



Environmental Chemistry Theory

CY1018



भारतीय प्रौद्योगिकी संस्थान हैदराबाद
Indian Institute of Technology Hyderabad

Department of Chemistry

CLASS LINK for B slot

CY1018 (CE+EE+ME+MnC+BME+BT+Comp.Engg.+IC)

MONDAY: 10:00 to 11:00

Join from the meeting link

<https://iithyd.webex.com/iithyd/j.php?MTID=m74bcd59b23cab53794b58f36f39f7680>

WEDNESDAY: 09:00 to 10:00

Join from the meeting link

<https://iithyd.webex.com/iithyd/j.php?MTID=m5984de3eb78aoaa1a03729440e3785co>

THURSDAY: 11:00 to 12:00

Join from the meeting link

<https://iithyd.webex.com/iithyd/j.php?MTID=m6486574d8c23166d15c03f6e7a846180>

CLASS LINK for S slot

CY1018 (AI+CH+CS+EP+ES+MS)

TUESDAY: 16:00 to 17:30

Join from the meeting link

<https://iithyd.webex.com/iithyd/j.php?MTID=m5db0a582b01e7b7dd668dfbfe408570d>

FRIDAY: 14:30 to 16:00

Join from the meeting link

<https://iithyd.webex.com/iithyd/j.php?MTID=m219fbc79bd86c2e9290b487f04cde25a>

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, NO_x, VOCs, SO₂, 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 (CO₂ sequestering, Nuclear energy). A project on environment related topic.

