In this paper we’ll look at NO reactions by reproducing a classic calculation that is widely used, then doing some further analysis.

Consider the paper by Marteney (link on the class website). Look at Figure 7 in the paper, which is reproduced in our class text.

(1)

In the original work from 1970, Marteney used a very reduced hydrocarbon/air combustion mechanism (15 reactions) to simulate nitric oxide production in simple flames. Use the ZeroD code to redo this calculation using modern chemical mechanisms. Use GRI 3.0, which is included in the ZeroD zip file. Select appropriate conditions to replicate the simulation. NOTE: Ignore the caption in the class textbook, and focus on that in the text of the Marteney paper. Run the calculation, then compare your results with the figure below. Select plotting parameters so that you can resolve the flame zone at the same temporal precision as the figure. Discuss possible sources of any discrepancies. You’re going to have to use non-standard procedures to get a comparable plot. You’ll find that the ignition time delay is much longer than what is suggested in the plot. To get a similar plot, I’d suggest finding the time (τ) at which a couple mole fractions match the values shown at 10⁻⁵ s, then reset your t = 0 such that τ = 10⁻⁵ sec. To keep output reasonable, you may have to stop your calculation, and restart it with a new output step, starting with the ending composition and thermodynamic parameters as the previous run. Or you might be able to brute force it with a 10⁻⁷ s output step.

(2)

Look at the relative contributions to NO production from the various routes for times greater than 10⁻⁵ s. First, use the X_NO data from your plot of your simulation and overall molar density from the calculation to estimate molar production rate of NO in moles/cm³/s. Plot this as a function of time for 10⁻⁵ < t < 10⁻².

(3)
Plot the forward reaction rates in moles/cm$^3$/s for each of the reactions below, using the rate constants in the mechanism file and the concentrations from your simulation. Only do the forward rates, not the backward rates.

\begin{align*}
N_2 + OH &\rightarrow NH + NO \\
N_2 + O &\rightarrow N + NO \\
N + O_2 &\rightarrow NO + O \\
NNH + O &\rightarrow NH + NO \\
C + N_2 &\rightarrow CN + N \\
CH + N_2 &\rightarrow HCN + N \\
CH_2 + N_2 &\rightarrow HCN + NH \\
CH_2(S) + N_2 &\rightarrow NH + HCN
\end{align*}

Discuss the results that you find in terms of the different mechanisms (thermal, prompt, NNH) that contribute to NO formation. This is just a quick-look at the NO kinetics. What other things could you do with your simulation data to better isolate and quantify the relative roles of each mechanism?

Simplification: For the first two reactions, only the reverse rate is given in GRI. Use these approximations (if you like) to avoid having to get the equilibrium constant.

\[ \ln [k] = b_0 + b_1 \cdot T + b_2 \cdot T^2 \quad \text{(T in Kelvin)} \quad k \text{ in cm}^3/\text{mol-s} \]

For $N_2 + OH$:
\begin{align*}
b_0 &= -30.7 \\
b_1 &= 0.028287 \\
b_2 &= -4.1784 \times 10^{-6}
\end{align*}

For $N_2 + O$:
\begin{align*}
b_0 &= -22.716 \\
b_1 &= 0.02557 \\
b_2 &= -3.81463 \times 10^{-6}
\end{align*}