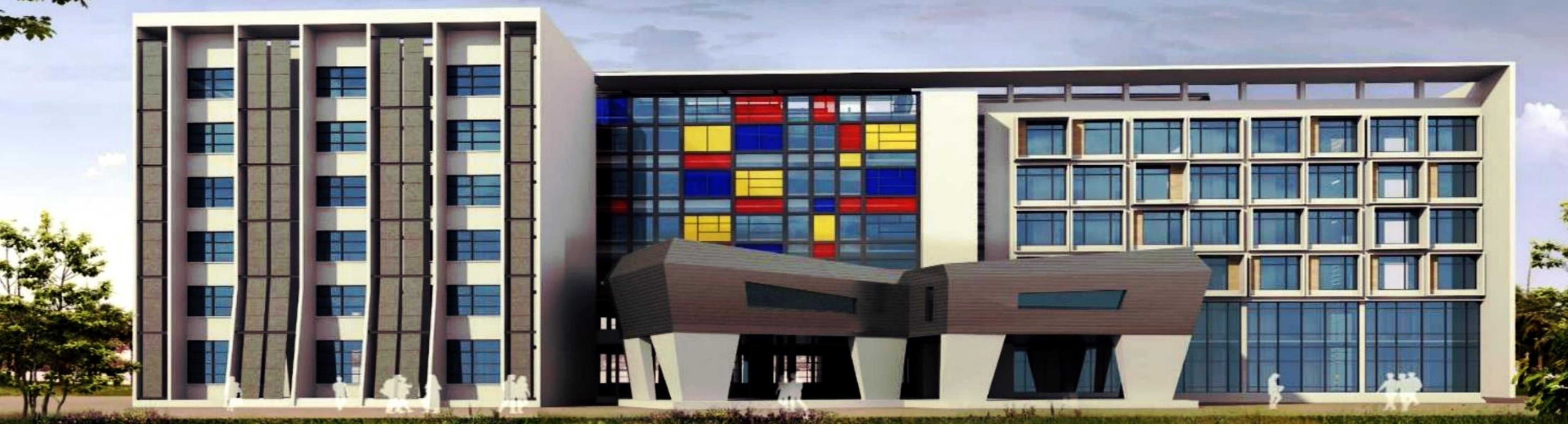


CY1018

भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

Course Content

Know our environment (chemistry of lithosphere, energy balance, sustainability and recycle), Know about global warming (infrared absorption, molecular vibration, atmospheric window, residence time of greenhouse gases, evidences and effects of global warming)

Deeper analysis of atmospheric pollution (Chemistry of CO, NOx, VOCs, SO_2, Industrial smog, photochemical smog), Ozone depletion (production, catalytic destruction)

Organic Chemicals in the Environment, Insecticides, Pesticides, Herbicides and Insect Control, Soaps, Synthetic Surfactants, Polymers, and Haloorganics. Fate of organic/inorganic chemicals in natural and engineered systems (fate of polymers after use, detergents, synthetic surfactants insecticides, pesticides etc. after use)

Aspects of transformations in atmosphere (microbial degradation of organics-environmental degradation of polymers, atmospheric lifetime, toxicity). Green Chemistry and Industrial Ecology. **Future challenges (CO_2 sequestering, Nuclear energy)**. A project on environment related topic.

Volatile Organic Compounds (VOCs)

❖ **Comparison**

1. A comparison of the emission from marine outboard two and four cycle engines of the same horse power was made. The result of those tests show that the exhaust of a two cycle engine contained more then 12 times the amount of HCs than a four cycle engine of the same power

Type of Marine outboard Engine	CO(g)	NOx(g)	HC(g)
Two cycle Engine	165	0.3	89
Four Cycle engine	127	0.7	7
Source: Juttner F. D. et al., Water Research **1995**, *29*, 1976-1982			

