

## Module 2: Genesis and Mechanism of Formation of Engine Emissions

### Lecture 4: Mechanisms of Nitrogen Oxides Formation

#### POLLUTANT FORMATION

The Lecture Contains:

- ☰ Formation of Nitrogen Oxides
- ☰ Thermal NO
- ☰ Rate Constants for Zeldovich Mechanism
- ☰ Rate of NO Formation
- ☰ NO Formation is a Function of Temperature and  $[O_2]$
- ☰ Prompt NO
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Formation of Nitrogen Oxides

Nitric oxide is the major component of NO<sub>x</sub> emissions from the internal combustion engines. During combustion, three probable sources of NO formation are:

(i)	Thermal NO	:	By oxidation of atmospheric (molecular) nitrogen at high temperatures in the post-flame burned gases.
(ii)	Prompt NO	:	Formed at the flame front within the flame reaction zone.
(iii)	Fuel NO	:	Oxidation of fuel-bound nitrogen at relatively low temperatures

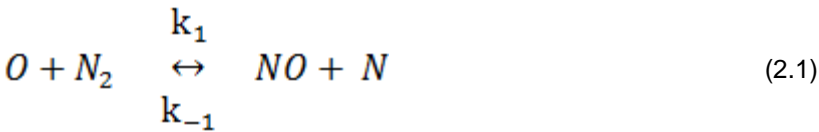
Thermal NO is the dominant source of nitrogen oxides in IC engines.

Thermal NO

NO is formed in the high temperature burned gases behind the flame front. The rate of formation of NO increases exponentially with the burned gas temperature although, it is slower compared to the overall rate of combustion.

Kinetics and Modelling of Thermal NO Formation

The following three reactions commonly referred to as the extended *Zeldovich* mechanism govern the formation of thermal NO



k<sub>1</sub>, k<sub>2</sub> and k<sub>3</sub> are the reaction rate constants for the forward reactions and k<sub>-1</sub>, k<sub>-2</sub> and k<sub>-3</sub> are for the reverse reactions

The original Zeldovich mechanism consisted of the first two reactions (2.1) and (2.2) and the third reaction (2.3) was added by Lavoie. The forward part of the first reaction (2.1) is highly endothermic with high activation energy of about 314 kJ /mol and is a rate determining reaction in NO formation.

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## Rate Constants for Zeldovich Mechanism

The rate constants for the above reactions in units of cm<sup>3</sup>/mol-s and temperature in K are given in Table 2.1

Table 2.1
Reaction rates for NO formation mechanism, cm <sup>3</sup> /mol-s, T in K

Reaction	Forward	Reverse
$O + N_2 \leftrightarrow NO + N$	$k_1 = 1.8 \times 10^{14} \times \exp(-38,370/T)$	$k_{-1} = 3.8 \times 10^{13} \times \exp(-425/T)$
$N + O_2 \leftrightarrow NO + O$	$k_2 = 1.8 \times 10^{10} T \times \exp(-4680/T)$	$k_{-2} = 3.8 \times 10^9 T \times \exp(-20,820/T)$
$N + OH \leftrightarrow NO + H$	$k_3 = 7.1 \times 10^{13} \times \exp(-450/T)$	$k_{-3} = 1.7 \times 10^{14} \times \exp(-24,560/T)$

## Rate of NO Formation

The rate of formation of NO using the three reactions (2.1) to (2.2) can be expressed by the following equation;

$$\frac{d}{dt} [NO] = k_1 [O][N_2] - k_{-1} [NO][N] + k_2 [N][O_2] - k_{-2} [NO][O] + k_3 [N][OH] - k_{-3} [NO][H] \quad (2.4)$$

[ ] denotes the concentration of species in moles/cm<sup>3</sup>.

Steady – state approximation of [N]: Rate of formation and destruction of N is small relative

- (i) to its concentration. Concentration of atomic N is of the order of 10<sup>-8</sup> mole fraction only, which is much smaller compared to the other reacting chemical species.

O, OH, O<sub>2</sub> and O concentrations are governed by chemical equilibrium considerations as the

- (ii) reactions governing concentration of these species are very fast at the combustion temperatures..

