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Temperature-Dependent Feature Sensitivity Analysis for Combustion Modeling

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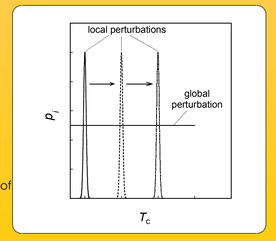
Motivation

- Sensitivity analysis is one of the most widely used tools in kinetic modeling.
- Typically, it is performed by perturbing the *A*-factors of the individual reaction rate or binary diffusion coefficients and monitoring the effect of these perturbations on the observables of interest.
- However, the sensitivity coefficients obtained in this manner do not contain any information on possible temperature dependent effects. Yet, in many combustion processes, especially in premixed flames, the system undergoes substantial temperature changes, and the relative importance of individual reaction rates and/or binary diffusion may vary significantly within the flame.
- An extension of conventional sensitivity analysis developed in the present work provides the means of identifying the temperatures at which individual reaction rate coefficients are most important as a function of input parameters and specific experimental conditions. The obtained information is demonstrated to be of critical relevance in optimizing complex reaction schemes against multiple experimental targets.

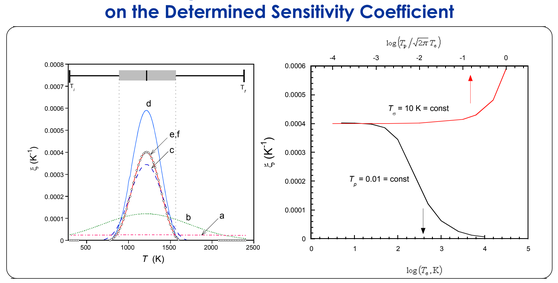
Temperature Dependent Sensitivity Analysis

- Conventional sensitivity analysis
  - — global perturbation $p_i = const.$
  - — sensitivity coefficient $s_i = \left.\frac{1}{F}\frac{\partial F}{\partial p_i}\right|_{p_i \to 0}$
  - ❖ No temperature-dependent information was revealed
- Temperature-dependent sensitivity analysis
  - — local perturbation $p_i = \frac{T_p}{\sqrt{2\pi}T_\sigma}\exp\left[-\frac{(T-T_c)^2}{2T_\sigma^2}\right]$

  where T_c is the center, T_s the width, and T_p the magnitude of the perturbation
  - — sensitivity coefficients $\xi_i(x_j^s) = \left.\frac{1}{F}\frac{\partial F}{\partial x_j^s}\right|_{x_j^s \to 0, \sigma \to 0}$
  - ❖ By gradually moving the center of this Gaussian perturbation, new, temperature-dependent sensitivity coefficients are obtained.



Effect of Magnitude and Width of Perturbation on the Determined Sensitivity Coefficient



- Sensitivity coefficient for reaction (R1), H + O_2 = OH + O, in H_2 kinetic model at stoichiometric, 1 atm, 298 K with different perturbation parameters, T_s and $T_p/\sqrt{2\pi}T_\sigma$: (a) = 2500 K and = 0.01; (b) = 500 K and = 0.01; (c) = 100 K and = 0.01; (d) = 10 K and = 1; (e) = 10 K and = 0.01; (f) = 10 K and = 10^{-4}, where $\xi(T)$ is the sensitivity coefficient.
- A robust numerical convergence is observed in both cases.

Acknowledgments

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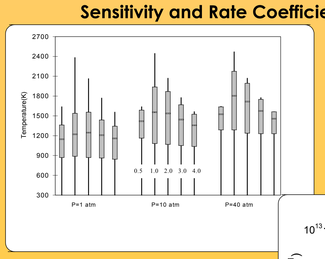
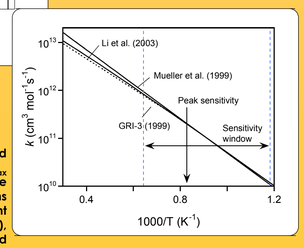
Sensitivity and Rate Coefficient of H_2 model



- Laminar flame speed is sensitive to H + O_2 = OH + O, (R1), over only a narrow sub-domain of the overall temperature range within each flame structure, and this sub-domain changes in both extent and location with equivalence ratio and pressure.

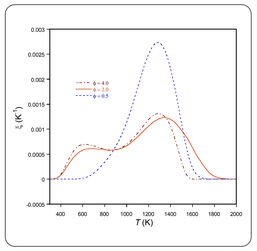
— The sensitivity temperature window for reaction rate of (R1) in H_2 kinetic model. The numbers in the figure refer to equivalence ratio.

