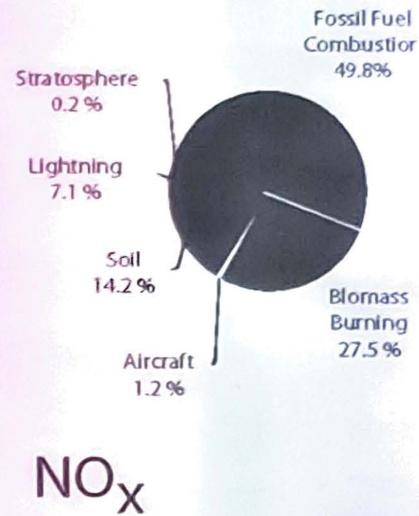
NO_x formation

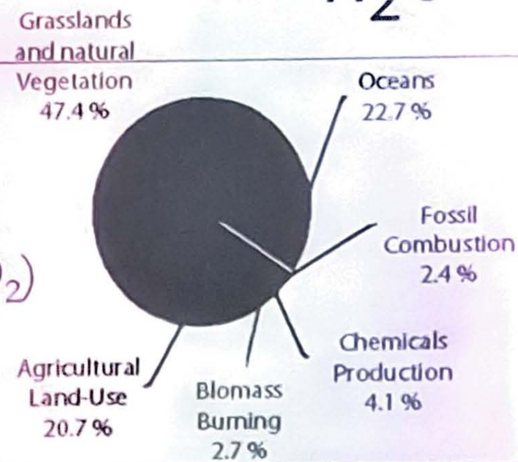
- What is NO_x?
- NO_x = Oxides of Nitrogen which are produced by combustion:
    - Nitric Oxide (NO)
    - Nitrogen Dioxide (NO_2)
    - Nitrous Oxide (N_2O)
- Nitric Oxide (NO)
    - Highly reactive due to lone pair of electron at N atom
    - Not particularly toxic
    - Major precursor of photochemical smog ($NO \rightarrow NO_2$)
    - It is produced by most of combustion systems



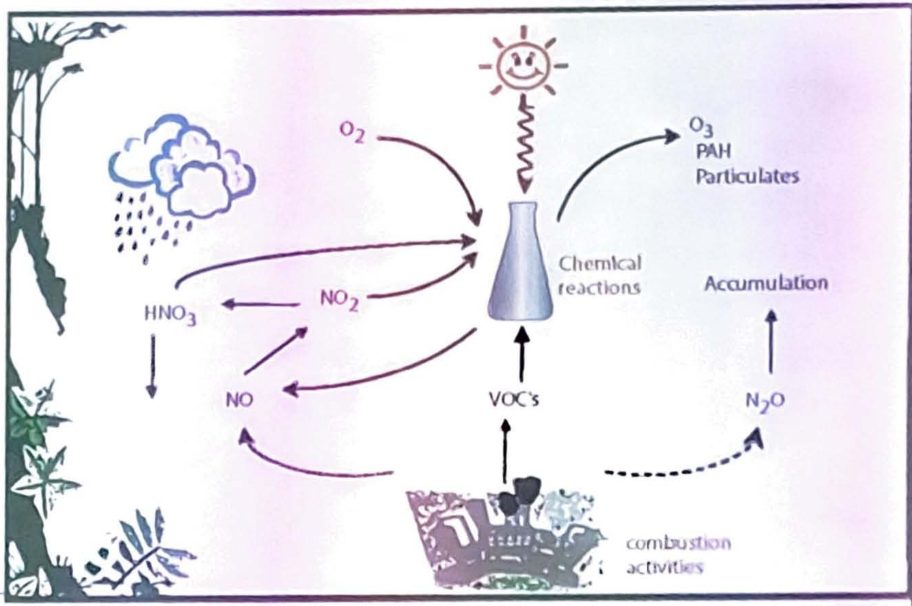
NO_x formation

- ✓ Nitrogen Dioxide (NO_2)
  - o Brown, poisonous gas
  - o Emissions of NO_2 from most combustion < 10% of NO_x
  - o Adverse health effects include: lung irritation, bronchitis, pneumonia and a lowering respiratory resistance
  - o Ambient limit = 120ppb [NEPC, 1998]
- ✓ Significant direct emissions of NO_2 occur from processes involving premixed flames:
  - o Indoor gas appliances (20-100% of NO_x)
  - o Gas turbines → yellow/brown plumes

Nitrous Oxide (N_2O)



