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Experimental and Numerical Study of Probe-Induced Perturbations of Mole Fraction Profiles of H and OH Radicals in a Burner-Stabilized CH₄/O₂/Ar Premixed Flame

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Abstract
Probe-induced perturbations of mole fraction profiles of H and OH radicals in a methane-oxygen-argon flame is studied both experimentally and numerically. This study is a continuation of our previous investigation focused on probe-induced perturbations of gas dynamic structure of the flow and the mole fraction profiles of stable species (CH₄, O₂, H₂O and CO₂) in the same flame [P.A. Skovorodko et al., Combust. Theory and Modelling, 2013 (17)(1) 1 - 24].

Introduction
Flame sampling molecular beam mass spectrometry (MBMS) is one of the most important methods of flame diagnostics. To interpret the sampling measurements correctly, an analysis of the probe-induced perturbations is needed. In the literature, there are many simplified theoretical approaches to account for probe-induced perturbations of the flame structure (see the references in [1]). As a rule, these approaches are based on approximating the flow field near the probe by incompressible fluid flow without considering the particular probe geometry. This study represents an attempt to model the real interaction between a probe (of a specific shape and size used specifically in flame probing experiments) and a real flame (with a description of the basic parameters of the flame).

Approach
A laminar premixed lean methane/oxygen/argon flame (CH₄/O₂/Ar = 0.06/0.15/0.79 in mole basis, equivalence ratio φ = 0.8) was stabilized on a Botha–Spalding burner 16 mm in diameter at a pressure of 1 atm (735-762 torr) and an unburned-gas temperature of about 368 K. The flow rate of the unburnt gases through the burner was 25 cm³/s at room temperature. The burner surface represents a perforated brass disc (diameter of holes 0.5 mm, hole separation 0.7 mm) placed in a brass housing with a cooling jacket. The burner was filled with 3 mm diameter stainless steel balls to uniform flow speed at the burner surface and to thoroughly heat the flow. The cooling jacket was thermostated by water at 95 °C. Inlet gas fluxes were set by mass flow controllers (MKS Instruments Inc.). The burner was moved along its axis of symmetry to provide sampling by a fixed probe at different heights above burner (HAB). The temperature profile of the flame was measured by a Pt–Pt+10%Rh thermocouple welded from wire 0.02 mm in diameter, covered with a thin layer of SiO₂ to prevent catalytic recombination of radicals on the thermocouple surface. The resulting thermocouple had a diameter of 0.03 mm and a shoulder length of about 5 mm, providing negligible heat losses to the cold ends. Mole fractions of H and OH radicals in the flame as a function of HAB were measured by MBMS. The molecular-beam setup based on an MS-7302 quadrupole mass-spectrometer was described in detail previously [1]. The flame-burning area was sampled by a quartz cone nozzle with a 0.08 mm orifice diameter at the tip, an inner cone angle of 40°, an outer cone angle of 51° and a tip diameter of 0.24 mm (wall thickness near the tip of 0.08 mm). The conical part of the probe from the tip to the base of the cone was 20 mm long. A tip of a skimmer with a 0.6 mm orifice was located at a distance of 20 mm from the probe tip. Temperatures of the probe tip and the cone walls at various distances from the tip were measured by the thermocouple. The error of the thermocouple measurements was within ±30 K.
The flow between the burner and the axisymmetric probe in the flow was simulated using the full set of unsteady Navier-Stokes equations. For an approximate consideration of the heat release due to the chemical reactions, a source term $Q_T$ is added to the energy equation to provide the given temperature distribution in the planar, undisturbed, isobaric flame, i.e. in the absence of the probe in the flame.

The simulations were performed for the burner-stabilized premixed flame studied in the experiments. The combustible gas mixture was assumed to be a single-component perfect gas with a molecular weight of 37.32 kg/kmol and a specific heat ratio $\kappa = 1.5747$ calculated from the real parameters of the flame at the burner surface. The temperature dependence of the dynamic viscosity $\mu$ of the gas was described by the Lennard-Jones $(6−12)$ potential with parameters $\sigma = 3.418$ Å and $\varepsilon / k = 124$ K typical of argon. Since the main component of the mixture is argon, the value of the Prandtl number ($Pr = \mu C_p / \lambda$) was assumed to be the same as for a monatomic gas, i.e., $Pr = 2/3$. The effect of bulk viscosity was neglected ($\mu'' = 0$).

