Topic: Air Pollution Date:

Major Sources of Air Pollution:

Carbon Monoxide: (CO):
Major Sources: Incomplete combustion of carbonaceous matter in automobile engines & defective furnaces, incomplete combustion of agricultural & slash matter, volcanic eruptions, forest fires.
Maximum permissible exposure in ppm during an average period of 8 hrs per day: 50 ppm.

Sulfur Dioxide (SO_2):
Major Sources: Combustion of sulphur-bearing fuels such as coal and oil, volcanic eruptions.
Maximum permissible exposure in ppm: 5ppm.

Nitrogen Oxides (NO, NO_2):
Major Sources: Combustion of fuel, interaction of N_2 and O_2 of the atmosphere at high temperatures.
Maximum permissible exposure in ppm = 5ppm.

H_2S: Major Sources: Biological decay of organic matter, oil refindries.
Maximum permissible exposer: 20 ppm.

Cl_2: Major sources: Industrial units producing paper, plastics, chlorinated hydrocarbons, dyes, chlorinated chemicals etc.
Maximum permissible exposer: 1 ppm

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Hydrocarbons:

Major sources: Combustion of fuel in automobiles, refinaries, anaerobic bacterial decomposition of organic matter, natural gas.

Maximum permissible exposure: 1000ppm.

Chlorofluorocarbons (CFCs):

Major sources: Industrial units manufacturing refrigerants, fire fighting agents, their use as solvents.

Maximum permissible exposure: 1030ppm.

Pesticides:

Major sources: Application of pesticides and their volatilization from soil, water treated surfaces & industrial units producing pesticides.

Particulates:

Major sources: Volcanic eruptions, fly ash, smelting and mining operations, smoke from incomplete combustion, dust from crushers & grinders.

$PbCl_2$, $PbBr_2$:

Major sources: Addition of $Pb(C_2H_5)_4 + C_2H_4Cl_2 + C_2H_4Br_2$ to gasoline to improve its antiknock property.

Carbon Dioxide (CO_2):

Major sources: Combustion of carbonaceous matter, biological decay etc.

Maximum permissible exposure: 5000 ppm.

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Carbon Monoxide (CO):

→ It is a colourless, odourless and tasteless gas.
bp. -192°C

→ 96.5% as heavy as air

→ Insoluble in water.

Reactions by which CO is Generated:

1. Incomplete combustion of fuels.

$$2C + O_2 \longrightarrow 2CO$$

2. Rxn between CO_2 and carbon at elevated temperature.

$$CO_2 + C \longrightarrow 2CO$$

3. Dissociation of CO_2 at high temperatures.

$$CO_2 \rightleftharpoons CO + \frac{1}{2}O_2$$

Sources of CO Pollution:

Sources
- → Natural Processes: Volcanic action, natural gas action, electrical discharge during storms, seed germination
- → Transportation: motor vehicles (59.2%), aircraft (2.4%), railroads (0.1%)
- → Miscellaneous (16.9%): forest fires (7.2%), agricultural burning (8.3%)
- → Industrial processes: mainly iron & steel industries, petroleum and paper industries.

Sinks of CO:

Soil micro-organisms e.g. fungi (Penicillium & Aspergillus)