- ✓ Relatively inert
- ✓ Uses: Dental anaesthetic
- ✓ Strong absorber of infrared radiation (~300 x CO_2)
- ✓ Stability = long atmospheric residence times (~150 yrs)
- ✓ Hence, potentially significant greenhouse gas
- ✓ Long life-time also allows its transportation into stratosphere and participates in ozone depletion
- ✓ Only significant from low-temperature processes (eg. Fluidised bed combustion)



Sources of Nitrogen

- ✓ Formation of NO_x requires a source of nitrogen
- ✓ Two sources of nitrogen:
  - **a.** Molecular nitrogen from air ($1/2\ N_2$ (from air) $+1/2\ O_2 \rightarrow NO$)
  - Thermal or Zeldovich Mechanism.
  - Prompt-Fenimore Mechanism ($HC + N_2$).
  - Other minor mechanisms
  - **b.** Nitrogen chemically bound within fuel
  - Fuel NO_x,
- ✓ Most of NO_x in the form of NO

Thermal NO

- ✓ One of the most important issues for combustion engineers is: 'What are my NOx emissions?'
- ✓ In most cases, unusually high NOx emissions are due to NO formed by the Thermal (Zeldovich) mechanism
- ✓ Thermal NO mechanism involves the attack of molecular nitrogen (N_2) and atomic nitrogen (N) by oxygen (O_2) and oxygen-containing radicals (O, OH). This can occurs in oxygen rich mixture.
- ✓ First identified by Zeldovich (1946) and extended by Fenimore and Jones (1957)
- ✓ Described by the following reactions:
  - o $N_2 + O \rightarrow NO + N$ (R.1)
  - o $N + O2 \rightarrow NO+O$ (R.2)
  - o $N + OH \rightarrow NO + H$ (R.3)

Thermal NO

✓ Westenberg (1971) invoked the steady-state approximation and determined that the maximum NO formation rate is given by:

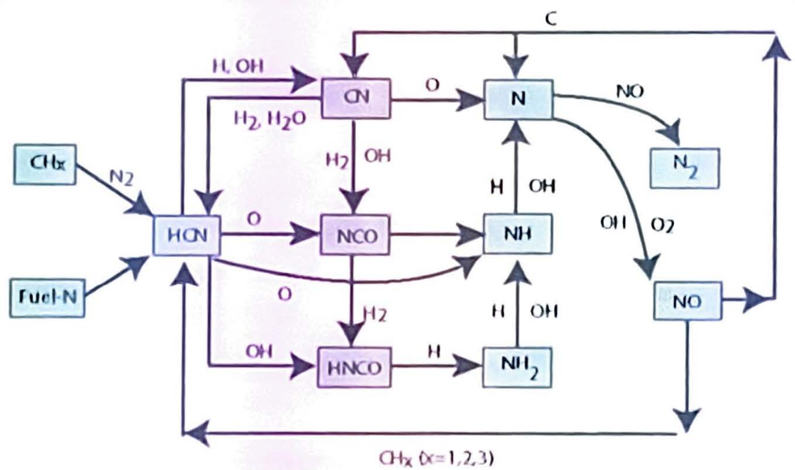
$$\frac{d[NO]}{dt} = 1.45 \times 10^{17} T^{-1/2} \exp\left[\frac{-69460}{T(K)}\right] \cdot [O_2]_{eq}^{1/2} \cdot [N_2]_{eq} \, mol/cm^3.s$$

✓ Hence, [NO] depends on:

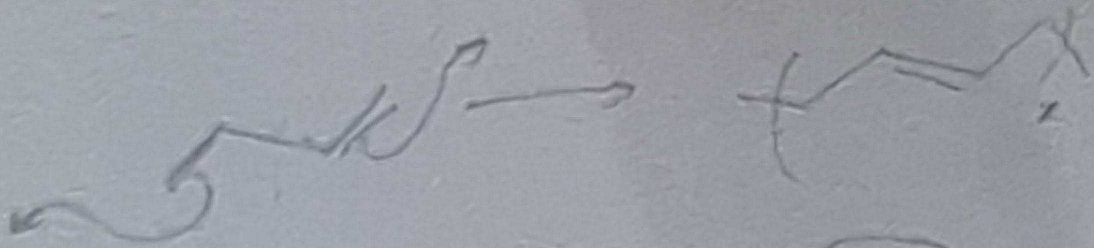
- Temperature (the higher the temp, strongly the higher the NO formed)
  ⇒ high temp environment
- O_2 concentration (the higher the oxygen conc, the higher the NO formed)
  ⇒ oxygen-rich environment
- Residence time