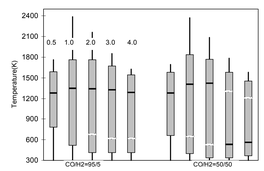
- At 1 atm, the sensitivity window is confined to the range of about 850-1550 K and $\xi(T)_{max}$ occurs at about 1210 K. As shown on the right figure, the rate coefficient expressions for reaction (R1) used in several recent H_2/O_2 mechanisms [Mueller et al. (1999), Smith et al. (1999), Li et al. (2004)] yield nearly the same specific rate values within the temperature sensitivity window, with all correlations intersecting close to the temperature of $\xi(T)_{max}$. The laminar flame speed predictions for atmospheric H_2/air flames are very similar for all three mechanisms and are in a good agreement with the experimental data even through different rate correlations were used.



— Rate coefficient of (R1), H + O_2 = OH + O, used in different H_2 kinetic models.

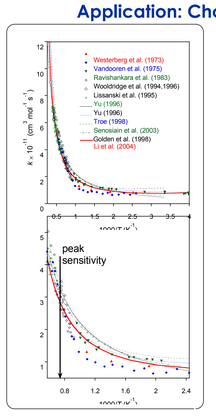
Sensitivity coefficient in CO/H_2 kinetic model



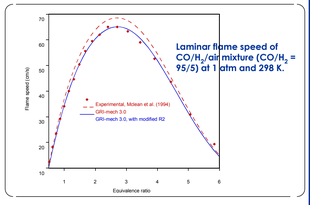


- Sensitivity coefficient for (R2), CO + OH = CO_2 + H, at 1 atm and 298 K (CO/H_2=95/5), Black and white horizontal lines within each bar indicate locations of first (highest) and second peak values, respectively. The numbers in the figure refer to equivalence ratio.
- The temperature-dependent sensitivity coefficient $\xi(T)$ for reaction (R2) is very interesting in that there are two maxima in the function at rich conditions that collapse into a single peak at lean conditions. The sensitivity window for (R2) is much wider and extends to much lower temperatures than for reaction (R1).

Application: Choice of the Rate Coefficient



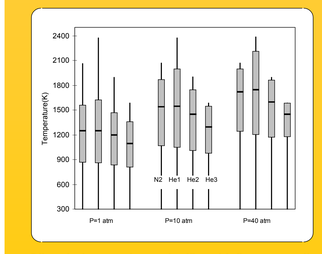
- Reaction (R2) exhibit a strong non-Arrhenius behavior and has been studied extensively.
- A large body of both experimental and theoretical results are available in the literature. Most of reported experimental data are from high-temperature shock-tube studies, and the vast majority of these data are outside of the sensitivity window for this reaction. On the low-temperature side, there are much fewer data points, however, the sensitivity of the flame speed to the specific rate constant at these temperatures still remains high.



Rate coefficient of (R2), CO + OH = CO_2 + H. The top-panel figure shows the compilation of all recent literature data, and the bottom-panel figure presents only the data within the sensitivity window for this reaction.

- Based on the observations reported here, Li et al. (2004) recently performed a modified Arrhenius fit of all experimental data, weighted by reported or estimated experimental errors.
- The substitution of this correlation for that used in the GRI-Mech 3.0 mechanism for the specific rate constant of (R2) brings the model predictions into excellent agreement with the experimental data.

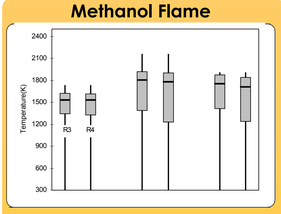
The Effect of Dilution on Sensitivity Windows



Sensitivity for (R1), H + O_2 = OH + O, in H_2 kinetic model for different diluents at equivalence ratio 2.0 (N_2: O_2/N_2 = 1/3.76, He1: O_2/He = 1/3.76, He2: O_2/He = 1/7.52, He3: O_2/He = 1/11.28).

- Diluent changes have significant influence on the sensitivity window for reaction (R1). For the same volume percentage of diluent, the sensitivity windows for H_2/He/O_2 flames are wider than those for H_2/air flames. When more diluent is used, the sensitivity window shifts toward lower temperatures following the decrease in the adiabatic flame temperature.
- These observations indicate that kinetic models verified against flame speed with one diluent, may not correctly predict the flame speed with another diluents depending on differences in the correlations used to predict (R1) as a function of temperature.