Automobile Pollutants

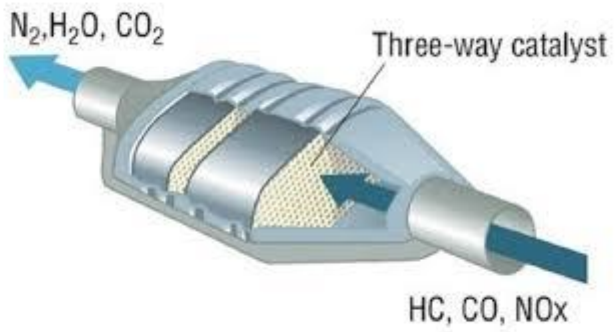
- Motor vehicles are a major source of CO, NOx and volatile HCs
- Since 1975, when all new cars in the USA were required by law to be equipped with a catalytic converter, emissions of those pollutant have been reduced significantly
- The table shows that today's car emits 95% less pollutant than pre-1970 vehicles despite the fact that the number of miles travelled has almost doubled in the last 20 years

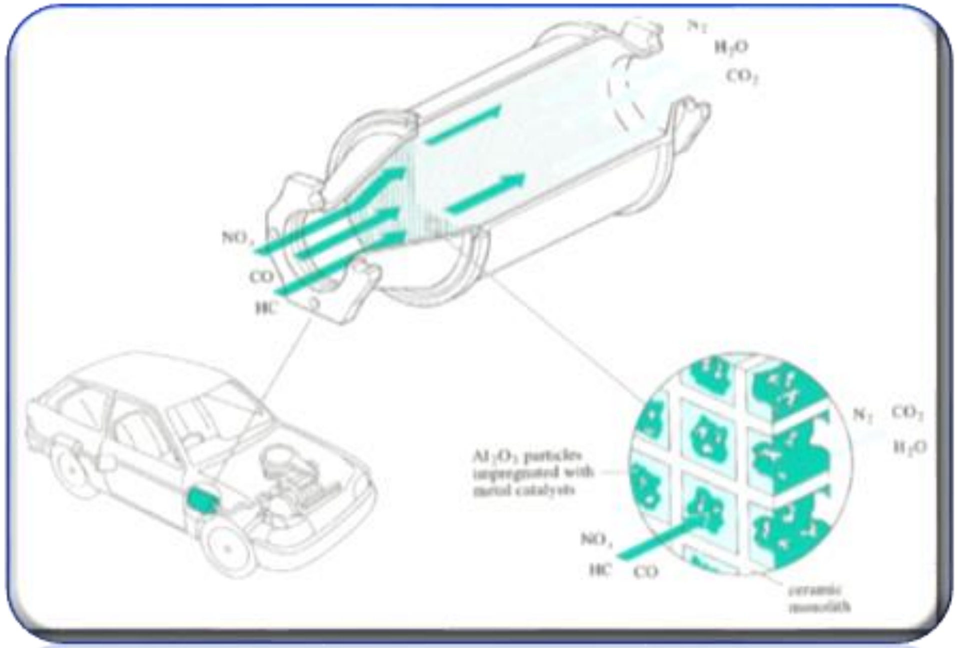
Emission Standards for Light duty Vehicles								
	Federal Standards				California Standards			
Year	HCs	CO	NOx	Evaporative HCs	HCs	CO	NOx	Evaporative HCs
<1970	10.6	84	4.1	> 45	10.6	84	4.1	>45
1970	4.1	34	-	-	4.1	34	-	2
1975	1.5	15	3.1	2	0.9	9	2.0	2
1980	0.41	7.0	2.0	2	0.39	9	1.0	2
1985	0.41	3.4	1.0	2	0.39	7	0.4	2
1990	0.41	3.4	1.0	2	0.39	7	0.4	2
1993	0.41	3.4	1.0	2	0.25	3.4	0.4	2
2000	0.41	3.4	0.4	2	0.25	3.4	0.4	2

All values reported in gms per mile except for evaporative HCs which are expressed as gms per tests

The Catalytic Converter

- The use of three-way catalytic converter (used since 1981) can reduce the emission drastically
- It is called three-way catalytic converter as it simultaneously reduces the amount of HCs, Nox and CO in the exhaust stream
- The converter is a very fine honeycomb structure made of ceramic coated with the precious metals like Pt, Pd, Rh which act as catalyst





