

Exercise 5 - Prediction of NO concentration at varying equivalence ratio

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1. Introduction & Problem

Nitrogen oxides (NO_x), comprising nitric oxide (NO) and nitrogen dioxide (NO_2), are gases produced by natural sources, vehicles, and fuel-burning processes. While NO is colorless, it oxidizes in the atmosphere to form NO_2 , an odorous, corrosive gas that contributes to photochemical smog and poses significant health and environmental risks. High NO_2 levels can damage the respiratory system, worsen asthma, impair senses, and harm vegetation and materials. Air quality standards from Queensland's government were set to a limit for NO_2 to 0.08 ppm over 1 hour and 0.015 ppm annually.

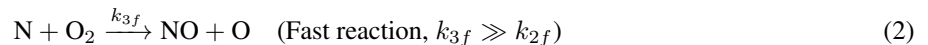
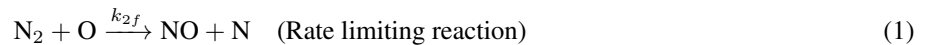
In hydrocarbon combustion, such as methane-air systems, NO formation is highly temperature-dependent and varies with operating conditions like the equivalence ratio (φ). So the interest to study the equivalence ratio effects on NO is of great importance to reduce pollution in the atmosphere. NO can also be produced by nitrogen bounded fuels where the present nitrogen gets oxidized to NO and flame generated NO which only occurs in the flame front due to intermediate combustion species.

2. Theory and Method

2.1 Assumptions

For this assignment, we assume the following to simplify the calculations:

- First we assume that NO is formed considering simple Zeldovich Mechanism (see equations 1 and 2).
Zeldovich or thermal mechanism for the formation of NO from atmospheric N_2 :



- $[\text{N}]$ is assumed to be in Quasi Steady State (QSSA). QSSA is a state where the change in certain species concentrations is considered negligible compared to the overall reaction rate.
- O_2 and 2O are assumed to be in equilibrium (applicable for high temperature system) (see equation 3):



- Reverse reaction rates in Zeldovich Mechanism are negligible as compared to forward reaction rates. Thus we will only calculate the forward reaction rate (k_{2f} and k_{3f}) and will ignore the backwards reaction rate (k_{2r} and k_{3r}).

We will also assume that the equivalence ratio (φ) varies between 0.6 to 2. The initial reactant temperature is 298 K and assume constant pressure of 101325 Pa. The initial mole fractions for nitrogen (X_{N_2}) is 0.79 and for oxygen (X_{O_2}) is 0.21. The initial reactant temperature is 298 K and the residence time (t) for the reaction is 5 ms.

2.2 Calculations

In order to calculate the nitrogen oxide formation, we need the setup of the reaction rate and formation per time unit. From the global reaction of nitrogen oxide formation (equation 4), we can get the rate law for the global reaction, see equation 5.



$$\frac{d[NO]}{dt} = k_G [N_2]^m [O_2]^n \quad (5)$$

Zeldovich mechanism, which explains the thermal formation of NO during high-temperature combustion. It involves two main reactions: nitrogen (N_2) reacts with atomic oxygen (O) to form nitric oxide (NO) and nitrogen atoms (N), followed by the rapid reaction of N with molecular oxygen (O_2) to form more NO and O. The first step is the rate-determining reaction, due to the second reaction occurring much faster ($k_{3f} \gg k_{2f}$). From this reaction we can get the reaction rate for the formation of NO and N, see equations 6 and 7.

$$\frac{d[NO]}{dt} = k_{2f} [N_2] [O] + k_{3f} [N] [O_2] \quad (6)$$

$$\frac{d[N]}{dt} = k_{2f} [N_2] [O] - k_{3f} [N] [O_2] \quad (7)$$

Where the reaction rate coefficient can be calculated from equations 8 and 9:

$$k_{2f} = 1.8 \times 10^{14} \exp\left(\frac{-318000}{RT}\right) \frac{\text{cm}^3}{\text{mol} \cdot \text{s}} \quad (8)$$

$$k_{3f} = 9.0 \times 10^9 \exp\left(\frac{-27000}{RT}\right) \text{cm}^3/(\text{mol} \cdot \text{s}) \quad (9)$$

Nitrogen can be assumed to be in a QSSA state as its reaction is almost instantaneous and is consumed as fast as it is produced. From the QSSA assumption, we can derive equation 10 which with substitution in equation 6 will provide equation 11.

$$[N]_{ss} = \frac{k_{2f} [N_2] [O]}{k_{3f} [O_2]} \quad (10)$$

$$\frac{d[NO]}{dt} = 2k_{2f} [N_2] [O] \quad (11)$$

We calculate the concentration of single oxygen through rearranging the standard equilibrium formula based on our previous assumption. That for any reaction $aA + bB \rightleftharpoons cC + dD$ in equilibrium can be written as (equilibrium equation):

$$K_p = \frac{\left(\frac{P_C}{P^0}\right)^c \left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a \left(\frac{P_B}{P^0}\right)^b} \quad (12)$$

And in our case, be rewritten as equation 13 using equation 3 as reference.