Steady state assumption of [N] leads to,

$$\frac{d}{dt} [N] = + k_1 [O][N_2] - k_{-1} [NO][N] - k_2 [N][O_2] + k_{-2} [NO][O] - k_3 [N][OH] + k_{-3} [NO][H] = 0 \quad (2.5)$$

$$[NO][H] = 0$$

Use of Eqs. 2.4 and 2.5 yield the rate of NO formation,

$$\frac{d}{dt} [NO] = 2 \{ k_1 [O][N_2] - k_{-1} [NO][N] \} \quad (2.6)$$

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and from Equation 2.5 steady state concentration of N,

$$[N]_{ss} = \frac{k_1 [O][N_2] + k_{-2} [NO][O] + k_{-3} [NO][H]}{k_{-1} [NO] + k_2 [O_2] + k_3 [OH]} \quad (2.7)$$

From the assumption of equilibration of O, OH, H and O<sub>2</sub>,

$$\frac{[O_2][H]}{[O][OH]} = \left( \frac{[N][O_2]}{[O][NO]} \frac{[NO][H]}{[N][OH]} \right)_{equilibrium} = \frac{k_{-2}}{k_2} \cdot \frac{k_3}{k_{-3}} \quad (2.9)$$

Eliminating [N] and [H] using equations 2.7 and 2.8, the equation 2.6 gives,

$$\frac{d}{dt}[NO] = 2k_1 [O][N_2] \frac{1 - [NO]^2 / \{K[O_2][N_2]\}}{1 + k_{-1}[NO]/(k_2[O_2] + k_3[OH])} \quad (2.10)$$

where  $K = (k_1/k_{-1})(k_2/k_{-2})$  is equilibrium constant for the reaction  $N_2 + O_2 \leftrightarrow 2NO$ .

The NO formation rates may be calculated by Eq. 2.10 using equilibrium concentrations of O, O<sub>2</sub>, OH and N<sub>2</sub>. Most of NO formation takes place in the burned gases behind the flame front after combustion is completed locally. The rate of NO formation being much slower than the combustion rates, the NO formation process may be decoupled from combustion process and rate of formation of NO can be calculated assuming equilibrium concentrations of O, O<sub>2</sub>, OH and N<sub>2</sub>.

By introducing equilibrium assumption in the calculations, the Eq. 2.10 is further simplified by using the following notations;

$$R_1 = k_1 [O]_e [N_2]_e = k_{-1} [NO]_e [N]_e$$

where  $R_1$  is the reaction rate using equilibrium concentrations for the reaction (2.1).

Similarly,

$$R_2 = k_2 [N]_e [O_2]_e = k_{-2} [NO]_e [O]_e, \quad \text{and}$$

$$R_3 = k_3 [N]_e [OH]_e = k_{-3} [NO]_e [H]_e$$

Using the above notations the Eq. 2.10 is simplified to give rate of formation of NO as below,

$$\frac{d}{dt}[\text{NO}] = \frac{2R_1\{1 - ([\text{NO}]/[\text{NO}]_e)^2\}}{(1 + w[\text{NO}]/[\text{NO}]_e)}$$

(2.11)

where  $w = R_1/(R_2 + R_3)$

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NO Formation is a Function of Temperature and  $O_2$ 

From Eq. 2.11 the initial rate of NO formation when  $[NO]/[NO]_e \ll 1$ ;

$$\frac{d}{dt}[NO] = 2 k_1 [O]_e [N_2]_e \quad (2.12)$$

The concentration of atomic oxygen at equilibrium, using reaction  $\frac{1}{2} O_2 \leftrightarrow O$  is given by;

$$[O]_e = \frac{K_{p(O)} [O_2]_e^{1/2}}{(P)^{1/2}} \quad (2.13)$$

Equilibrium constant  $K_{p(O)}$  is

$$K_{p(O)} = 3.6 \times 10^3 \exp\left(\frac{-31090}{T}\right) \quad (2.14)$$

Using value of  $k_1$  from Table 2.2 and, the Eqs. 2.13 and 2.14 the initial rate of NO formation then reduces to

$$\frac{d[NO]}{dt} = \frac{1.3 \times 10^{18}}{P^{1/2}} \exp\left(\frac{-69,460}{T}\right) [O_2]_e^{1/2} [N_2]_e \quad (2.15)$$

Temperature being in exponential term in Eq.2.15, it strongly influences NO formation rates. From Eq. 2.15 it follows that the NO formation is maximized under the conditions of high temperature and high oxygen concentrations. These conditions occur at fuel-air equivalence ratios 5-10% leaner than stoichiometric mixture.