The Catalytic Converter

- The catalytic converter has two chambers in succession. As the gases enter, **Rh** catalyzes the reduction of NOx to nitrogen gas by hydrogen generated at the surface of the **Rh** catalyst by the reaction of H_2O and unburned HCs

$$\text{HCs} + H_2O \longrightarrow H_2 + CO\ ; \qquad 2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

- Then air is injected into the exhaust stream to produce oxygen and **CO** oxidized to $\mathbf{CO_2}$ in the presence of **Pt** and **Pd** catalyst

$$2\,CO + O_2 \longrightarrow 2\,CO_2\ ; \quad HC + 2O_2 \longrightarrow CO_2 + 2\,H_2O$$

❖ Thus, overall reaction for reduction of NO and oxidation of CO can be written as

$$2\,NO + 2\,CO \xrightarrow{\text{Rh, Pt, Pd Cat}} N_2 + 2\,CO_2$$

- Oxidation of a typical gasoline HC, Octane occurs as

$$2\,C_8H_{18} + 25\,O_2 \xrightarrow{\text{Pt, Pd Cat}} 16\,CO_2 + 18\,H_2O$$

- Automobiles using catalytic converters must have their air/fuel ratio set as 14.8:1 to get optimum result. At room temp, the efficiency of the catalytic converter is nearly zero

Sulfur Dioxide

- The release of SO_2 to the atmosphere is the primary cause of acid rain
- Fossil fuel combustion accounts for 70% of the emission
- Industrial sources contribute approximately 23% of SO_2
- Coal, oil and all other fossil fuels naturally contain some sulfur (FeS). When sulfur containing coal is burned, the sulfur is oxidized to SO_2: $S + O_2 \longrightarrow 2SO_2 + 2H_2O$
- H_2S (produced an end product of anaerobic decomposition of sulfur containing organic matter by microorganism) enter to the atmosphere to form SO_2

$$2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$

- Volcanic eruptions are another more localized natural source of SO_2; e.g. eruption of Mt. Pinatubo in Philippines in June 1991 contribute 25 million tons of SO_2 into atmosphere, where it was converted into sulfuric acid aerosols

Fate of atmospheric SO_2: Acid Rain

- SO_2 in the atmosphere reacts with oxygen to form SO_3 which then readily react water vapor or water droplets to forms H_2SO_4(g). The mechanism involves hydroxyl radicals and the eqns.