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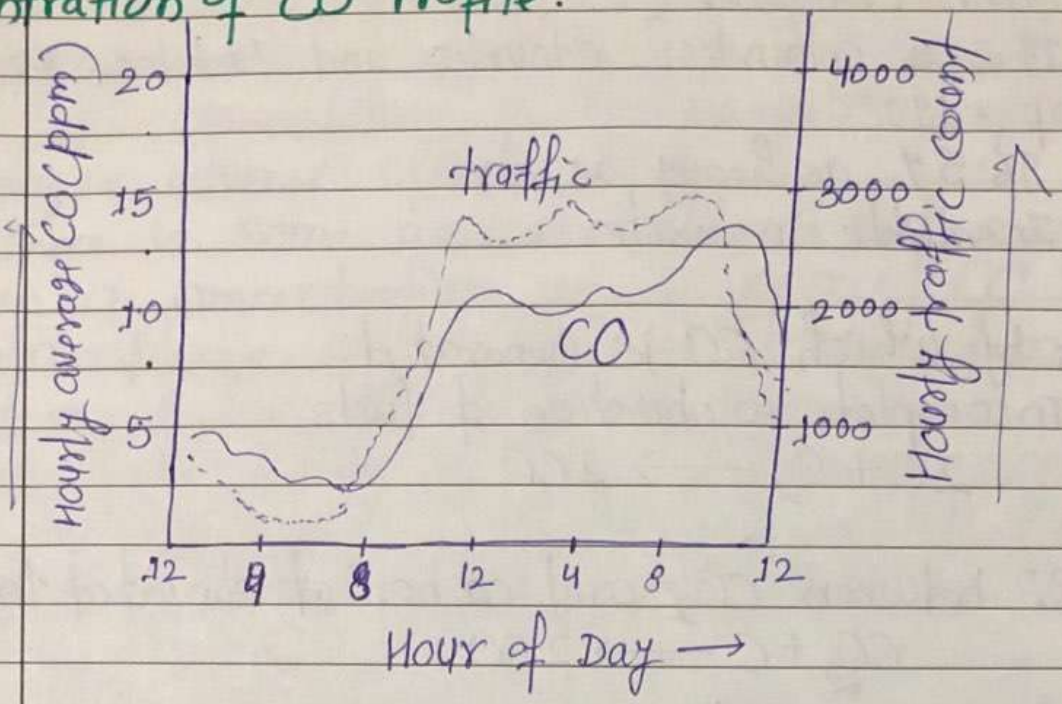
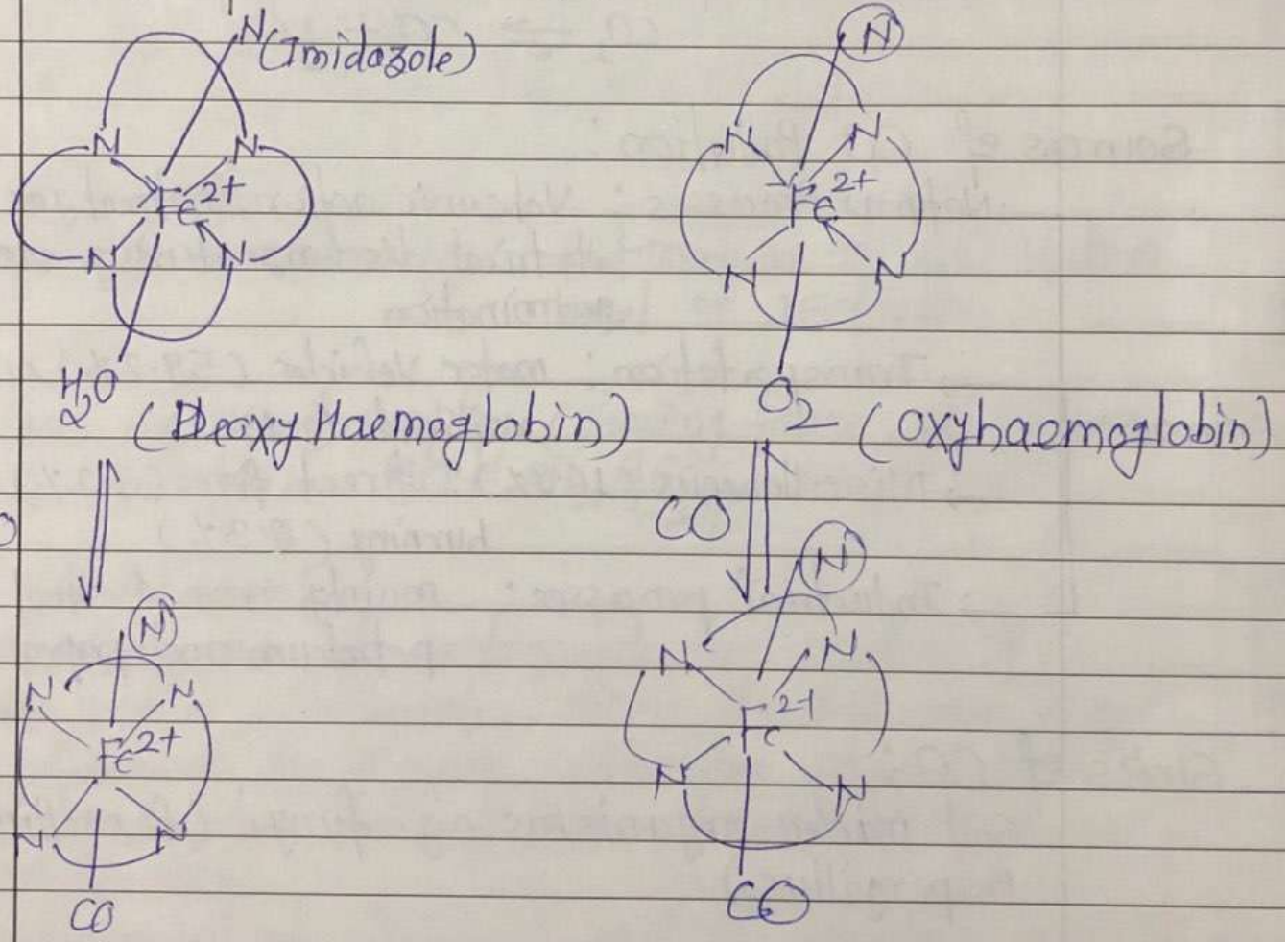
Concentration of CO Profile:



