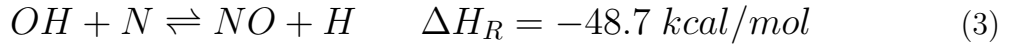
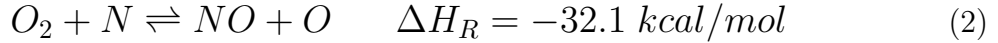
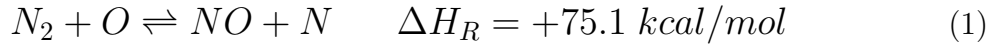


NO Mechanism

1 Zeldovich Mechanism

1.1 Overview

Zeldovich mechanism is also called thermal NO mechanism. It describes the formation of nitrogen oxides (NOx) in combustion processes, particularly those that occur at high temperatures. The reactions include:



1.2 Steady State Assumption

It is important to know any of these reactions much slower or faster than others, therefore we need to know the characteristic time of the reaction. Take a bimolecular reaction as an example:



Then, we define characteristic time by reaction rate and change in reactant concentration:

$$\tau_{chem} = \frac{[N] - [N]_0}{d[N]/dt} \quad (5)$$

$$\frac{d[N]}{dt} = -k_{2f}[O_2][N] \quad (6)$$

Assume **fractional** $[O_2]$ change much less than for $[N]$ and little $[N]$ initially:

$$\tau_{chem} = \frac{[N] - 0}{k_{2f}[O_2]_0[N]} = \frac{1}{k_{2f}[O_2]_0} \quad (7)$$

We can observe that characteristic time depends on rate constant and initial species concentration.

Now we continue to analyze the net production rate:

$$\frac{d[NO]}{dt} = k_{1f}[N_2][O] - k_{1r}[NO][N] + k_{2f}[O][N] - k_{2r}[NO][O] \quad (8)$$

$$\frac{d[N]}{dt} = k_{1f}[N_2][O] - k_{1r}[NO][N] - k_{2f}[O][N] + k_{2r}[NO][O] \quad (9)$$

Now we introduce the **steady state assumption** to solve the ODEs. This assumption only applies to specific species not reactions. It usually associates with condition where species concentration determined by instantaneous balance between formation and destruction rates.

Assume $[N]$ in steady state because $[N]$ is destroyed almost immediately as it is created. Therefore:

$$0 = k_{1f}[N_2][O] - k_{1r}[NO][N] - k_{2f}[O][N] + k_{2r}[NO][O] \quad (10)$$

$$k_{1f}[N_2][O] - k_{1r}[NO][N] = k_{2f}[O][N] - k_{2r}[NO][O] \quad (11)$$

$$[N]_{ss} = \frac{k_{1f}[N_2][O] + k_{2r}[NO][O]}{k_{1r}[NO] + k_{2f}[O_2]} \quad (12)$$

Simplified NO Rate

- Use assumptions/definitions in NO rate equation

$$\begin{aligned} \frac{d[NO]}{dt} &= \underbrace{k_{1f}[N_2][O] - k_{1r}[NO][N]}_{\text{Formation} - \text{Destruction}} + \underbrace{k_{2f}[O][N] - k_{2r}[NO][O]}_{\text{Formation} - \text{Destruction}} \\ \frac{d[NO]}{dt} &= 2(RR_1 - k_{1r}[NO][N]) \quad [N]_{ss} = \frac{RR_1 + RR_2}{k_{1r}[NO] + k_{2f}[O_2]} \\ &= 2RR_1 \left(1 - \frac{1 + RR_2/RR_1}{1 + k_{2f}[O_2]/k_{1r}[NO]} \right) \\ &\quad \left\{ \begin{aligned} \frac{k_{2f}[O_2]}{k_{1r}} &= \frac{k_{2r}[NO]^2}{k_{1f}[N_2]} \quad \leftarrow \\ \frac{k_{1f}}{k_{1r}} &= K_{p1} = \frac{[NO]^*[N]^*}{[N_2][O]} \\ \frac{k_{2f}}{k_{2r}} &= K_{p2} = \frac{[NO]^*[O]}{[O_2][N]^*} \end{aligned} \right. \end{aligned}$$

$[NO]^*$ is concentration that would occur if NO in partial equilibrium with N_2, O_2

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Simplified NO Rate (con't)

$$\begin{aligned}\frac{d[NO]}{dt} &= 2RR_1 \left(1 - \frac{1 + RR_2/RR_1}{1 + k_{2f}[O_2]/k_{1r}[NO]} \right) \\ &= 2RR_1 \left(1 - \frac{1 + RR_2/RR_1}{1 + \left\{ [NO]^*/[NO] \right\}^2 \left\{ k_{2r}[NO]/k_{1f}[N_2] \right\}} \right) \\ &= 2RR_1 \left(1 - \frac{1 + RR_2/RR_1}{1 + \left\{ [NO]^*/[NO] \right\}^2 \left\{ RR_2/RR_1 \right\}} \right)\end{aligned}$$

$$\alpha \equiv [NO]/[NO]^* \quad RR'_2 \equiv k_{2r}[NO]^*[O] \quad RR_1, RR'_2, [NO]^* = f(T, [N_2], [O_2])$$

$$\frac{d\alpha}{dt} = \frac{1}{[NO]^*} \frac{d[NO]}{dt} = \frac{2RR_1}{[NO]^*} \left(\frac{1 - \alpha^2}{1 + \alpha RR_1/RR'_2} \right) \quad \begin{array}{l} \text{okay for hot air,} \\ \text{lean combustion;} \\ \text{[O] partial equil?} \end{array}$$

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Simplified NO Formation Result