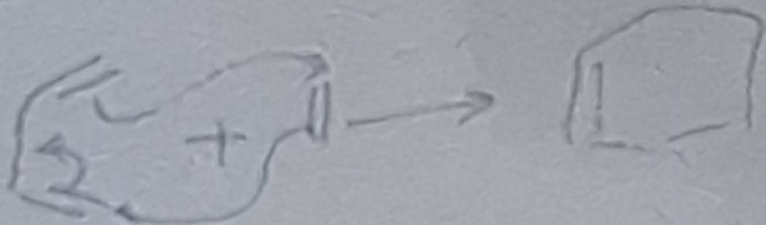
Prompt NO

- Fenimore (1971) observed an additional formation of NO which could not be explained by the thermal mechanism
  - NO formed close to the burner (hence - "prompt' NO)
  - Effect is not observed under very fuel-lean conditions or in systems with H_2 or CO as fuel
  - Mechanism involves the attack of N_2 by hydrocarbon fuel fragments, mainly CH radicals and C-atoms.
  - The Prompt-Fenimore mechanism is initiated mainly by R.4 (the formation of HCN) with a lesser contribution from R.5
    $:CH + N_2 \rightarrow HCN + N$ (R.4)
  - $C + N_2 \rightarrow CN + N$ (R.5)
  - HCN is subsequently oxidised to NO (see diagram)
  - Prompt mechanism dominates for hydrocarbon combustion in fuel-rich, in both premixed and diffusion flames



Reaction path diagram illustrating the major steps in **prompt NO formation**, the conversion of volatile nitrogen in flames, and reburning. (Bowman, 1992)





Volatile Organic Compounds

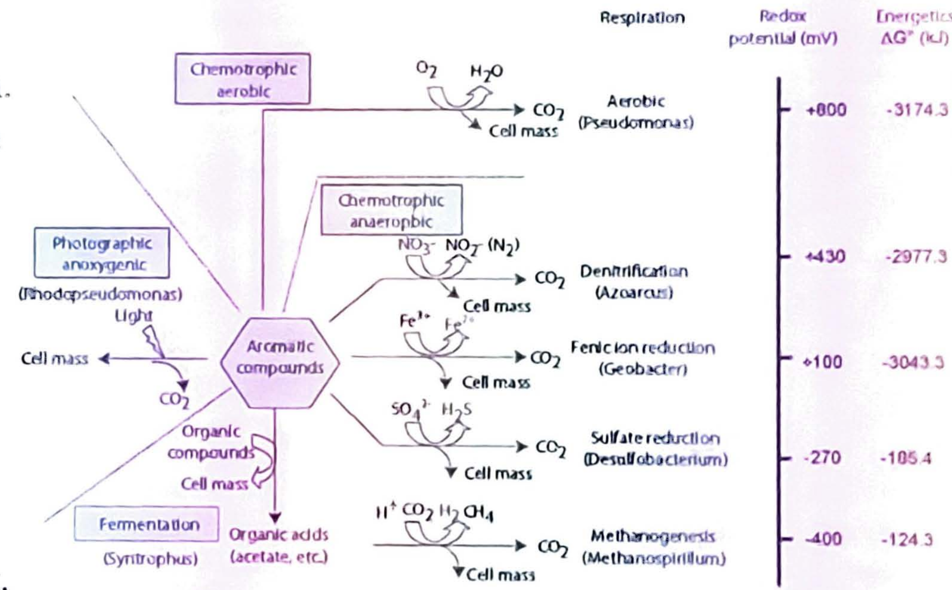
- ✓ The term volatile organic compounds (VOCs) refers to carbon-containing compounds that exist as gases or that vaporize easily. **Some examples of VOCs are benzene, formaldehyde, toluene, xylene, hexane, ethylbenzene, 1,3-butadiene, and a group of compounds known as polycyclic aromatic hydrocarbons (PAHs)**.
- ✓ **The vast majority of VOCs are hydrocarbons**, often represented by the chemical formula RH, where R may represent either an alkyl or an aryl group.
- ✓ Volatile organic chemicals are released during a number of industrial and manufacturing operations.
- ✓ For example, 1,3-butadiene is an important raw material in the manufacture of synthetic rubber: During manufacture small amounts of the chemical escape into the air.
- ✓ Formaldehyde is a raw material used in the manufacture of a variety of building materials, such as phenol-formaldehyde and melamine resins.
- ✓ Many household products, such as cleaning products, varnishes, waxes, paints, and organic solvents, contain VOCs, which vaporize and escape easily into the atmosphere when they are used. For this reason, VOCs often build up indoors.
- ✓ About 40 percent of all VOCs released into the atmosphere are from on-road vehicles, an additional 32 percent from solvent use and evaporation, about 12 percent from combustion operations, and the remaining 17 percent from a variety of other sources.
- ✓ Because they tend to build up indoors and to react with and damage living tissue, VOCs constitute an important element in the special problem of indoor air pollution.
- ✓ Exposure to low concentrations of VOCs produces a number of annoying but relatively benign symptoms, such as irritation of the eyes, nose, throat, and respiratory system; headache, fatigue, dizziness, and nausea; visual problems; impairment of memory and other thought processes; and skin reactions.
- ✓ Some VOCs, such as benzene, formaldehyde, perchloroethylene, and derivatives of xylene and toluene, pose more serious concerns in that they have been found to be carcinogenic. Long-term exposure to these compounds may, therefore, pose a serious health risk.