Toxic Effects of Carbon Monoxide:



→ The combination of Hb with CO inhibits its oxygen carrying capacity in the blood, thereby reducing the availability of oxygen for the body cells resulting in anoxia (oxygen starvation).

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→ The maximum permissible concentration of CO in the atmosphere is 50 ppm for an exposure of 8 hrs.
→ If the concentration is higher or the exposure is longer adverse effect start.
→ There is some medical evidence that even as low a concentration as 10 ppm of CO in the atmosphere may produce increased mortality amongst haspitalised heart patients.
→ The higher rate of heart disease in smokers is also beleived to be due to CO which the smoker inhales from the cigarette smoke.

Treatment for CO Poisoning: is to confine the victim in a chamber having oxygen at 2 to 2.5 atm pressure.

$$Hb{\cdot}CO + O_2 \rightleftharpoons HbO_2 + CO$$

Monitoring of CO:

Two methods:
→ By IR spectroscopy: Estimation of CO upto a level of 150 ppm.
→ Gas Chromatography (having flame ionisation detector): $CO + 3H_2 \xrightarrow[\text{catalyst}]{360^\circ C} CH_4 + H_2O$

Control of CO Pollution:

Ⓐ Directive use of automobiles or control of automotive emissions along the following lines.
1. Modification of internal combustion engines to reduce the amounts of pollutants formed during fuel combustion.
2. Development of exhaust system reactors which will complete the combustion process and change potential pollutants into more acceptable materials.

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3. Development of substitute fuels for gasoline, which will yield low concentration of pollutants upon combustion.
4. Development of pollution-free power sources to replace the internal combustion engine.

