LLP Research Report

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Background:

Previously in the combustion literature, the evaluation of the reaction rate used imprecise methodology when considering experimental data. For a given reaction, such as $H + O2 = O + OH$, experimental results would list their temperature range in Kelvin and their calculated Arrhenius parameters, A, n, E, as well as their respective uncertainties for the parameters. The Arrhenius equation is as follows: $k = A * T^n * e^{\frac{-E}{RT}}$

The drawback with previous statistical analyses is the lack of weights assigned when considering the significance of experimental data and calculating the average. Simply calculating a normal average and standard deviation is misleading because experiments that have lower parameter relative uncertainty and a wider breadth of temperatures are given the same weight as experiments with higher parameter relative uncertainty and a thinner breadth of temperatures. With our methodology, lower relative uncertainty and a wider temperature range are given more significance. Thus, the purpose of our research is to conduct a more thorough statistical analysis on combustion data to calculate more accurate parameters and reaction rates. The impact of our research is introducing better statistical methodology when developing a mechanism based on experimental data. Moreover, our results have demonstrated that applying robuster statistical methodology makes rate and Arrhenius parameter evaluation more accurate.

Rate Evaluation and development of new mechanism

Simulations were performed with Python Spyder and visualized with the package, matplotlib. Additionally, the packages SciPy, uncertainties, and Cantera were all extensively used. Simulation programs conducted rate evaluation for fourteen reactions by calculating new rates and their respective A, n, E parameters.

The methodology begins with extracting each reaction's experimental temperature range as well as their calculated parameters and respective uncertainties. Considering each temperature spaced ten Kelvin apart in the experimental range, a rate along with its uncertainty is calculated with the experimental parameters using the Arrhenius equation and the uncertainties package. With a list of rates for each temperature, a weighted average along with a variance to the mean is calculated by considering the uncertainty of the rates as weights. After performing this methodology for all experimental data, the list of weighted averages and their uncertainties are fitted with a least squares function utilizing curve_fit in the SciPy package. The function outputs fitted A, n, E parameters which are then used to calculate an evaluated rate for each temperature from 300-2500K. The final rate evaluation along with each reaction's parameters creates our new mechanism. This methodology takes into account both the breadth of temperature range and relative experimental uncertainty which results in a more accurate model.

Additionally, there are three reactions ($H_2O_2 + OH = HO_2 + H_2O$, $HO_2 + HO_2 = H_2O_2 + O_2$, $HO_2 + OH = H_2O + O_2$) that utilizes a modified Arrhenius with two equations. The experimental data did not fit well with the original Arrhenius equation hence the need for a modified double Arrhenius equation. The formula for double equation Arrhenius is as follows: $k = A * e^{\frac{-E}{RT}} + A_2 * e^{\frac{-E_2}{RT}}$

The mechanism, including the modified double equation Arrhenius, consists of twenty-two distinct reactions and their respective A, n, E parameters. In order to further determine the accuracy of our mechanism, it is important to compare our mechanism's rate evaluation with previously established mechanisms, HP-Mech and FFCM. The tables below show our mechanism compared with HP-Mech and FFCM at temperatures 1000K, 1500K, and 2000K with the following reactions. The reaction rate units for reactions without (+M) are $cm^3/mole/s$ while the reaction rate units for reactions with with (+M) are $cm^6/mole^2/s$. Our mechanism is consistently within 20% of HP-Mech or FFCM which shows the accuracy of our mechanism compared to previously established results.