Methanol Flame

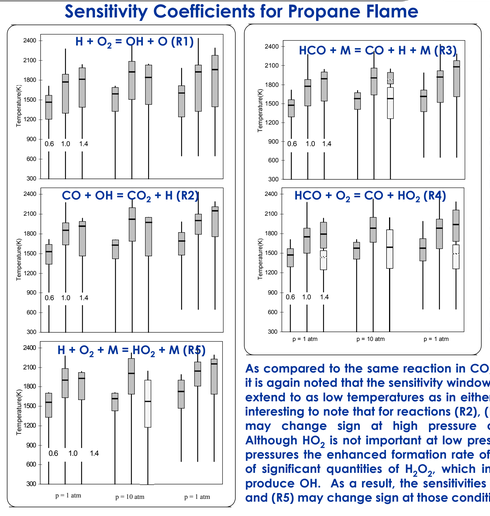


Sensitivity coefficient for (R3) and (R4), HCO + M= CO + H + M and HCO + O_2 = CO + HO_2, at 1 atm and 298 K

For methanol flames, the flame speed is most sensitive to R3. In contrast to CO flames, the temperature dependent sensitivity for this reaction and the competing reaction, R4, are located at very high temperatures. In methanol flames, the major source for HCO is CH_2O, which is generated in the high-temperature reaction zone.

The sensitivity window for reaction (R2) in hydrocarbon flame systems is considerably narrower than for CO flames, primarily because CO is an intermediate species formed at higher temperatures in the flame zone (not an initial reactant). Due to the different origins of CO and HCO, the temperature dependent sensitivity spectrums of the CO flame will generally differ from those for hydrocarbon fuels.

Sensitivity Coefficients for Propane Flame



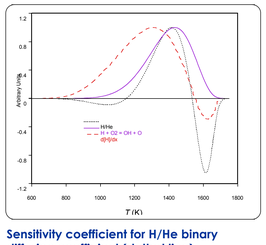
Propane is generally considered to be the smallest hydrocarbon molecule with combustion characteristics similar to larger hydrocarbon fuels. Because the flame speeds for molecules larger than C_3 are primarily controlled by the C_3 sub-mechanism, it is reasonable to expect that for large molecule hydrocarbon fuels, that conventional sensitivity, temperature-dependent sensitivity, and temperature sensitivity window patterns for small species interactions will be similar to those found for propane flames.

As compared to the same reaction in CO/H_2 and hydrogen flames, it is again noted that the sensitivity windows are narrower and do not extend to as low temperatures as in either of these cases. It is also interesting to note that for reactions (R2), (R4) and (R5) the sensitivity may change sign at high pressure and fuel-rich conditions. Although HO_2 is not important at low pressure conditions, at higher pressures the enhanced formation rate of HO_2 results in production of significant quantities of H_2O_2, which in turn can decompose to produce OH. As a result, the sensitivities for reactions such as (R2) and (R5) may change sign at those conditions.

Summary and Conclusions

- A novel applied sensitivity analysis method using perturbation with a temperature-dependent Gaussian-shaped profile to determine the range of temperatures over which a predicted observable is sensitive to a particular input parameter has been demonstrated.
- Results obtained analyzing the temperature sensitivity of flame speed predictions to the most significant reactions in H_2, H_2/CO, CH_3OH and C_3H_8 oxidation systems have been presented.
- The methodology in analyzing the effects of temperature dependence of binary diffusion coefficients on predicted H_2/He/O_2 flames have been demonstrated.
- The sensitivity parameters for almost all reactions are very temperature dependent. Our results also explain the cause of the sign change in binary diffusion coefficient to burning velocities.
- The temperature dependent sensitivity approach not only provides new insights for flame modeling, but may also serve as a tool to identify the most significant temperature range in which parameters should be experimentally and theoretically studied to reduce uncertainties important to a particular set of predictions.
- Application of the temperature dependent sensitivity analysis in helping to choose the elementary reaction rates for mechanism development was also demonstrated.

Sensitivity of Binary Diffusion Coefficient

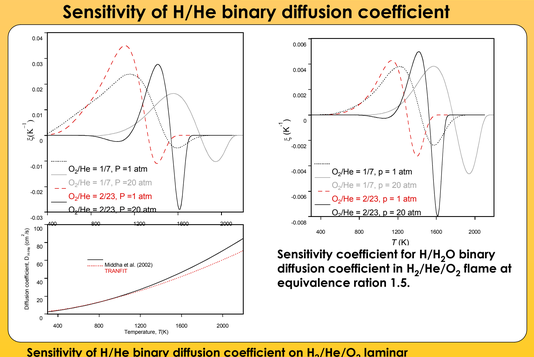


Sensitivity coefficient for H/He binary diffusion coefficient (dotted line), reaction rate of (R1), H + O_2 = OH + O, (solid line) and H concentration gradient (dashed line) for H_2/He/O_2 (He/O_2 = 23/2) flame at equivalence ratio 1.5 and 20 atm pressure. All presented quantities are normalized by the respective maximum values.