Fate of atmospheric SO_2: Acid Rain

$$SO_2 + OH^{\bullet} \longrightarrow HSO_3^{\bullet}$$

$$HSO_3^{\bullet} + O_2 \longrightarrow SO_3 + HOO^{\bullet}$$

$$SO_3 + H_2O \longrightarrow H_2SO_4\,(g)$$

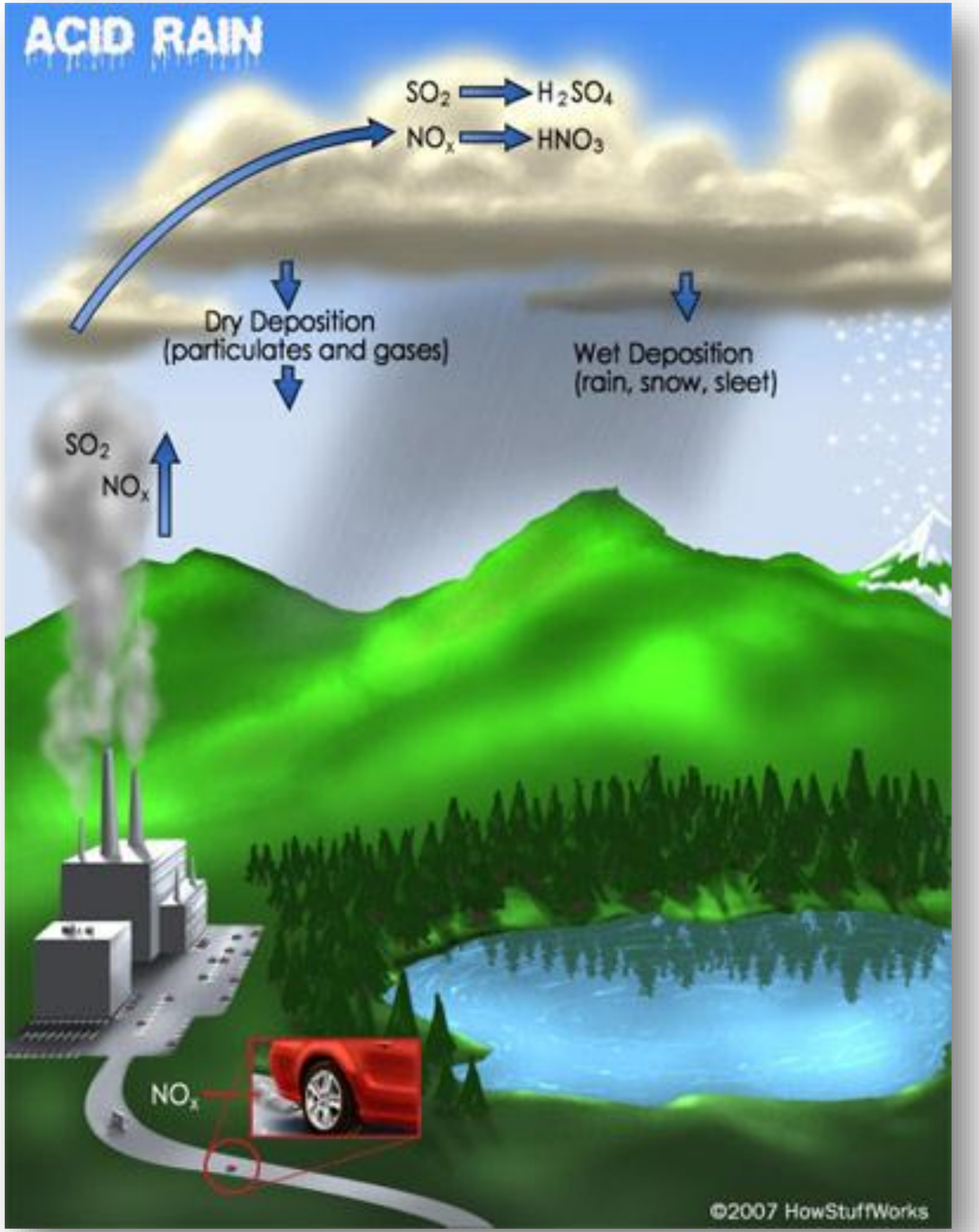
$$H_2SO_4 + H_2O \longrightarrow H_2SO_4\,(aq)$$

- Sulfuric acid in the atmosphere becomes concentrated near the base of clouds where PH level as low as 3 (PH of orange juice)
- Some of the atmospheric SO_2 dissolves if there is a significant water in the air to form sulfurous acid

$$SO_2(g) + H_2O\,(aq) \longrightarrow H_2SO_3(aq)$$

- The dissolved SO_2 is oxidized by trace amount of H_2O_2 and Ozone that are also present in the aerosol droplets to sulfate ions (SO_4^{2-})
- $HSO_3^- + H_2O_2 \longrightarrow H_2O + HSO_4^-$

$HSO_3^- + O_3 \longrightarrow O_2 + HSO_4^-$



Effect of Acid Rain

Original color of Taj Mahal

Taj Mahal after the constant effect of acid rain

Effect of SO_2 on Human Health and Environment

- SO_2 is colorless, toxic gas with sharp acrid odor
- Exposure to it causes irritation of eyes, respiratory passages and aggravates symptoms of respiratory disease. Children are susceptible to its effects
- SO_2 also harmful to plants. Crops such as barley, alfalfa, cotton and wheat are particularly adversely affected

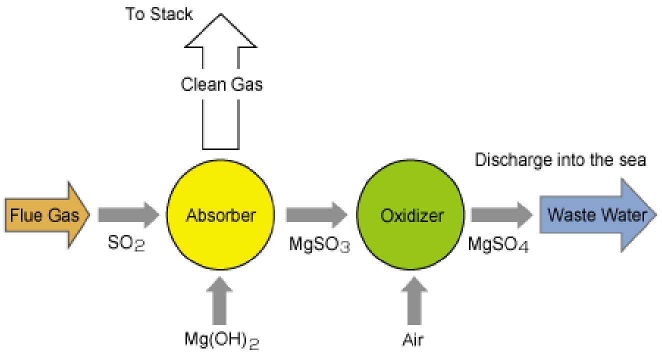
❖ How to control SO_2 emissions

1. Sulfur can be removed from coal before combustion
2. SO_2 can be removed from the smoke stack after combustion but before it reaches to atmosphere