$H + O_2 = O + OH$	Our Mechanism	HP-Mech	FFCM
1000 K	4.7E10 $cm^3/mole/s$	4.72E10	4.44E10
1500 K	6.15E11	6.21E11	5.78E11
2000 K	2.13E12	2.21E12	2.09E12

$HO_2 + OH = O_2 + H_2O$	Our Mechanism	HP-Mech	FFCM
1000 K	2.13E13 $cm^3/mole/s$	1.74E13	1.46E13
1500 K	2.41E13	2.09E13	2.21E13
2000 K	3.80E13	3.74E13	3.87E13

$HO_2 + H = OH + OH$	Our Mechanism	HP-Mech	FFCM
1000 K	5.87E13 $cm^3/mole/s$	6.10E13	5.06E13
1500 K	6.42E13	6.41E13	5.33E13
2000 K	6.85E13	6.57E13	5.46E13

$HO_2 + H = H_2 + O_2$	Our Mechanism	HP-Mech	FFCM
1000 K	1.36E13 $cm^3/mole/s$	1.38E13	1.12E13
1500 K	2.58E13	2.53E13	2.04E13
2000 K	4.15E13	4.09E13	3.29E13

$H + O_2(+M) = HO_2(+M)$	Our Mechanism	HP-Mech	FFCM
1000 K	2.29E15 $cm^6/mole^2/s$	2.34E15	3.39E15
1500 K	1.41E15	1.49E15	1.84E15
2000 K	9.88E14	1.08E15	1.17E15

Note: FFCM is using a different diluent (N_2) hence the larger discrepancy.

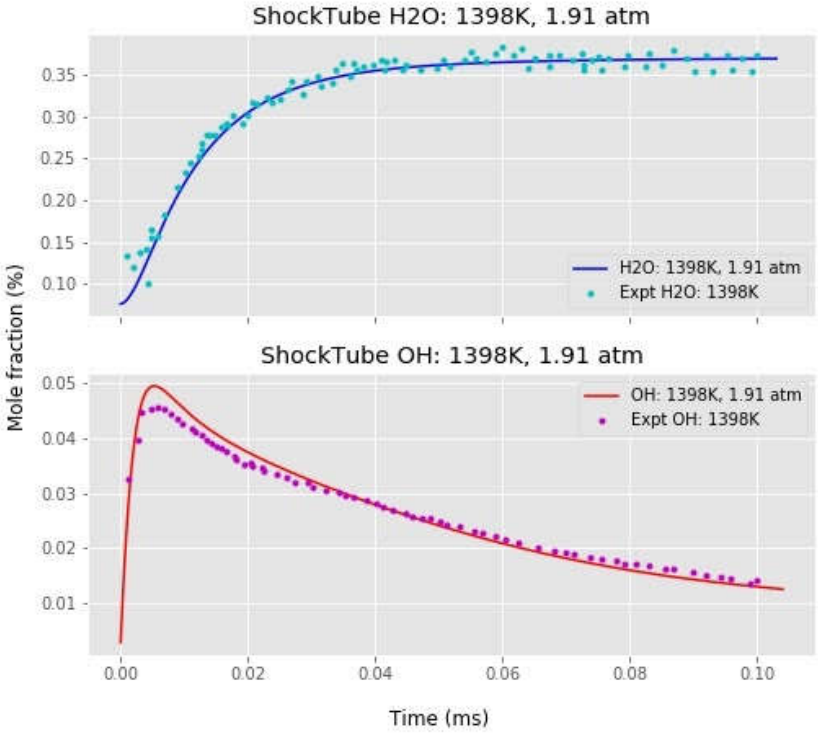
Flow Reactor, Shock Tube, Flame Speed simulations