1. Use of Catalytic Converters:
Helps to eliminate pollutants from exhaust gases in two steps.

(i) Reduction of $(NO)_x$:

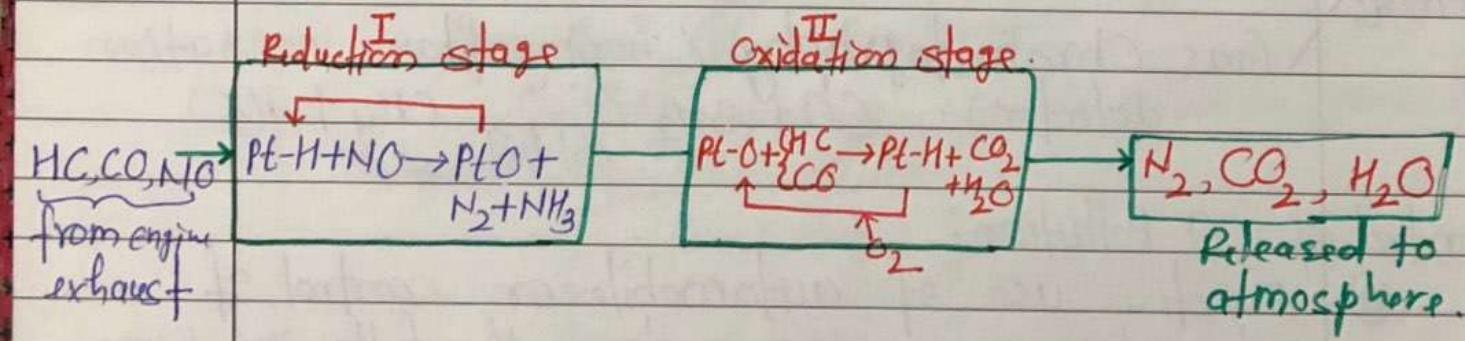
$$NO_x + e^- \xrightarrow[CO,\ RH]{Pt\ Catalyst} N_2 \text{ and } NH_3$$

(ii) Oxidation of HC and CO:

$$CO + \frac{1}{2}O_2 \xrightarrow{Pt} CO_2$$

$$RH + H_2O \longrightarrow CO_2 + H_2O$$

Drawback of catalytic converters:
→ Pt catalyst is poisoned by heavy metals (e.g. Pb) present in gasoline itself.
→ Hence Pb-free gasoline must be used for proper function of catalytic converters.



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Role of TEL [$Pb(C_2H_5)_4$]:

→ To reduce knocking (preignition)

→ Knocking creats small explosions, which decrease the efficiency of the engine.

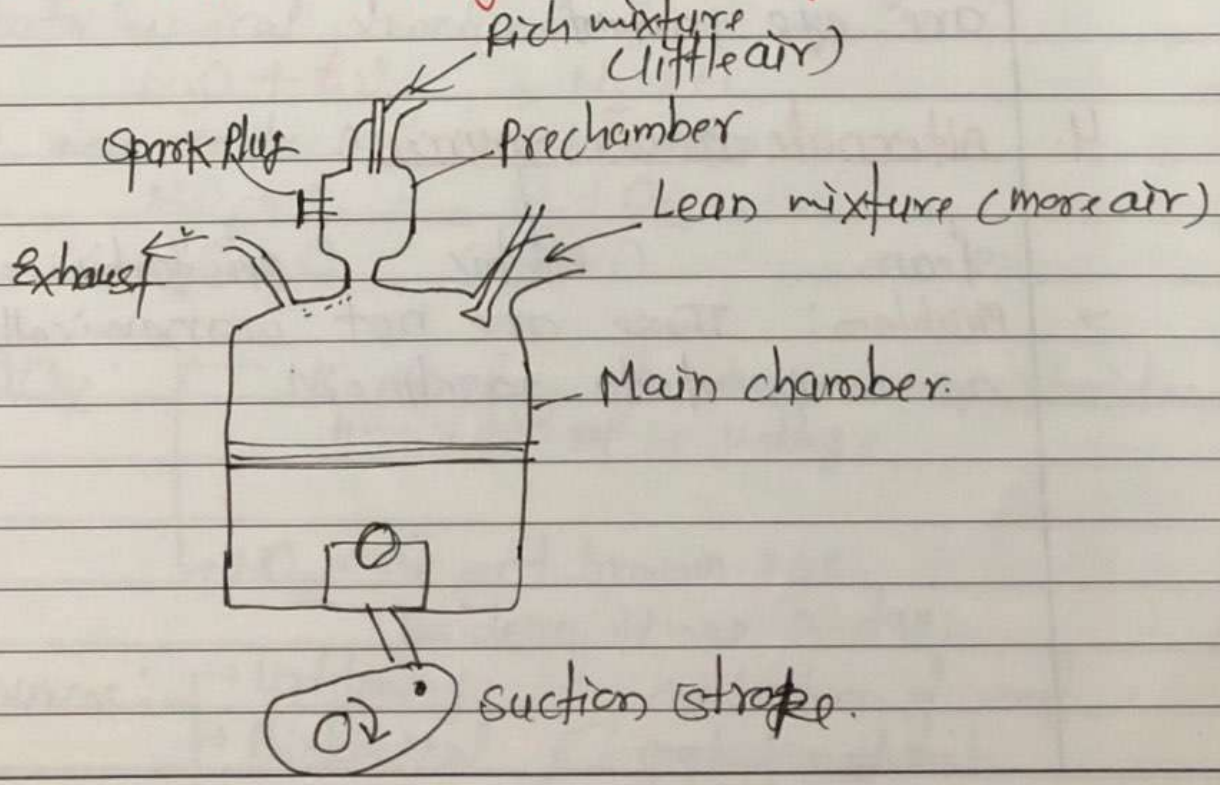
→ $Pb(C_2H_5)_4$ acts as scavenger of free radicals.

