpy profile in flat hydrogen–air flame fronts under normal initial conditions is numerically characterised.

In the previous studies[1–3] of an enthalpy distribution in a flat flame front, it has been assumed that, if the diffusion coefficient of a deficient component is not equal to the thermal diffusivity, chemical energy diffuses at a rate different from that of thermal energy, and their sum may vary in different flame regions; that is, in some regions, the enthalpy may be higher or lower than in others. In lean hydrogen–air mixtures, the deficient component, molecular hydrogen, which carries chemical enthalpy, has a high diffusion coefficient and, hence, transfers chemical enthalpy to more heated regions of the front. Since the thermal diffusivity of the mixture is lower than the diffusion coefficient of hydrogen, in a region from which chemical enthalpy was lost, the total enthalpy is lower than the initial value. Therefore, for this case, the plots of enthalpy in the flame front have a dip.[1,2] These ideas have arisen in attempts to solve the system of equations describing flame propagation. In this approach, it was natural to use a simple approximation for the heat release term – the global kinetics approximation, where a complex multistep reaction was replaced by a single reaction. Accordingly, only the deficient component was assumed to transfer chemical enthalpy. In the case of multistep reaction when numerous intermediate components arise, their contributions to the mixture enthalpy should be considered in more detail.

Note that a change in the enthalpy of a system during passage of this system through the flame front was out of the question.[1,2] It is obvious that, in passing through the front, any prescribed system in the initial mixture will change due to loss or gain of particles (H, OH, O_2, H_2 *etc*.) through the boundary. It is reasonable to consider different thermodynamic systems in each unit volume at different points of the front to which particular enthalpies correspond. Thus, we can speak of the concentration profile of enthalpy in the same way as we speak of the concentration profile of any component of the mixture.

Clearly, molecular hydrogen without oxygen does not carry chemical energy. In other words, we should also consider the behaviour of oxygen in the flame front and its diffusion coefficient. It suffices to recall that, with other oxidizers (NO, NO_2, N_2O and Cl_2), different amounts of energy are released. In addition to the initial components, other components appear in the flame front; their contribution to the chemical enthalpy is unknown, but they can also have it. Previously,[1–3] there was no precise information on the kinetics of reactions at high temperatures, and the transport coefficients were not known with sufficient accuracy. Therefore, Lewis and von Elbe,[1] considering the subject of study difficult and complex, proposed to postpone its consideration until a later stage in the development of our knowledge of gas combustion. Moreover, it has been claimed[4] that previous attempts to solve the equation for flame propagation based on global kinetics are now largely of historical interest.

The aim of this work was to numerically study the enthalpy concentration profile in the flame front of hydrogen–air mixtures over a range of hydrogen concentrations from lean to rich conditions.

The easiest way to elucidate the enthalpy concentration profile in the flame front is the summation of the enthalpies of each component at each point of the front. Numerical simulation makes it possible to determine the composition and temperature of the mixture in any section of the front. This is sufficient to determine the heat content (enthalpy) of each component and, after summation, to obtain the enthalpy at a particular location of the flame front. We consider hydrogen–air mixtures because hydrogen has a sufficiently large diffusion coefficient in comparison with other gaseous fuels; therefore, the nature of an enthalpy distribution for these mixtures should be most pronounced.

The numerical simulation of flame propagation in hydrogen–air mixtures was performed using a software package[5] and Konnov's kinetic scheme.[6] The accuracy of the calculation and the convergence of the solutions are determined by the number of points in the domain of integration, which was more than 200. The positions of the cold and hot boundaries were –8 cm and 20 cm, respectively. The origin of coordinate was at the point with a temperature of 400 K in the flame front.

The following four characteristic hydrogen concentrations in mixtures with air were used: 15 and 20% H_2 in lean mixtures, 42% H_2 in rich mixtures with a maximum normal velocity, and 70% H_2 in rich mixtures (T_0 = 300 K, P_0 = 0.1 MPa). In accordance with published data,[1–3] the enthalpy profile in the flame front of lean hydrogen–air mixtures should have one enthalpy minimum. However, the numerical simulation gives a completely different result. Figure 1 shows the enthalpy profiles for the four above hydrogen concentrations. For all of the test concentrations, the enthalpy initially increased, then decreased below the initial value and subsequently approached the initial value from below, including the case of a very rich mixture.