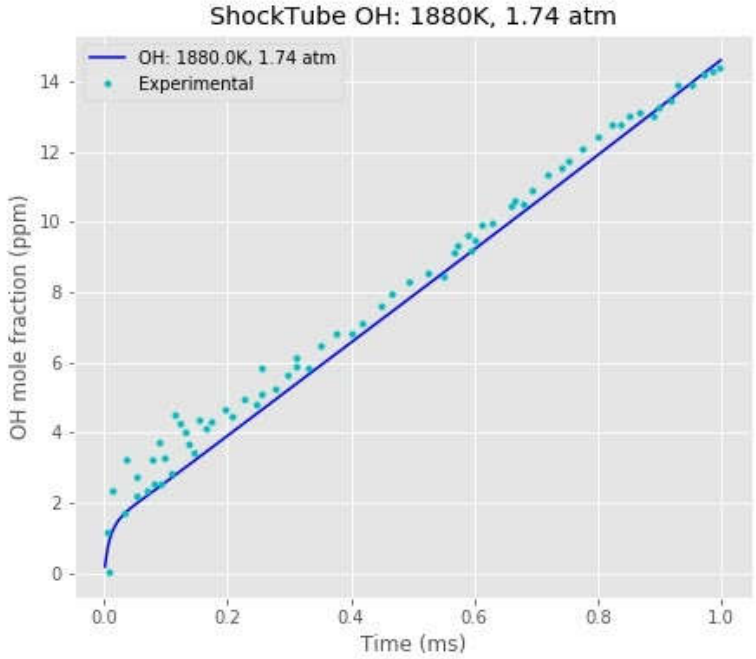
To improve the mechanism and the rate parameters, Cantera simulations were conducted involving flow reactors, shock tubes, and flame speed comparing the outputted model with previous experimental data. Flow reactors and shock tubes are devices in which chemical reactions take place. A key distinction between them is that flow reactors have constant pressure and shock tubes have constant volume. The simulations were conducted employing our mechanism and using Cantera's ReactorNet to make time steps and recording the state of the solution at each time step. For flow reactors and shock tubes, the model graphed time in seconds to mole fraction percentage.

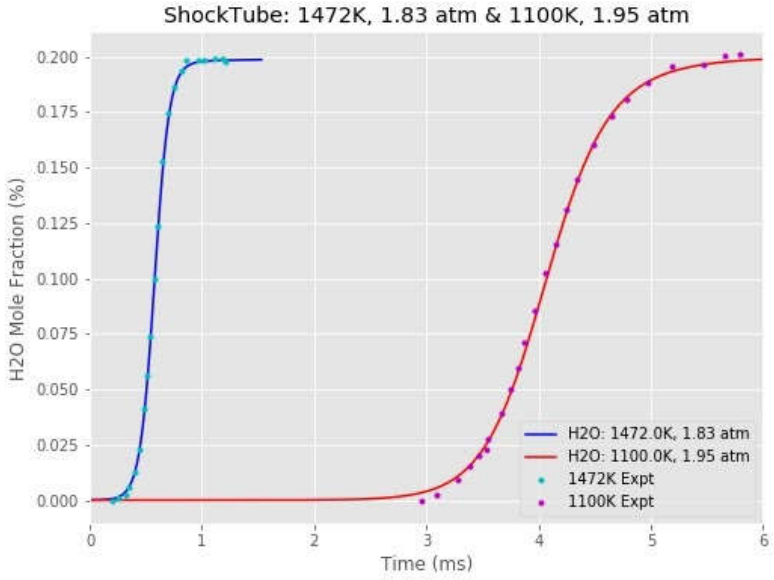
Along with these simulations, a sensitivity analysis was performed, showing the reactions with the greatest effect on the model. At each time step, each reaction's sensitivity was obtained using Cantera. The top five highest sensitivity reactions were determined by calculating the

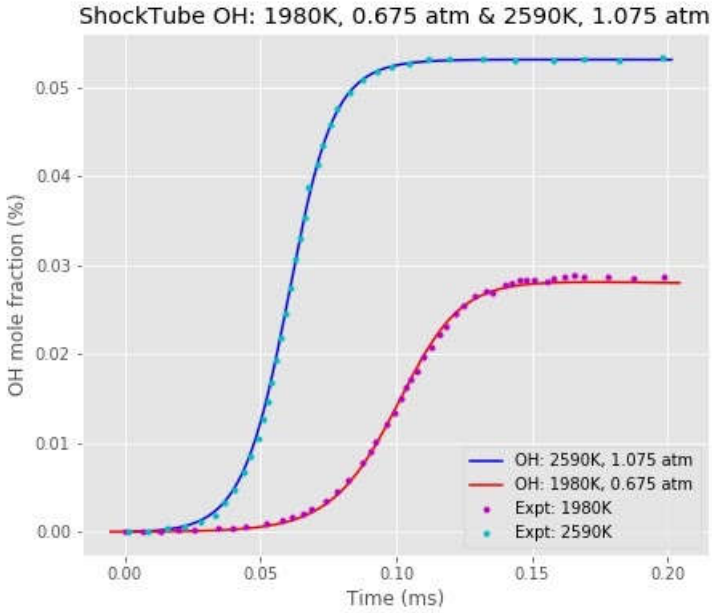
highest average sensitivities within the simulation time. While some simulations resulted in a near-match to experimental data, some simulations required the adjustment of the parameter A (which would proportionally adjust the rate) to the highest sensitivity reaction. Thus, to best fit the model to match experimental data for some simulations, adjustments to the reaction were made and recorded. Repeating this process for all flow reactor and shock tube simulations, a summary of all the changes was compiled. The summary was made to ensure that no adjustment of the parameter went beyond 20%, which held true for all simulations. Because our mechanism did not have to be adjusted by more than 20% to match experimental data, our mechanism was shown to be accurate.

