TEMPERATURE-DEPENDENT FEATURE SENSITIVITY ANALYSIS OF FLAMES

Z. Zhao*, J. Li, A. Kazakov, F.L. Dryer
Mechanical and Aerospace Engineering Department, Princeton University NJ USA
zzhao@princeton.edu

Typically, sensitivity studies are performed by perturbing the *A*-factor for individual reaction rate coefficients and monitoring the effect of these perturbations on the observable(s) of interest. The sensitivity coefficients obtained in this manner do not contain any information on possible temperature dependence effects. In many combustion processes, e.g. in premixed flames, the system undergoes substantial temperature changes, and the importance of individual reaction rates may be confined to specific ranges of temperature within the flame structure itself. In this work, temperature dependent sensitivity characteristics for key reaction rates and for binary diffusion coefficients on laminar flame speed were determined by perturbing the most sensitive specific reaction rates or the binary diffusion coefficients by small values at multiple points in the flame temperature profile. A Gaussian function perturbation profile was utilized, where the center of the Gaussian profile moves with the assigned temperature of interest.

Using an updated H_2 oxidation kinetic model, the sensitivity spectrum of reaction $H + O_2 = OH + H$ (R1) is found to be dominant in determining flame speed based upon rate constant values in a relatively narrow temperature range 850 – 1550 K. This temperature “window” shifts to higher values with increasing system pressure. The selected diluent species and concentration are found to influence the temperature window size and location, being broadened by helium substitution for nitrogen and shifted toward lower temperatures as overall dilution is increased. As a result, kinetic models verified against flame speed data with one diluent condition may yield disparities at other diluent conditions, based entirely on the temperature dependent characteristics of an important reaction. A similar investigation of the importance of $CO + OH = CO_2 + H$ (R2) on CO/H_2 flame speed at atmospheric pressure shows that the most sensitivity to this reaction is at temperatures lower than 1900 K. For carbon monoxide flames, the range of the temperature window extends to 300K, but for hydrocarbon flames, the temperature window lower limit is above 800 K. Recent RRKM models of the rate constants for (R2) differ substantially from experimental results at these intermediate temperatures. Premixed flame speeds of small-hydrocarbon oxygenate/air mixtures (methanol, dimethyl ether, ethanol) are also particularly sensitive to the reactions $HCO + M = H + CO + M$, (R3) and $HCO + O_2 = HO_2 + CO$, (R4). Similar studies showed that flame speeds are most sensitive to the values of (R3) and (R4) in the temperature ranges 1350-2000 K and 1200-1900 K, respectively, well above the range of conditions of the more recent rate constant measurements. In other work, we utilized this information in developing an updated C_1 mechanism in with alternative reaction rate expressions for reactions (R2)-(R4). The updating significantly improves the ability to predict laminar flame speeds while maintaining excellent predictive comparisons for shock tube and flow reactor results.

The temperature dependent sensitivity features of binary diffusion coefficients on laminar flame speed were also demonstrated using hydrogen air flames. The temperature dependent sensitivity of H/He binary diffusion coefficient on the predicted $H_2/O_2/He$ laminar flame speed exhibits a non-monotonic trend. The shape of the obtained curve is a result of complex reaction/transport interactions within the flame structure. At lower temperatures, an increase in the diffusion coefficient causes an enhanced transport of H atoms toward the cold region where they do not contribute to chain branching kinetics (primarily, via R1). Consequently, the sensitivity with respect to of H/He binary diffusion coefficient is negative. As the temperature increases, the H/He diffusion sensitivity becomes positive and peaks close to the point where the sensitivity with respect to R1 has its maximum. Here, the diffusion flux brings H atoms to the regions where chain branching is active, resulting in an increase in the flame speed. At even higher temperatures, the sensitivity with respect to the H/He binary diffusion coefficient goes through zero again (around the point where H concentration has its peak, indicative of directional change in H diffusion flux). From this point, the diffusion flux carries H atoms away from the chain-branching region toward the post-flame zone, and the sensitivity becomes negative again. Non-monotonic behaviour of binary diffusion coefficient sensitivity with respect to temperature has significant implications for detailed flame modelling. For example, Middha et al. (Proc. Combust. Inst., 2002, 29, 1361) recently reported improved values of H/He binary diffusion coefficient which are generally higher than those computed with the CHEMKIN II database over the entire temperature range of interest. However, it was also reported that the resulting flame speeds did not change significantly. The present study shows that the difference in binary diffusion coefficient may be compensated by the sensitivity sign change with the temperature, resulting in a minor difference in predicted flame speed.