Volatile Organic Compounds

- ✓ PAN, ozone, and many of the other compounds formed in the series of reactions just described are strong oxidants and are responsible for some of the initial and most aggravating features of smog, including nose, eye, and throat irritation.
- ✓ The primary system for controlling VOC emissions from automotive vehicles is the catalytic converter.
- ✓ A number of different technologies have been developed for removing VOCs from flue gases of stationary sources. They include thermal and catalytic incineration, adsorption, absorption, and biofiltration.
- ✓ Incineration systems are based on the principle that all volatile organic compounds are combustible and can, in principle, be eliminated simply by being burned.
- ✓ Combustion can be achieved without catalysts (thermal systems) or with catalysts (catalytic systems). In either case, flue gases are passed into a chamber where they are heated in an excess of air, resulting in the oxidation of VOCs.
- ✓ Thermal systems operate at temperatures of 750°C–1,000°C, while catalytic systems operate at temperatures of about 350°C–500°C.
- ✓ Adsorption systems make use of the fact that VOCs are attracted to and will adsorb to (attach to the surface of) certain special materials, the most common of which is activated charcoal.
- ✓ Flue gases containing VOCs are passed through a chamber and over a bed of the adsorbent, where they collect on its surface. The system may be designed such that the VOCs can then be removed from the adsorbent, which can then be reused or the adsorbent with VOCs attached is simply discarded.

Volatile Organic Compounds

- ✓ Absorption systems operate as scrubbers.
- ✓ Flue gases are directed into and upward through a large cylindrical tank, where they encounter a downward spray of some solvent, in which they dissolve.
- ✓ The solvent can then be removed, evaporated, and collected for future use. Or it can be incinerated or otherwise discarded, destroying the VOCs in the process.
- ✓ In the past two decades, a number of novel systems for the control and removal of VOCs have been developed.
- ✓ One such technology is biofiltration. In this type of system, flue gases are passed through a large tank containing microorganisms that digest and degrade the organic chemicals in the gases.
- ✓ The waste products of this process are carbon dioxide and water, harmless compounds that can be released directly to the environment.



Water Pollution

- ✓ Key Ideas
  - o What is water pollution?
  - o What are major types and effects of water pollution?
  - o How do we measure water quality?
  - o Point versus Nonpoint sources
  - o What are the major sources of pollution?

- ✓ What is water pollution?
- ✓ Any chemical, biological, physical change in water quality that has a harmful effect on living organisms or makes water unsuitable for desired usage.

- ✓ WHO:
  - 3.4 million premature deaths each year from waterborne diseases
  - 1.9 million from diarrhea
  - U.S. 1.5 million illnesses
  - 1993 Milwaukee 370,000 sick

- ✓ Infectious Agents: bacteria and viruses often from animal wastes

- ✓ Oxygen Demanding Wastes: organic waste that needs oxygen often from animal waste, paper mills and food processing.

- ✓ Inorganic Chemicals: Acids and toxic chemicals often from runoff, industries and household cleaners

- ✓ Organic Chemicals: oil, gasoline, plastics, detergents often from surface runoff, industries and cleaners

What is water pollution?

- ✓ Plant Nutrients: water soluble nitrates, ammonia and phosphates often from sewage, agriculture and urban fertilizers

- ✓ Sediment: soils and silts from land erosion can disrupt photosynthesis, destroy spawning grounds, clog rivers and streams

- ✓ Heat Pollution and Radioactivity: mostly from powerplants

How do we measure water quality

✓ Bacterial Counts: Fecal coliform counts from intestines of animals

- None per 100 ml for drinking
- ~200 per 100 ml for swimming

✓ Sources: human sewage, animals, birds, raccoons, etc.