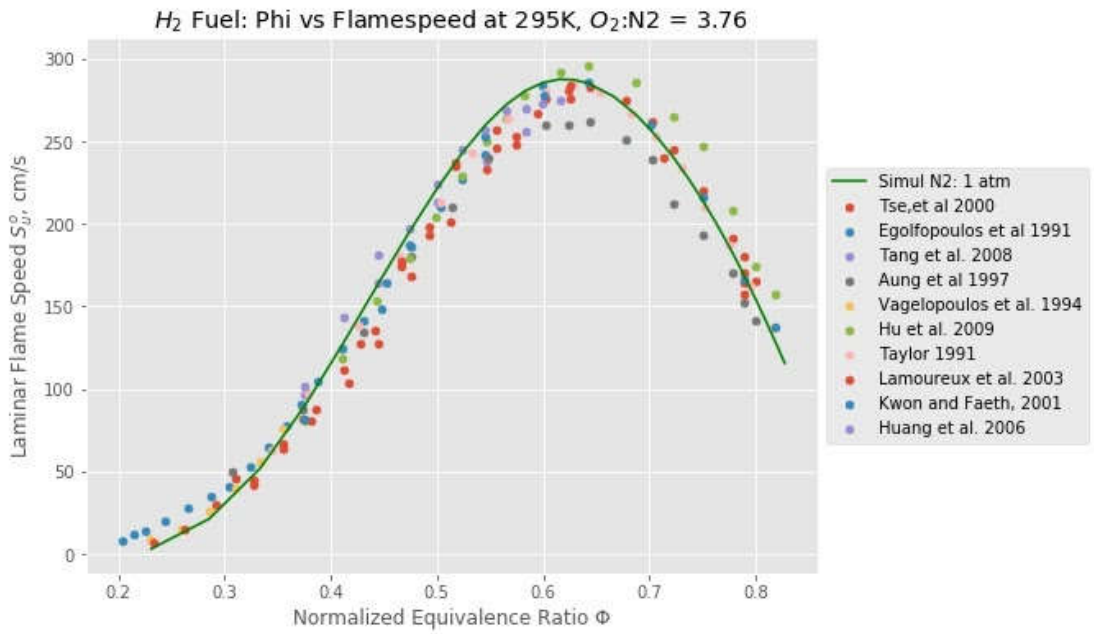
Flame speed simulations measured fuel-air equivalence ratio (φ) to flame speed in cm/s. Flame speed simulations were done with Cantera's FreeFlame and our mechanism's reaction parameters. All simulations used H_2 as the fuel with varying pressures (1, 3, 5, 10, 15, 20 atm) and varying diluents (Nitrogen, Argon, Helium) as well as the diluent to oxygen ratio (3.76, 7, 11.5). The simulation is performed with an initial grid and Jacobian matrix which is continuously refined and evaluated with the transient and steady age criteria as parameters. After numerous time steps, flame speed is calculated. In simulations where experimental data is given, the mass burning rate (MBR) is calculated by multiplying flame speed and density. The results of the flame speed simulations demonstrate the accuracy of our mechanism by closely matching experimental data. The following graphs display the results of the simulations involving flow reactors, shock tubes, and flame speed as well as their respective sensitivity graphs showing the top five most impactful reactions to the simulation.