The obtained gas dynamic structure of the flow near the probe under conditions similar to those in a real perturbed flame was used to evaluate the probe-induced perturbations of species concentrations – the most important problem from an experimental point of view. Since the main component of the investigated flame is chemically neutral argon, the evolution of the concentration of some flame species in the flow field was simulated using the diffusion equation for binary gas mixtures of these species with argon. The effect of chemical reactions was approximately described by a source term $Q_c$, which provided a given species concentration distribution in the unperturbed flame, i.e. in the absence of the probe in the flame.

The temperature dependence of the diffusion coefficients $\rho D_{12}$ for the investigated mixtures was described by the Lennard-Jones $(6−12)$ potential with parameters $\sigma = 2.05$ Å, $\varepsilon / k = 145$ K for H and $\sigma = 2.75$ Å, $\varepsilon / k = 80$ K for OH using the conventional combination rules for describing the interaction between unlike molecules. The effects of pressure and thermal diffusion on the concentration distribution in the flow field were also studied though they are small compared to pure concentration diffusion.

In the considered case of radicals H and OH, the boundary conditions for concentration at the solid surfaces were revised to account for the possible quenching of radicals on the surface of the probe due to their recombination there. By introducing the probability of radical loss upon collision with the probe surface ($K$), we proposed the boundary conditions that for limited cases provided no diffusion flux for $K = 0$ and zeroth concentration of the considered radical at the surface at $K = 1$.

Further details of numerical procedure may be found in [1]. Temperature profile and mole fraction profiles of H and OH radicals in undisturbed flame were simulated using CHEMKIN II collection of codes with inclusion of ENRG keyword to obtain a solution for the coupled energy-species equations.

**Results and discussion**

Mole fraction profiles of H and OH radicals in undisturbed flame calculated using CHEMKIN II as well as measured mole fraction profiles for these species are illustrated in Fig. 1. As it is seen from this figure, the measured profiles are shifted downstream by about 1 mm with maximum measured values of concentrations being noticeably lower compared to the profiles in undisturbed flame.

The axial dependencies of source terms $Q_c(z)$ for H and OH radicals obtained with and without accounting for thermal diffusion are shown in Fig. 2. The small values of $Q_c(z)$ at $z \leq 0.2$ mm are indicative of the predominantly diffusive nature of this region of the flame front. In contrast with the source terms for stable components which are positive for the combustion products CO$_2$ and H$_2$O and negative for the reagents CH$_4$ and O$_2$ [1], the source terms for H and OH change the sign inside the flame front – positive values of these terms take place only in
some range of distances from the burner (0.5 mm \( \leq z_0 \leq 1.5 \) mm) while outside this region the terms are negative that corresponds to the sink process. Such behavior of source terms reflects the chemical structure of the flame front. Small difference between the data shown in Fig. 2 by solid and dashed lines reveals small effect of thermal diffusion on the H and OH concentration distributions in the considered flame.

The effect of the probability of radical loss upon collision with the probe surface (\( K \)) on the mole fraction of H in the probe orifice section is illustrated in Fig. 3 for the probe-burner distance \( z_0 = 1.6 \) mm (the shown data are obtained with accounting for concentration diffusion only). Both shown values of concentrations - in the center of the orifice, and the mean value of concentration over the probe orifice section reveal the same dependence on \( K \) – the decrease by about order of magnitude with increasing \( K \) from 0 to 1. For considered case the agreement between the model and the measured results is achieved at \( K \approx 0.05 \).

![Fig. 1. Distributions of H and OH concentrations in undisturbed flame (lines) and experimental data for these species concentrations (symbols).](image1.png)

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![Fig. 2. Source terms in non-dimensional form for the diffusion equation for H and OH radicals obtained without (solid lines) and with (dashed lines) accounting for thermal diffusion.](image2.png)

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Conclusions

The performed investigation favours to understanding of the peculiarities of the gas flow near the probe in the conditions similar to real ones, and allows more correct statement of the problem of the parameters distribution in undisturbed flame recovering based on the data obtained by mass-spectrometric probe sampling technique.

References