INSTRUCTORS

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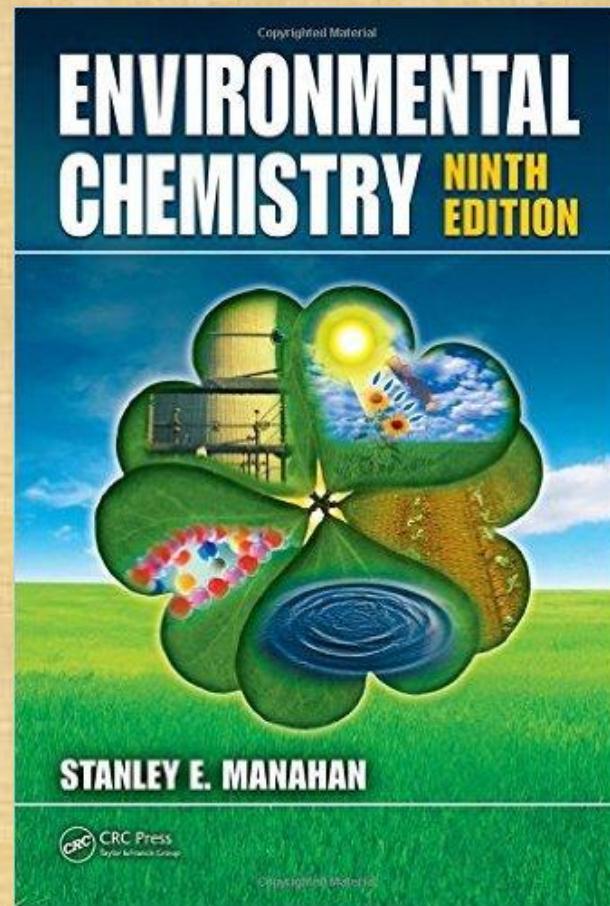
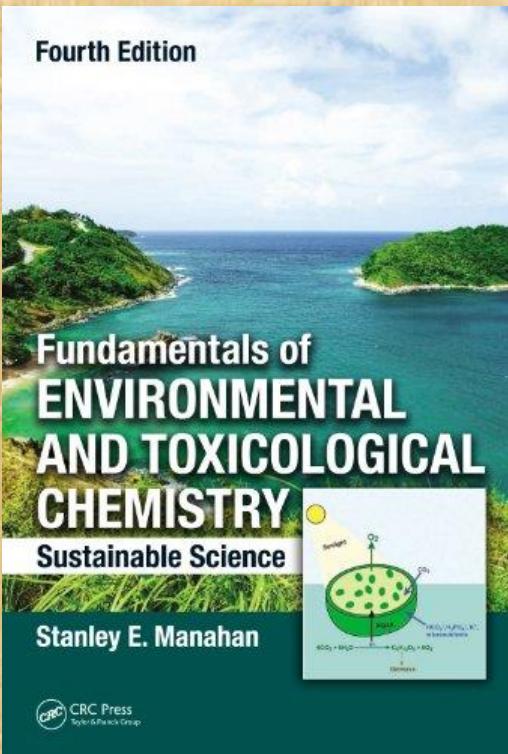
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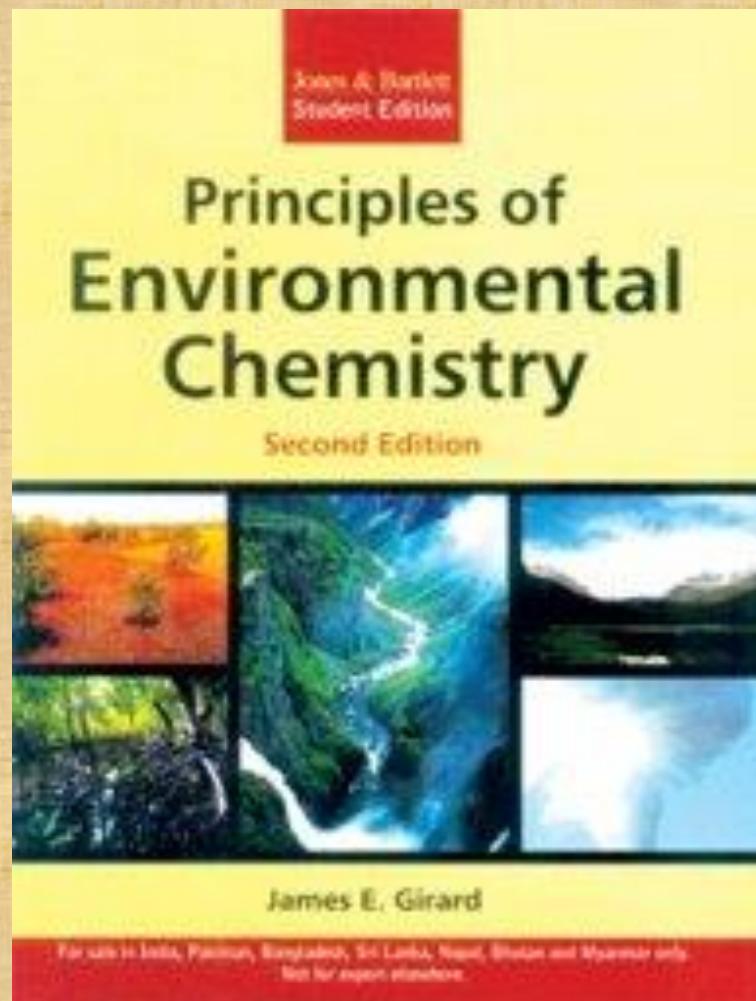
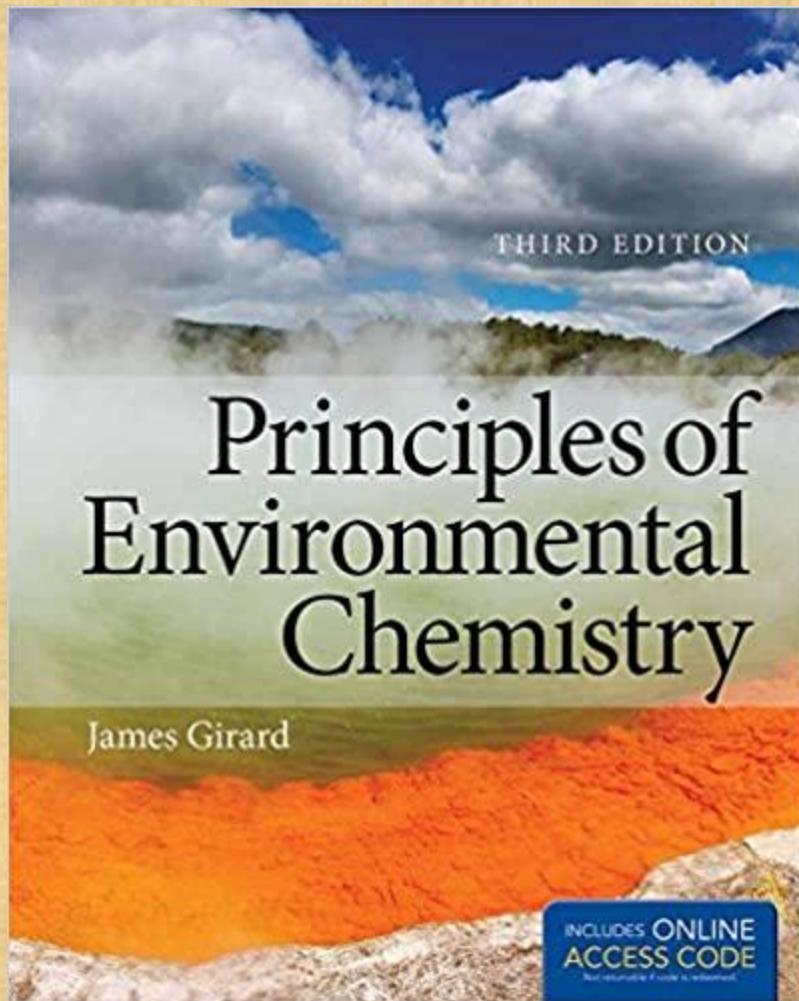
Environmental Chemistry Theory