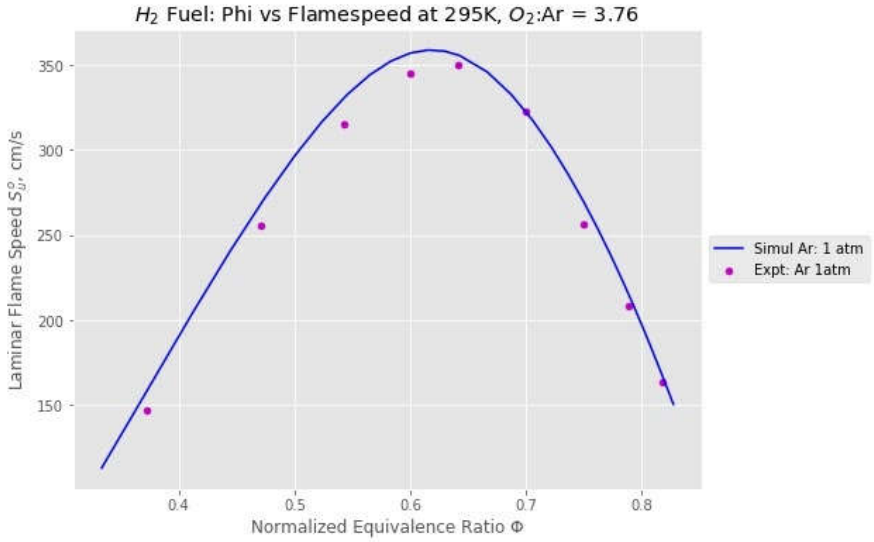

ShockTube H2O: 1398K, 1.91 atm
H2O: 1398K, 1.91 atm
Expt H2O: 1398K
ShockTube OH: 1398K, 1.91 atm
OH: 1398K, 1.91 atm
Expt OH: 1398K
Mole fraction (%)
Time (ms)

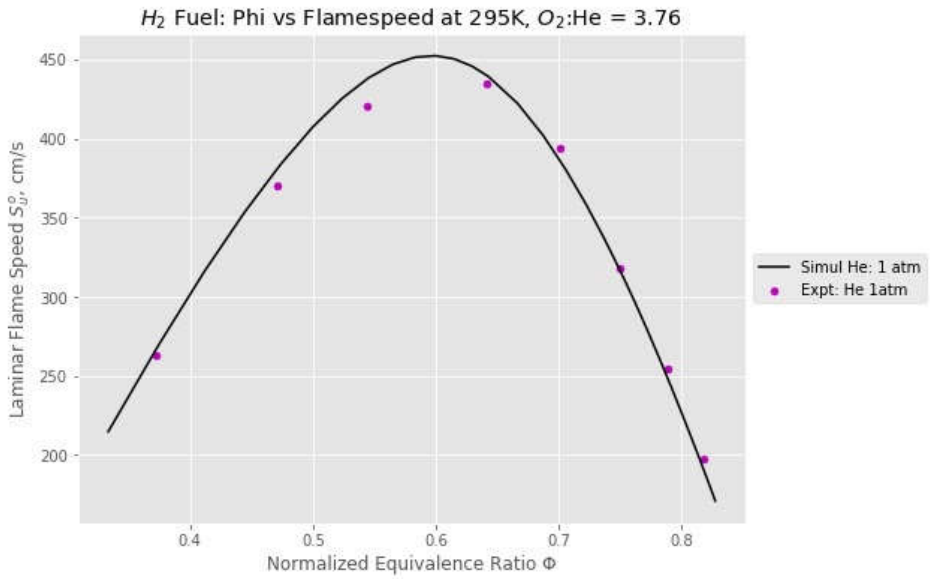

ShockTube OH: 1880K, 1.74 atm
OH: 1880.0K, 1.74 atm
Experimental
OH mole fraction (ppm)
Time (ms)