$$Pb(C_2H_5)_4 + O_2 \longrightarrow PbO_2\cdot$$
$$PbO_2\cdot + RCH_2\cdot \longrightarrow PbO + RCH_2O\cdot$$
$$RCH_2O\cdot + O_2 \longrightarrow RCHO + HO_2\cdot$$
$$HO_2\cdot + PbO \longrightarrow PbO_2 + OH\cdot$$
$$PbO + OH\cdot \longrightarrow PbO(OH)$$
$$PbO(OH) + OH\cdot \longrightarrow PbO_2 + H_2O$$

→ Gasoline containing $Pb(C_2H_5)_4$ is the major source of Pb pollution in the environment.

→ Pb-free gasoline has come into vogue in USA and in Europe. It is little costlier than leaded gasoline.

2. Catalytic Converters Used by Honda Corporation:



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→ Compared to normal catalytic converters it has extra combustion where a fuel rich mixture is introduced & ignited with spark & this acts as relatively low temperature as a result of which NO_x formation is minimized.

→ The burning mixture is then fed into the larger main chamber where it gets mixed with a lean fuel mixture which contains excess air.

→ The presence of excess air ensures complete combustion of HC and CO but the temperature remains low enough to limit the build up of NO_x.

3. **Substitute fuel for Gasoline:**

Sustitute fuel → CNG, LNG, Alcohols → Pollution free

Problem: Supply and storage.

→ Combustion products of alcohols is aldehydes are eye irritants.

4. **Alternate Power Sources:**

Steam, Electric, Gas turbine engines

→ Problem: These are not economically viable as compared to gasoline.

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Nitrogen oxides (NO_x):

- Nitrous oxide — N_2O
- Nitricoxide — NO
- NO_2
- Nitrate Radical (NO_3^-)
  - → Involved in nighttime chemistry of photochemical smog
  - → In daytime it dissociates.

NO_x = NO + NO_2

N_2O: used as anesthetic (laughing gas)

→ Produced by microbiological processes and is a component of the unpolluted atmosphere at a level of approximately 0.3 ppm.

→ Unreactive gas, probably does not contribute chemical reaction in lower atmosphere.

→ Its concentration decreases rapidly with altitude in the stratosphere owing to the photochemical reaction.

$$N_2O + h\nu \longrightarrow N_2 + O$$

It also reacts with singlet oxygen

$$N_2O + O \longrightarrow N_2 + O_2$$

$$N_2O + O \longrightarrow 2NO$$

NO_x:

- → NO colourless, odourless, average residence time of NO is 4 days
- → NO_2 → Pungent brown gas. Residence time 3 days.

