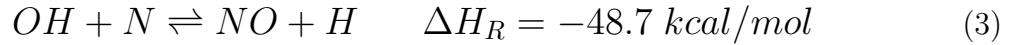
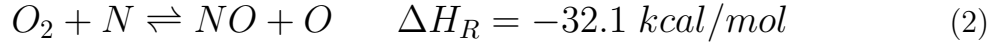
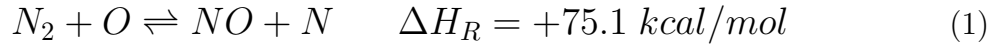


# NOx Mechanism

## 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<sub>2</sub>, O<sub>2</sub>**

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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

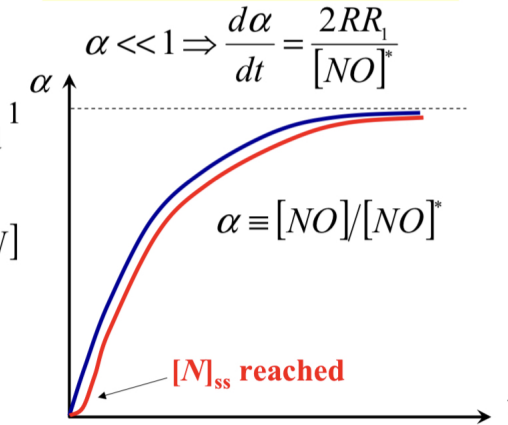
- Solution for
  - $T, [N_2], [O_2]$  constant
  - $[NO]_0 = 0$

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

- 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:

	<b>1000 K</b>	<b>1500 K</b>	<b>2000 K</b>
$\tau_{If}$	$3 \times 10^7$ s	100 s	0.2 s
$\tau_{2f}$	2 $\mu$ s	0.5 $\mu$ s	0.2 $\mu$ 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 ( $> 1800K$ ), 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  $NO$ :



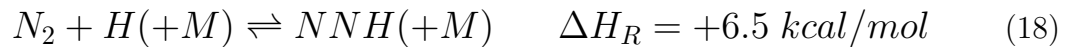
### 2.2 Application Condition

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.



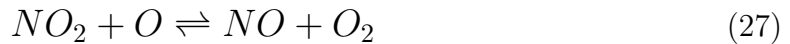
### 4.2 Application Condition

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

## 5 NO<sub>2</sub> Mechanism

### 5.1 Reactions

NO<sub>2</sub> can also be converted to NO during the combustion process.



### 5.2 Application Condition

1. No NO<sub>2</sub> from hot region
2. NO<sub>2</sub> from NO mixing into low T regions

## 6 Master Graph

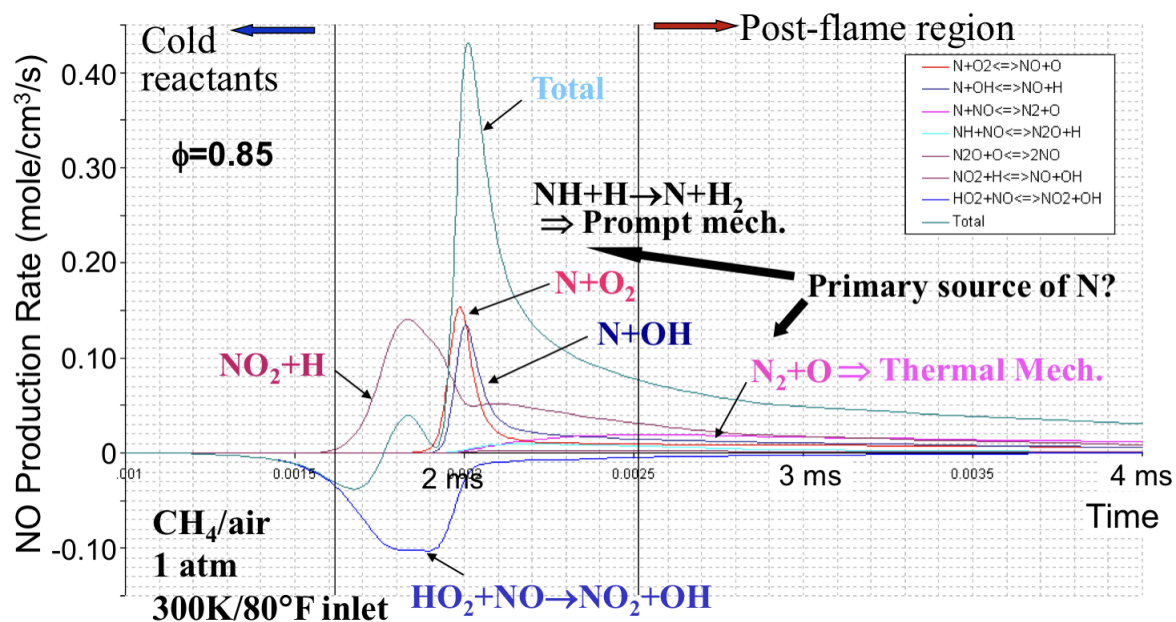


Figure 2: Master Graph.