❖ The second approach is cheaper and chosen

❖ The most commonly used method is fuel gas desulfurization (FGD) in which sulfur containing compounds are washed out by passing the Chimney (flue) gases through a slurry of water mixed with finely ground lime stone ($CaCO_3$) or dolomite [$Ca{\bullet}Mg(CO_3)_2$] or both. On heating the basic $CaCO_3$ with acidic SO_2 in presence of O_2 to form $CaSO_4$

$$2\,SO_2 + 2\,CaCO_3 + O_2 \longrightarrow 2\,CaSO_4 + 2CO_2$$



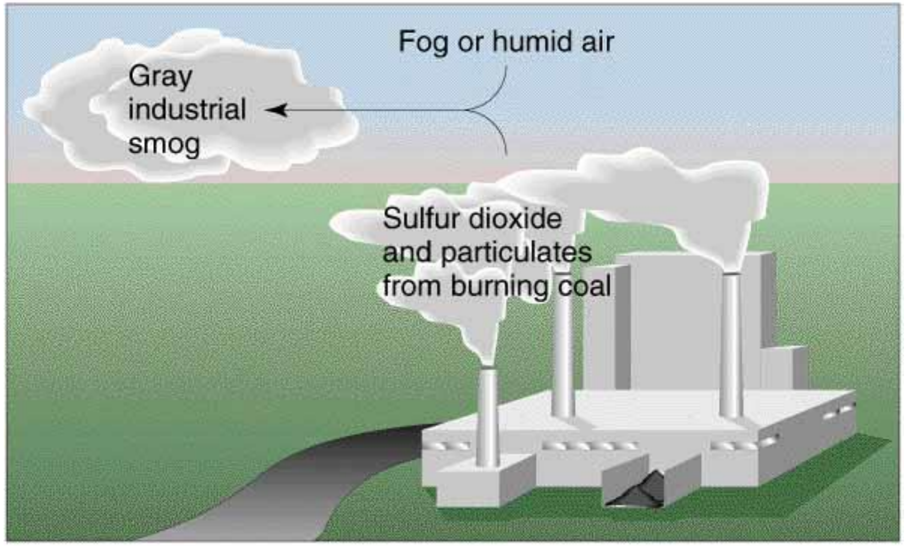
Industrial Smog

- Particulate matter and **SO_2** can be a deadly combination. Released into the atmosphere together when coal is burned, they can form **industrial smog** a mixture of fly ash, soot, SO_2 and some VOCs
- It is formed in winter, typically in cities where the weather was cold and wet. Visibility was often reduced to a few yards and people in factory towns lived under a pall of black smoke