Sources:

- → Lightening
- → Biological
- → Man-made:
  - → combustion of coal.
  - → combustion of oil
  - → Natural gas
  - → gasoline.

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Natural
- ~~Biological~~ → micro organism decomposition of nitrogen fertilizers
- → Biomass burning
- → Lightening
- → Atmospheric oxidation of NH_3

How NO is generated?

Combustion of fuels in engines.

$$N_2 + O_2 \xrightarrow{1210-1800^\circ C} 2NO$$

$$2NO + O_2 \longrightarrow 2NO_2$$

Mechanism of formation of NO:

$$O_2 + M(\text{energized body}) \longrightarrow O + O + M$$

$$N_2 + M \longrightarrow N\cdot + N\cdot + M$$

$N \equiv N$ → Bond dissociation energy = 225 KCal/mol

$O = O$ → 118 KCal/mol

$$N_2 + O \longrightarrow NO + N$$

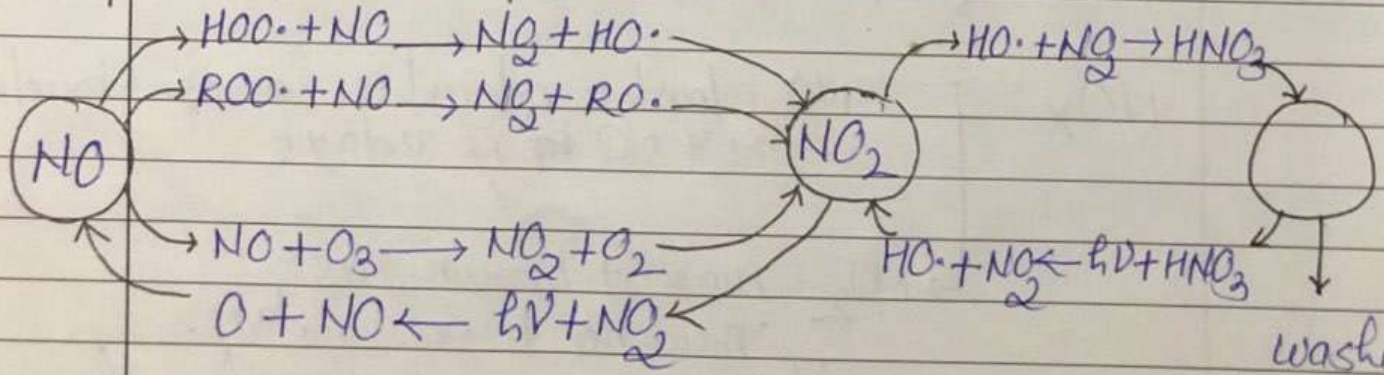
$$N + O_2 \longrightarrow NO + O$$

Net Rx^n: $N_2 + O_2 \longrightarrow 2NO$

$$RH + O \longrightarrow R\cdot + HO\cdot$$

$$N + HO\cdot \longrightarrow NO + H\cdot$$

Atmospheric Reactions of NO_x:



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Atmospheric Reactions of NO_x:

$$NO_2 + h\nu \xrightarrow[398nm]{\text{Below}} NO + O \quad \text{---(1)}$$

Photodissociation

$$NO_2 + h\nu \xrightarrow{\text{Above 430nm}} NO_2^* \quad \text{---(2)}$$

Photo excitation

$$O + O_2 + M \text{ (Third body)} \longrightarrow O_3 + M \quad \text{---(3)}$$

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad \text{---(4)}$$

→ In the night photodissociation is absent, NO_2 predominates over NO.

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad \text{---(5)}$$

The NO_3 product undergoes rapid photodissociation in daytime, but builds up at night.