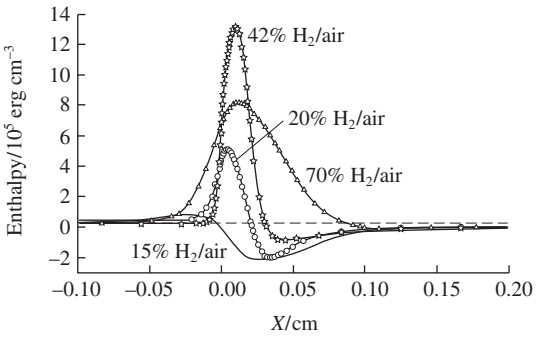

Figure 1 Enthalpy profiles in flames of 15, 20, 42 and 70% hydrogen and air at T_0 = 300 K and P = 0.1 MPa.

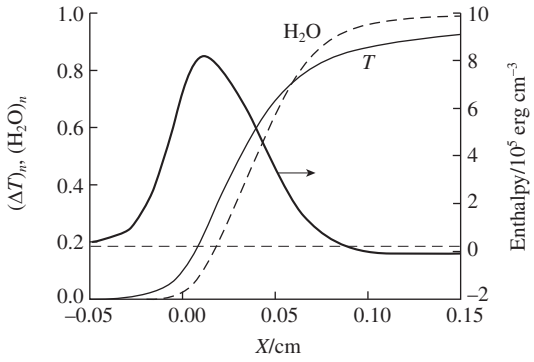

Figure 2 Profiles of the enthalpy, normalized temperature increase and normalized water concentration in a 70% hydrogen–air flame.

The numerical simulation revealed that the main components of the lean mixture with significant enthalpy values at the front with a maximum enthalpy are molecular hydrogen, molecular oxygen, water and molecular nitrogen. For the mixture of 42% H_2, atomic hydrogen is added to these components. All components other than water have a positive enthalpy.

For a very rich mixture of 70% H_2, the calculated enthalpy profile can be explained using a classical model; *i.e.*, the excess enthalpy is due to the higher thermal diffusivity of the mixture (0.83 cm^2 s^{-1}) compared to the diffusion coefficient of oxygen (0.66 cm^2 s^{-1}). The coefficients are given for the fresh mixture under the initial conditions. Figure 2 depicts the dependence of the normalized temperature increase $\Delta T_n = (T - T_0)/(T_{eq} - T_0)$ and the normalized water concentration $(H_2O)_n = H_2O(x)/H_2O_{eq}$ on the coordinate in the flame front of this mixture. The temperature rise is faster than the increase in the concentration of water – the main source of heat. However, note that the faster temperature rise may also be due to the diffusion of hydrogen atoms to a low-temperature zone. There are many hydrogen atoms in the reaction zone of rich mixtures, where they react with oxygen or recombine with heat release, producing an excess of enthalpy in the heating zone. As found previously,[7] the diffusion of H atoms to the low-temperature zone leads to the formation of HO_2, followed by the reaction $H + HO_2 \rightarrow 2\,OH$. Hydroxyl reacts with hydrogen to form water. These reactions with the formation of HO_2, OH, and H_2O involve heat release. The formation of OH from HO_2 and the formation of H_2O from OH are shifted relative to each other on the coordinate. In other words, the diffusion of H atoms transfers chemical energy from the high-temperature zone to the low-temperature zone. Figure 3 shows the concentration profiles of H, OH and HO_2 for the flame of a mixture of 42% H_2 with air.

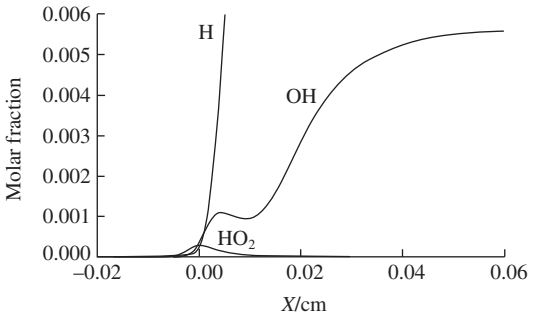

Figure 3 Concentration profile of H atoms, OH and HO_2 in the 42% H_2/air flame front.

The OH profile has two peaks. The first peak in the low-temperature region is related to the diffusion of hydrogen atoms, which leads to the formation of HO_2. The peak in the HO_2 profile is before the first peak in the OH profile since the formation of OH is followed by the formation of HO_2.

Thus, the numerical simulation of flame propagation taking into account the detailed kinetics of hydrogen oxidation demonstrates that the use of single-step kinetics (or global kinetics) does not always give correct results. The chemical enthalpy is determined not only by the deficient component. The intermediate components formed in the flame front also have chemical enthalpy and transfer it by diffusion. The enthalpy profile of a particular flame can show both an increase and a decrease in the enthalpy relative to the initial value.

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