$$[O] = [O_2] \left[\frac{K_p P^0}{R_u T} \right]^{1/2} \quad (13)$$

The equilibrium constant can be calculated using the equilibrium equation 14. The theta values are calculated from $(\theta = T/1000)$ and the alpha values are, $a_1 = 6.434$, $a_2 = -0.2755$, $a_3 = 0.02396$, $a_4 = -0.111 \times 10^{-2}$, $a_5 = 0.8258$, $a_6 = -25.80$

$$\log_{10} K_p = a_1 + a_2 \theta + a_3 \theta^2 + a_4 \theta^3 + a_5 \ln(\theta) + \frac{a_6}{\theta} \quad (14)$$

Substituting equation 13 in equation 11 will give equation 15.

$$\frac{d[NO]}{dt} = 2k_{2f} \left(\frac{K_p P^0}{R_u T} \right)^{1/2} [N_2][O_2]^{1/2} \quad (15)$$

If we take into account the average time the reactants spend in the high-temperature combustion zone where the reaction takes place, we get the final equation to calculate the concentration of nitrogen oxide, see equation 16.

$$[NO] = \frac{d[NO]}{dt} \times \text{residence time} \quad (16)$$

Comparing the rate of formation reaction for nitrogen oxide (eq 15) with the rate law for the global reaction (eq 5), we can get the values for the overall reaction coefficient K_G through equation 17 and the exponential values $m = 1$ and $n = 1/2$ for the rate law for the global reaction.

$$k_G = 2k_{2f} \left(\frac{K_p P^0}{R_u T} \right)^{1/2}, m = 1 \text{ and } n = 1/2 \quad (17)$$

3. Results

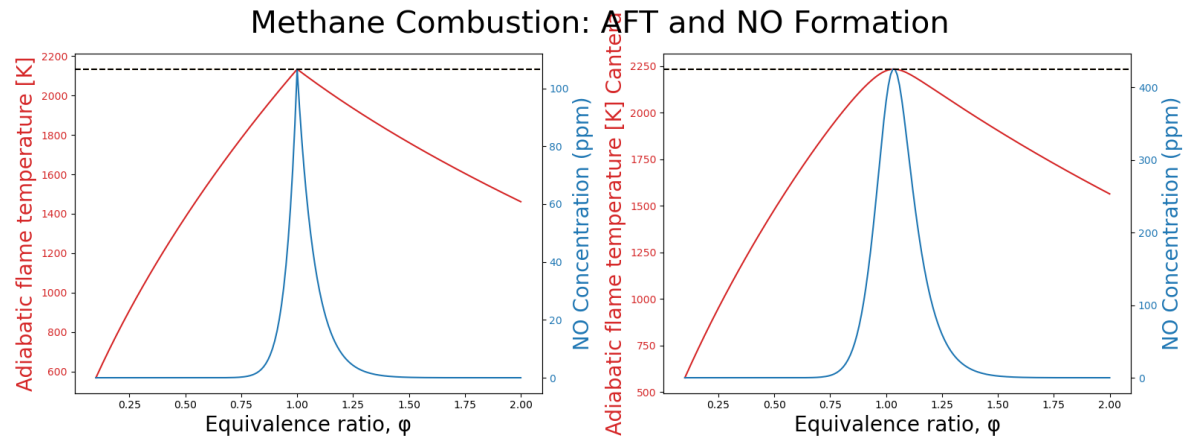


Figure 1: The red lines represent the adiabatic flame temperature in kelvin calculated from the previous task and the blue lines represent the concentration of NO in parts per million against the equivalence ratio. The left figure shows the calculations made through python and the right figure shows the values calculated with the Cantera software.

Table 1: Maximum Values and Corresponding Equivalence Ratios

Parameter	Max Value	at $\phi =$
Max temp for Python (K)	2134.08	1.000
Max temp for Cantera (K)	2232.72	1.030
Max NO ppm for Python	106.60	1.000
Max NO ppm for Cantera	425.16	1.030

4. Discussion and Conclusion

From figure 1 we see that the NO is mainly formed when the equivalence ratio φ is between 0.8-1.30, where the AFT values differ between roughly 1850K and 1900K for python calculations. With a maximum at the same φ value as the maximum AFT temp.

This is expected as our calculations are based on the Zeldovich mechanism which is founded on the dissociation of N_2 in air at temperatures beyond 1850K. To achieve this temperature, there needs to be an optimal balance of oxygen and fuel present. Low φ values (lean conditions) provide excess oxygen but insufficient fuel, resulting in lower combustion temperatures due to the heat sink effect of excess air and incomplete fuel utilization. Conversely, high φ values (rich conditions) provide excess fuel but insufficient oxygen for complete combustion, which reduces flame temperatures as more fuel gets heated up without fully reacting to release all available chemical energy. The optimal φ range of 0.8-1.3 achieves the necessary high temperatures ($>1850K$) and provides sufficient oxygen atoms for the Zeldovich mechanism reactions, with peak NO formation occurring near stoichiometric conditions where combustion efficiency and temperature are maximized.

The difference in NO concentration between Cantera and python is likely due to the calculations steps and chemical reactions that differ between the two methods. Python's calculation steps are described above under Calculation while Cantera's steps are far more sophisticated and detailed. We only take into consideration the Zeldovich mechanism for the NO formation while cantera also takes into account several other present elementary reactions and intermediate pathways.

So to summarize, the formation rate of nitric acids is directly related to the equivalence ratio through the different adiabatic flame temperatures generated through the methane-air combustion. We can also conclude that φ affects the formation of nitric acids in other ways than just Zeldovich mechanism from comparing the values between python and Cantera, where cantera has almost four times higher concentration of nitric acids than the python calculations.