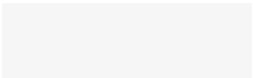
Typical combustion duration is about 1 to 2 ms in SI engines operating close to stoichiometric conditions at 3000 -5000 rpm. NO formation at peak pressure and temperature conditions may reach close to equilibrium [NO] concentrations as illustrated below;

The characteristic time ( $t_{NO}$ ) necessary to reach equilibrium concentration of NO may be approximated as,

$$t_{NO} = \frac{[NO]_e}{d[NO]/dt} \quad (2.16)$$

The mole fraction  $[NO]_e$  can be estimated from the reaction  $O_2 + N_2 \leftrightarrow 2NO$ , as

$$x_{[NO]_e} = \left( K_{NO} x_{[O_2]_e} x_{[N_2]_e} \right)^{1/2} \quad \text{,mole fraction} \quad (2.17)$$



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$K_{NO}$  is given by

$$K_{NO} = 20.3 \times \exp(-21,650 / T)$$

and mole fraction of  $N_2$  at equilibrium,  $x_{[N_2]e} \sim 0.71$

From the above,

$$t_{NO} = \frac{3.38 \times 10^{-16} T \exp(58,635 / T)}{P^{1/2}} \quad (2.18)$$

Time  $t_{NO}$  is in seconds, pressure,  $P$  is in atmospheres and temperature,  $T$  is in K.

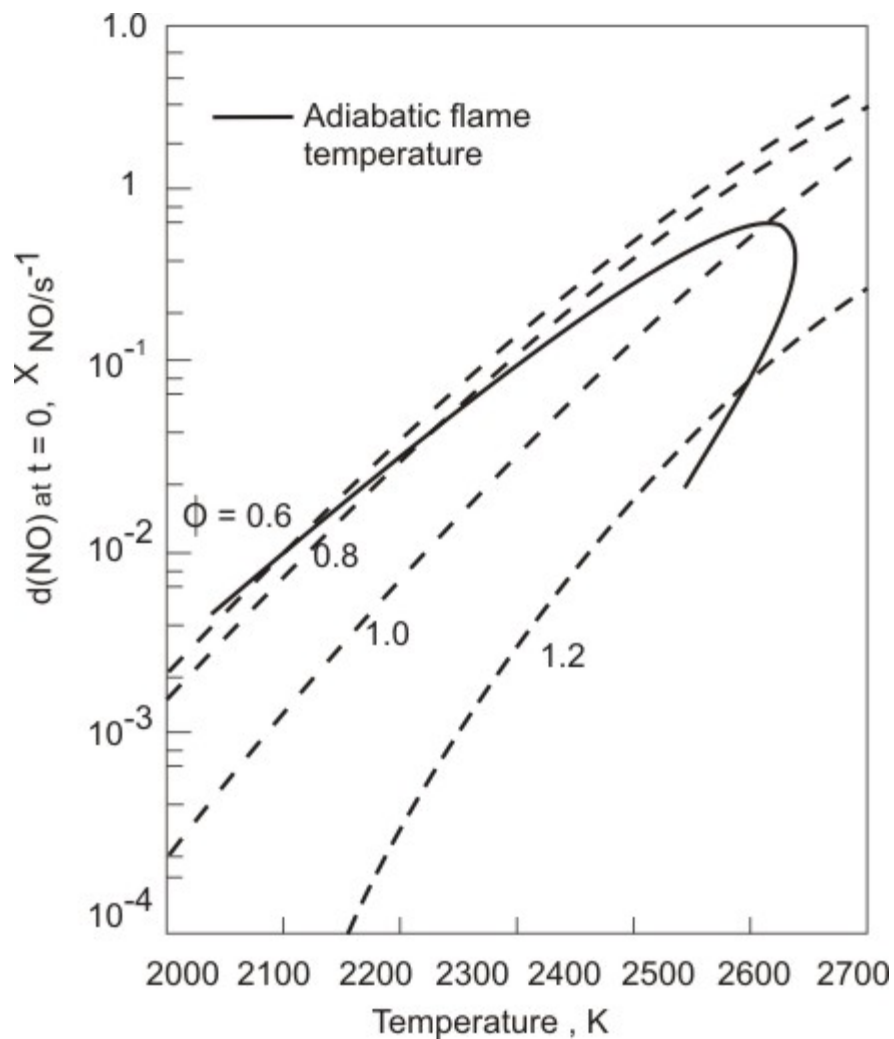


Fig. 2.4 Dependence of initial rate of NO formation on temperature and fuel-air equivalence ratio ( $\phi$ ). The



dashed line shows adiabatic flame temperature line for different values of  $\phi$ . The maximum NO formation rate occurs at slightly leaner than stoichiometric mixture.