→ NO_3 plays a role in atmospheric chemical processes at night, including those involved in photochemical smog formation.

$$O + NO_2 \longrightarrow NO + O_2$$

$$O + NO_2 + M \longrightarrow NO_3 + M$$

$$NO_2 + NO_3 \longrightarrow N_2O_5$$

$$NO + NO_3 \longrightarrow 2NO_2$$

$$O + NO + M \longrightarrow NO_2 + M$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

In the stratosphere NO_2 reacts with OH· to produce HNO_3

$$HO\cdot + NO_2 \longrightarrow HNO_3$$

In this region HNO_3 can also be destroyed by OH·

$$HO\cdot + HNO_3 \longrightarrow NO_3 + H_2O$$

or by photochemical reaction.

$$HNO_3 + h\nu \longrightarrow HO\cdot + NO_2$$

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Sinks of NO_x in Environment:

→ HNO_3 is the temporary sink of NO_2 in stratosphere.

$$HNO_3 + h\nu \longrightarrow HO\cdot + NO_2$$

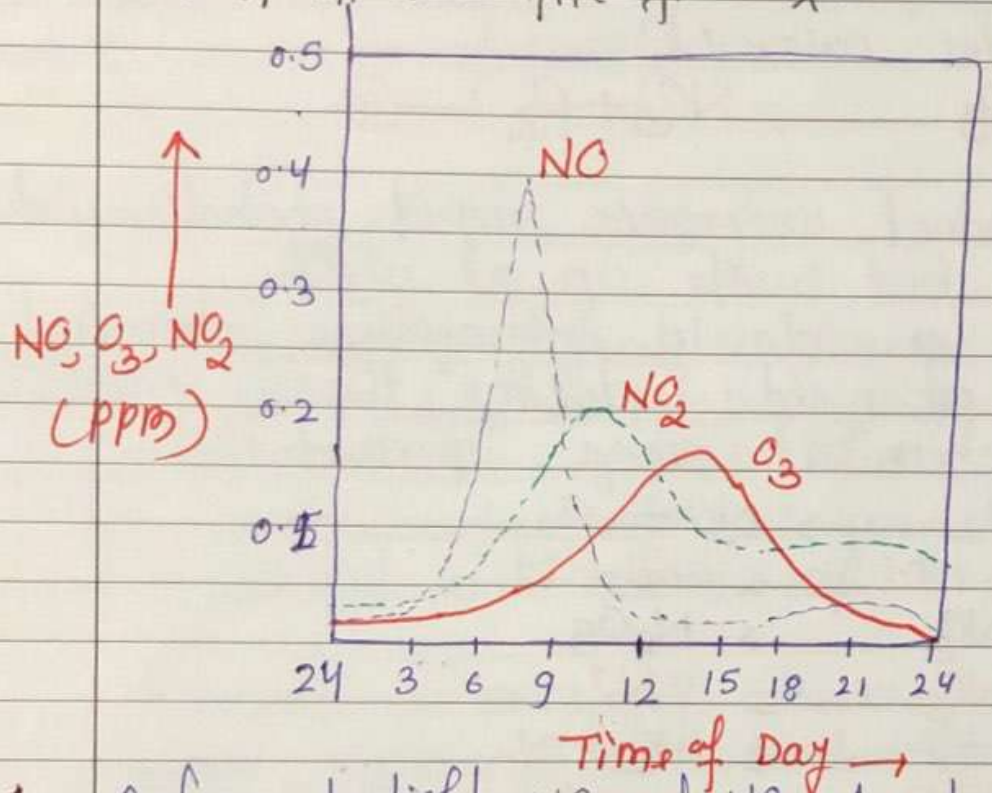
$$HO\cdot + NO_2 \longrightarrow HNO_3$$

$$O_3 + NO_2 \longrightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \longrightarrow N_2O_5$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3$$

Concentration Profile of NO_x:



1. Before daylight NO and NO_2 levels remain fairly stable at concentrations slightly higher than the daily minimum.
2. As the traffic rush begins and increases (6 to 8 A.M.) the level of NO increases ~~(9 to 10 A.M.) due to conversion of NO and NO_2~~ and becomes maximum.
3. At mid-morning with increased UV light, the NO_2 level increases (9 to 10 A.M.) due to conversion of NO into NO_2.