The shape of the computed $\xi(T)$ function 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), H + O_2 = OH + O). Consequently, the sensitivity with respect to the 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 rate of (R1) reaches a maximum. Here, the diffusive flux of H atoms to the region where chain branching is active results in and 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. The temperature range and sensitivity value of this non-monotonic shape may cause the overall binary diffusion coefficient sensitivity to even change sign with initial conditions.

•The non-monotonic behavior of binary diffusion coefficient sensitivity with respect to temperature has significant implications for detailed flame modeling. For example, Middha et al. (2002) 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. One of the reasons is clearly the relatively small difference (as compared to uncertainties in reaction rate coefficients) between the TRANFIT expression and the result of Middha et al. Another reason discovered in the present study is that the difference in binary diffusion coefficient (which is uniformly positive with slight increase with the temperature) may be compensated by the sensitivity sign change with the temperature, resulting in a minor difference in predicted flame speed .

Sensitivity of H/He binary diffusion coefficient

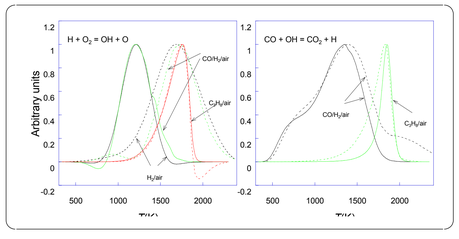


Sensitivity coefficient for H/H_2O binary diffusion coefficient in H_2/He/O_2 flame at equivalence ration 1.5.

Sensitivity of H/He binary diffusion coefficient on H_2/He/O_2 laminar flame speeds at equivalence ratio 1.5, and the diffusion coefficient of H-He for different expressions .

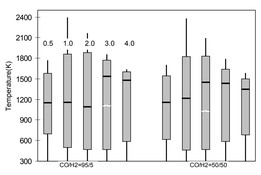
- Temperature dependent sensitivity coefficients for binary diffusion coefficients can be determined in a manner similar to that used in investigating kinetic parameters.
- Similar to the case of specific rate analyses, the sensitivity with respect to a particular binary diffusion coefficient correlation is also concentrated in a narrow temperature range and may change sign. The shape of the computed $\xi(T)$ function is a result of complex reaction/transport interactions within the flame structure.

Sensitivity Coefficients and Reaction Rates



Comparison of temperature-dependent sensitivity coefficients with the corresponding net reaction rates; solid lines – sensitivity coefficient, dotted lines – net reaction rate. All flame calculations were performed at stoichiometric conditions at 1 atm and 298 K. For CO/H_2/air flame, CO/H_2 volumetric ratio is 95:5.

•The rate curves closely follow the corresponding sensitivity coefficients for the C_3H_8/air case. Clearly, in such cases, one can simply evaluate the reaction rates to approximately identify the sensitivity windows instead of following a complex series of steps involved in the evaluation of the temperature sensitivity coefficients themselves. A similar observation was reported by Rumminger et al. (2002). However, this reasoning does not hold for all circumstances. As evidenced by the example of (R2) for CO/H_2 flame, the reaction rate, while closely following the corresponding sensitivity coefficient at lower temperatures, extends to much higher temperatures where the actual sensitivity is nearly zero. Therefore, the sensitivity window estimated based on the reaction rate curve would be substantially wider than the exact result based on the temperature sensitivity analysis. Furthermore, the analyses for reaction (R1) in cases of H_2 and CO/H_2 flames show distinct differences between the net reaction rate and the temperature sensitivity coefficient results. While similarity shaped, the curves exhibit peaks at very different temperatures, almost 500 K apart with the peak in the sensitivity coefficient occurring at lower temperature. Because the sensitivity window width for these cases is about 700 K, the sensitivity window for (R1) estimated based on the reaction rate curve for these cases would not only be misleading but also would have almost no overlap with the actual sensitivity window.



Sensitivity coefficient for (R3), HCO + M = CO + H + M, at 1 atm and 298 K.

- In CO/H_2 flames, the sensitivity windows for reaction R3 and R4 are very wide and start at a very low temperature. HCO is formed at very early stages by reaction of CO and H atom, where H can be transported by diffusion from the high temperature flame regions to the initial flame regions where CO, the initial reactant, is present.

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