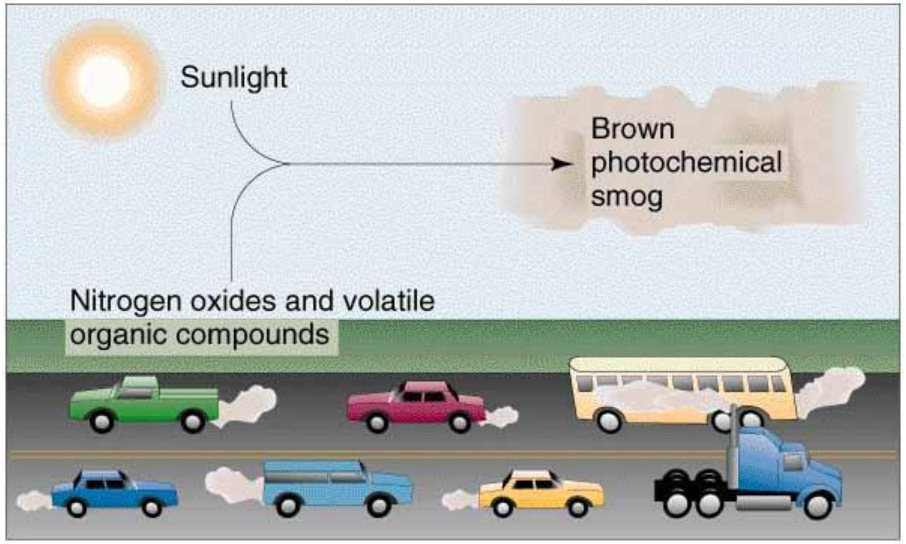
Photochemical Smog

- The origin of photochemical smog is quite different from that of industrial smog. Typically, photochemical smog develops as a yellow brown haze in hot slurry weather in cities like Los Angels where automobile traffic is congested
- The reaction that led to its formation are initiated by sunlight and involve the HCs and NO_x emitted in automobile exhaust.
- NO_2 is responsible for the brownish color of the haze

Industrial Smog



(a) Industrial smog



(b) Photochemical smog

Production of Hydroxyl Radicals

- By the time sunlight reaches the surface of the Earth, all of the light energy UV light has been absorbed in the stratosphere
- NO_2 is the only automobile emission that is capable of absorbing visible light that reaches the Earth surface
- NO_2 + sunlight (< 320 nm) $\longrightarrow$ NO + O ; O + O_2 $\longrightarrow$ O_3
- O_3 + NO $\longrightarrow$ NO_2 + O_2
- The ozone produced absorbs light in the blue region of the visible spectrum (< 320 nm) and photo dissociates: $O_3 \longrightarrow O_2 + O$
- The oxygen atom produced (having six electrons) reacts with water vapor in the atmosphere and abstract a hydrogen atom to produce hydroxyl radical (seven electrons)
- O + H_2O $\longrightarrow$ $2OH^{\bullet}$ By this way one NO_2 molecule produces two hydroxyl radicals
- The concentration of hydroxyl radicals does not continue to increase out of control because there are termination reactions that remove it from the troposphere. It can react with other radical species in the troposphere

Production of Hydroxyl Radicals

$$^{\bullet}OH + {}^{\bullet}NO_2 \longrightarrow HNO_3$$

$$^{\bullet}OH + HOO^{\bullet} \longrightarrow H_2O + O_2$$

$$2\,{}^{\bullet}OOH \longrightarrow H_2O_2 + O_2$$

❖ The products are very soluble in water and are removed from troposphere during precipitation

- Unburned HCs in automobile exhausts (RCH_3) react with hydroxyl radical to form a number of secondary pollutants including HC radicals $RO_2^{\bullet}$. This radical then reacts with NO to form aldehydes and the hydro peroxide radical $HO_2^{\bullet}$

$$RCH_3 + {}^{\bullet}OH \longrightarrow RCH_2^{\bullet} + H_2O$$

$$RCH_2^{\bullet} + O_2 \longrightarrow RCH_2OO^{\bullet} \quad \text{(Peroxy alkyl radical)}$$

$$RCH_2OO^{\bullet} + NO \longrightarrow RCH_2O^{\bullet} \quad \text{(Alkoxy radical)}$$

$$RCH_2O^{\bullet} + O_2 \longrightarrow RCHO + {}^{\bullet}OOH \quad \text{(Hydroperoxyl radical)}$$

$$HOO^{\bullet} + NO \longrightarrow NO_2 + {}^{\bullet}OH$$

Production of Hydroxyl Radicals

- Each step in this reaction produces a radical. The overall reaction is can be summarized as

$$RCH_3 + 2\,O_2 + 2\,NO \longrightarrow RCHO + 2\,NO_2 + H_2O \qquad (1)$$

$$2\,NO_2 + 2\,H_2O \longrightarrow 2\,NO + 4\,\dot{O}H \qquad (2)$$

$$RCH_3 + 2\,O_2 + H_2O \longrightarrow RCHO + 4\dot{O}H$$

- This reaction produces four hydroxyl radicals for every HC reacted. This is a catalytic reaction. A very small number of radicals can produce a large amount of product through the production of four radicals per cycle

Reaction of Hydroxyl Radicals with HCs

- Abstraction of Hydrogen
  - Hydroxyl radicals will react with certain unburned HCs from the automobiles exhaust depending on the number and type of C-H bonds in the HCs