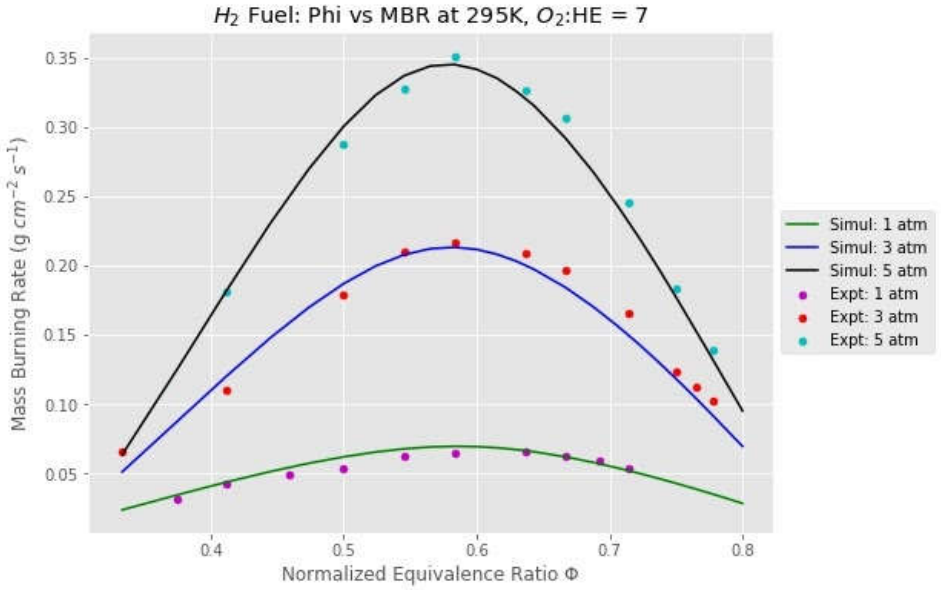

ShockTube: 1472K, 1.83 atm & 1100K, 1.95 atm
H2O Mole Fraction (%)
Time (ms)
H2O: 1472.0K, 1.83 atm
H2O: 1100.0K, 1.95 atm
1472K Expt
1100K Expt


ShockTube OH: 1980K, 0.675 atm & 2590K, 1.075 atm
OH mole fraction (%)
Time (ms)
OH: 2590K, 1.075 atm
OH: 1980K, 0.675 atm
Expt: 1980K
Expt: 2590K


H_2 Fuel: Phi vs Flamespeed at 295K, O_2:N2 = 3.76
Laminar Flame Speed S_u^o, cm/s
Normalized Equivalence Ratio Φ
Simul N2: 1 atm
Tse,et al 2000
Egolfopoulos et al 1991
Tang et al. 2008
Aung et al 1997
Vagelopoulos et al. 1994
Hu et al. 2009
Taylor 1991
Lamoureux et al. 2003
Kwon and Faeth, 2001
Huang et al. 2006


H_2 Fuel: Phi vs Flamespeed at 295K, O_2:Ar = 3.76
Laminar Flame Speed S_u^o, cm/s
Normalized Equivalence Ratio Φ
Simul Ar: 1 atm
Expt: Ar 1atm





Conclusion

Our new mechanism employs the addition of weights when considering the significance of experimental data. Lower relative uncertainty and a wider range of temperature are given more magnitude which results in a more accurate reading of experimental data. Through many simulations testing our mechanism involving flow reactors, shock tubes, and flame speed, our

mechanism has shown its accuracy with its models that closely emulate experimental data. Our mechanism demonstrates that a robuster statistical methodology can more accurately evaluate reaction rate and Arrhenius parameters from past experimental data.

Acknowledgement

My summer research at Princeton University Combustion Lab would not have been possible without the tutelage and opportunity provided by Professor Law. I would also like to thank my mentor Dr. Yang for his invaluable advice and for guiding my research this summer. Because of this opportunity, I have developed a deep passion for research and science as I have learned how to wield computer science as a tool to apply onto scientific research.