- Solution for
 - $T, [N_2], [O_2]$ constant
 - $[NO]_0 = 0$

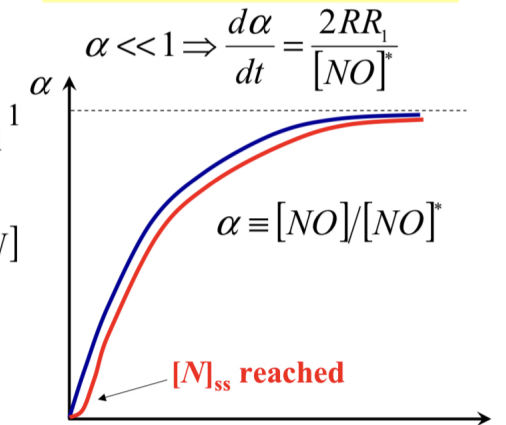
$$\frac{d\alpha}{dt} = \frac{2RR_1}{[NO]^*} \left(\frac{1 - \alpha^2}{1 + \alpha RR_1/RR'_2} \right)$$

- Maximum relative change at $t=0$

- not true; time required to reach $[N]_{ss}$

$$\frac{d[NO]}{dt} = RR_1 + k_{2f}[O_2][N]$$

- Asymptotes to equilibrium NO
 - $d\alpha/dt = 0$ @ $\alpha = 1$



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1.3 Time Scale

In the previous section, using the rate expression we can keep calculating the time constant. For the NO formation reactions:



Based on simulation result:

	1000 K	1500 K	2000 K
τ_{If}	$3 \times 10^7 \text{ s}$	100 s	0.2 s
τ_{2f}	$2 \mu\text{s}$	$0.5 \mu\text{s}$	$0.2 \mu\text{s}$

Figure 1: Time Constant.

We can observe that the formation of NO from Zeldovich will be relatively slow except at very high temperatures.

1.4 Application Condition

1. Dominates in high T ($> 1800\text{K}$), lean environment
2. Requires long residence time (usually in postflame)

2 Intermediate N_2O Mechanism

2.1 Reactions

In this mechanism, N_2 converted to N_2O then NO :



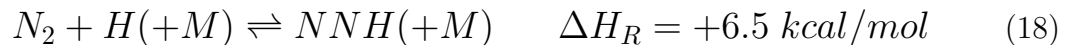
2.2 Application Condition

1. Important in low T, fuel lean systems

3 NNH Mechanism

3.1 Reactions

NO can also be produced via NNH intermediate:



3.2 Application Condition

1. For $T > 2200K$, important for stoichiometric and rich, low residence time systems.
2. For $T < 1900K$, most impact near stoichiometric.

4 Fenimore/Prompt Mechanism

4.1 Reactions

In the previous three mechanisms, NO produced via conversion from attack on N_2/O_2 via radicals containing N, O, H nuclei. However, NO can also be produced in hydrocarbon combustion via C species.



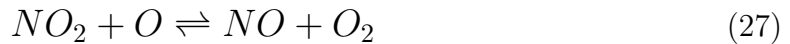
4.2 Application Condition

1. Normally in rich mixtures so there are extra C species for the reactions.

5 NO_2 Mechanism

5.1 Reactions

NO_2 can also be converted to NO during the combustion process.



5.2 Application Condition

1. No NO_2 from hot region
2. NO_2 from NO mixing into low T regions

6 Master Graph

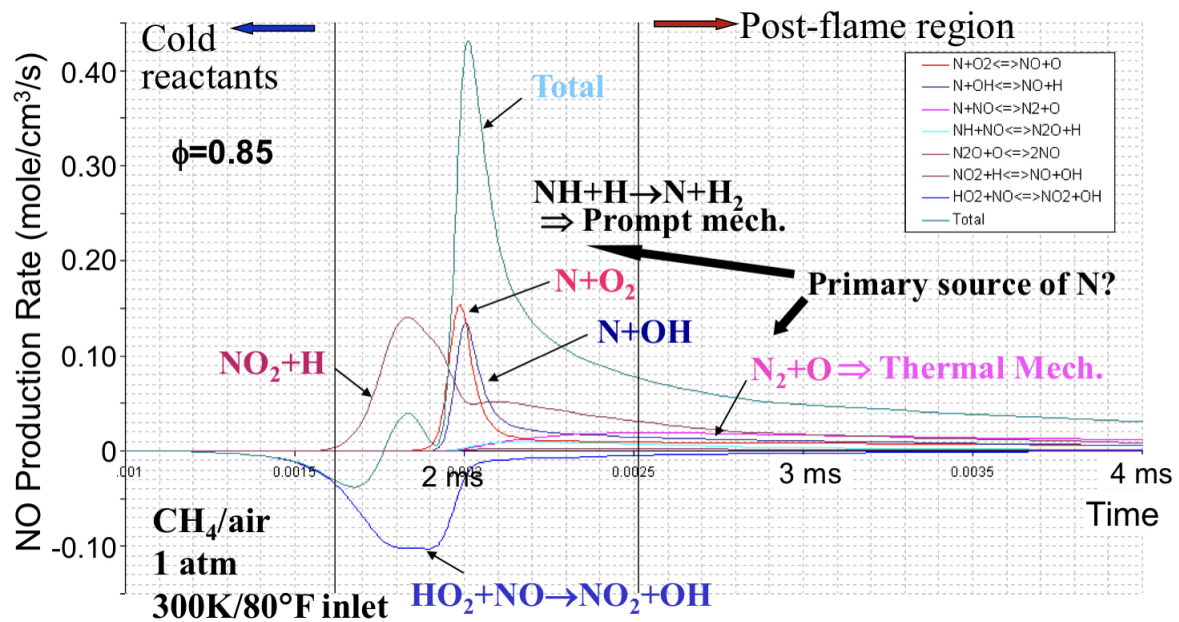


Figure 2: Master Graph.