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4. O_3 builds up as NO levels drop below 0.1 ppm.
5. In the evening (5 to 8 PM) the NO level again goes up during the evening rush.
6. O_3 accumulated during daytime reacts with NO during night with the result that NO_2 concentration goes slightly up and O_3 level drops.

Control of NO_x Pollution:

- By use of catalytic converters
- Two stage combustion of fuels in power plants.
- Chemical absorption → by use of acidic or alkaline scrubbing

Two Stage Combustion of fuels in Power Plants:

1. The fuel is fired at a relatively high-temperature with a stoichiometric amount of air, say 90-95% of the stoichiometric requirement. This yield of NO is limited in the absence of excess O_2.
2. Fuel burnout is completed at relatively low-temperature in excess air. Under this condition NO is not formed.

Chemical Absorption: A possible approach to NO_x removal from stack gas is the chemical absorption process using H_2SO_4 solution or alkaline scrubbing solution containing $Ca(OH)_2$ & $Mg(OH)_2$. Simultaneously SO_2 is also removed. NO is converted into N_2O_3 which is easily absorbed. Then $NO_2 + NO \longrightarrow N_2O_3$ NO_2 is recycled. 4 steps are involved in this scrubbing process.

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(i) Flue gas and NO_2 are introduced into an oxidiser. $$NO_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + NO$$

(ii) NO and NO_2 react to form N_2O_3 which is scrubbed by H_2SO_4 in a scrubber. The cleaned flue gas is released into the atmosphere.

$$NO + NO_2 \longrightarrow N_2O_3$$
$$N_2O_3 + 2H_2SO_4 \longrightarrow 2NOHSO_4 + H_2O$$

(iii) The reaction product from the scrubber is next decomposed in a decomposer and the resulting H_2SO_4 recycled to the scrubber.

$$2NOHSO_4 + \frac{1}{2}O_2 + H_2O \longrightarrow 2H_2SO_4 + 2NO_2$$

(iv) NO_2 produces HNO_3 in the HNO_3 reactor.

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

and excess NO_2 and NO are recirculated through the oxidiser in step (i)

Harmful Effects of Nitrogen oxides:

→ NO attaches to Hb and reduces oxygen transport efficiency.

→ NO_2 exposure upto 150-200ppm causes bronchiolitis fibrosa obliterans.

→ NO_x are known to cause fading of dyes and inks used in some textiles.

→ causes acid rain.

→ In the upper stratosphere and in the mesosphere, molecular oxygen is photodissociated by UV light of less than 242 nm wavelength.

$$O_2 + h\nu \longrightarrow O + O$$

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In the presence of energy absorbing third bodies the atomic oxygen reacts with molecular oxygen to produce ozone.

$$O_2 + O + M \longrightarrow O_3 + M$$

$$O_3 + O \longrightarrow O_2 + O_2$$

$$O + O + M \longrightarrow O_2 + M$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow NO + O_2$$

$$O + O_3 \longrightarrow O_2 + O_2$$

$$O + H_2O \longrightarrow HO\cdot + HO\cdot$$

$$HO\cdot + O_3 \longrightarrow HOO\cdot + O_2$$

$$NO_2 + h\nu \longrightarrow NO + O \quad (\lambda < 420\,nm)$$

$$NO + HOO\cdot \longrightarrow NO_2 + HO\cdot$$

Monitoring of oxides of Nitrogen:

→ Estimated through chemiluminescence

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$

→ The intensity of the light emitted is measured with the help of photomultipliers.

→ Since intensity is directly related to the concentration of the excited species and hence of NO molecules the concentration of NO can be easily determined.