Fig. 2.4 shows the initial NO formation rate as a function of temperature for different fuel-air equivalence ratios. For a given value of  $\phi$  NO formation increases with temperature. And as  $\phi$  is reduced more oxygen is available resulting in higher NO formation for a fixed reactant temperature. In the real combustion systems, the burned gas temperature also depends on the value of  $\phi$ . On this figure, the adiabatic flame temperature for a hydrocarbon fuel-air mixture initially at 700 K and combustion at constant pressure at 15 atm for different fuel-air ratios is also shown. The adiabatic constant pressure combustion of a charge element as an acceptable model for an internal combustion engine. The initial NO formation rate is seen to be highest for a mixture slightly leaner than stoichiometric.

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## Example 2.1:

Using the Eq. 2.18 based on initial rate of NO formation estimate whether during typical SI engine combustion the kinetically formed NO could reach the level of equilibrium concentrations

## Solution

For the charge that burns early in the cycle the peak burned gas temperatures of 2700 K or higher could be obtained. At full load maximum cylinder pressure is of the order of 30 – 40 atm. Under real engine conditions, the rate of NO formation changes with time as the temperature and pressure change with time during the cycle and also the NO concentration (Eq. 2.11). However, for an approximate analysis let us assume that the average temperature and pressure of the charge elements burnt early are 2700 K and 35 atm. At  $T = 2700$  K and  $P = 35$  atm for an early burn charge element

$$(t_{NO})_{earlyburn} = \frac{3.38 \times 10^{-16} (2700) \exp(58365 / 2700)}{(35)^{1/2}} = 0.38 \times 10^{-3} s$$

For an engine operating at 4500 rpm, it would take  $10.3^\circ$  CA to reach equal to equilibrium NO concentrations. This time period is well within the typical combustion duration being in the range  $30 - 40^\circ$  CA

For the charge elements burning later in the cycle the temperatures reached may be around 2300 K and pressure may be down to 20 atm. At these conditions,

For a late burn element :

$$(t_{NO})_{lateburn} = \frac{3.38 \times 10^{-16} (2300) \exp(58365 / 2300)}{(20)^{1/2}} = 4.07 \times 10^{-3} s$$

For a late burn element on the other hand it needs about 4.07 ms i.e.,  $110^\circ$  CA which is too long a period in the engine cycle. Due to expansion, the burned gas temperatures would have fallen by then to further low levels of around 1300-1400 K and in the late burn elements the kinetically formed NO would never reach equilibrium concentrations. The NO formation in the late burn elements is frozen at a value higher than that predicted by the equilibrium considerations. This is demonstrated later in this module in Fig. 2.7.

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#### Prompt NO

In the flame reaction zone NO may be formed rapidly. The **prompt** NO is formed in the flame by reaction of intermediate chemical species of CN group with O and OH radicals. The hydrocarbon radicals CH, CH<sub>2</sub>, C, C<sub>2</sub> etc. formed in the flame front react with molecular nitrogen to give intermediate species such as HCN and CN by the reactions (2.19) to (2.21). Large concentrations of HCN near the reaction zone in fuel rich flames have been observed and rapid formation of NO has been seen to be associated with rapid decay of HCN.



The contribution of **prompt** NO in the stoichiometric laminar flames is estimated to be about 5 to 10 percent only. In the engines as the combustion occurs at high pressures, the thickness of flame front is very small (~ 0.1 mm) and the residence time of chemical species in this zone is very short. Moreover, the burned gases produced by the charge elements that burn early during the combustion process are compressed to a much higher temperature than the temperatures attained immediately after combustion. The formation of thermal NO in the burned gases behind the flame front therefore, is much higher compared to any NO formation in the flame front. However, contribution of **prompt** NO may be significant under lean engine operation or engine operation with high dilution such as use of exhaust gas recirculation.

#### Fuel NO

Fuel NO is formed by combustion of fuels with chemically bound nitrogen. The fuel nitrogen produces at first intermediate nitrogen containing compounds and reactive radicals such as HCN, NH<sub>3</sub>, CN, NH etc. These species are subsequently oxidized to NO. Although petroleum crude may contain about 0.6 % nitrogen but gasoline has negligible nitrogen. Diesel fuels have higher nitrogen content than gasoline, but this too is usually less than 0.1% by mass. The fuel nitrogen therefore, does not make significant contribution to NO formation in automotive engines operating on gasoline, diesel, natural gas and alcohols etc.