Reference books

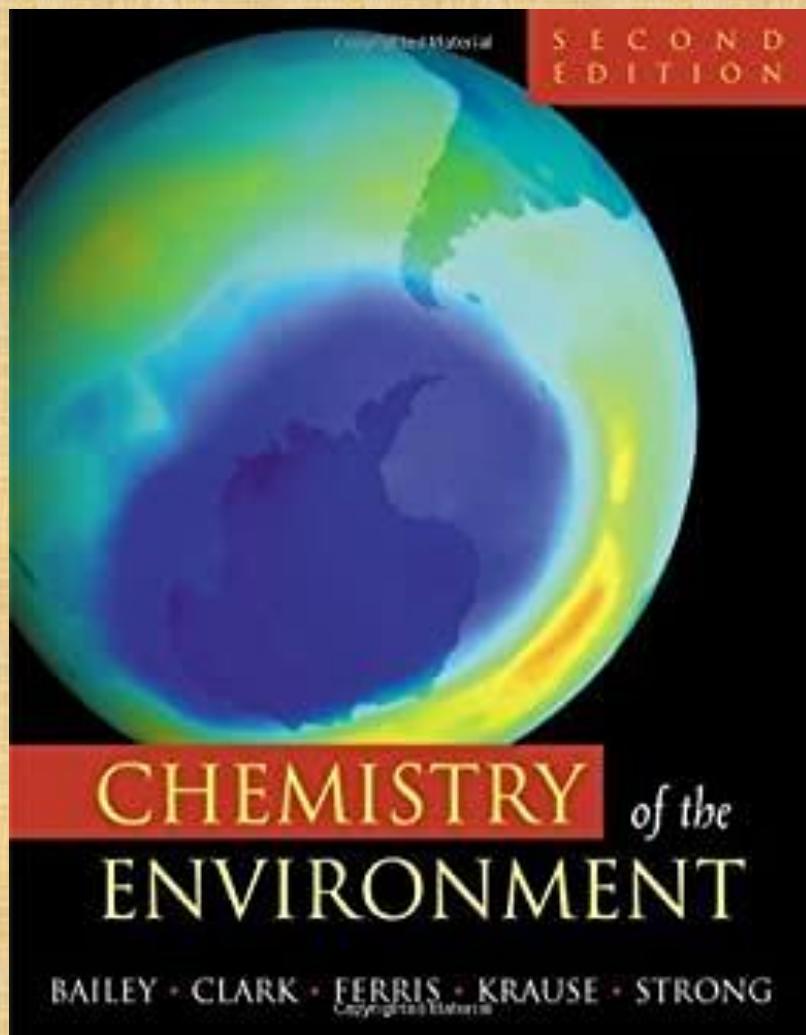
Fundamentals of Environmental and Toxicological Chemistry: Sustainable Science, Fourth Edition Kindle Edition



Principles of Environmental Chemistry By James E. Girard



**Chemistry of the Environment, Second Edition by R. A. Bailey,
H. M. Clark, J. P. Ferris, S. Krause, R. L. Strong**



GRADING and EXAMS:

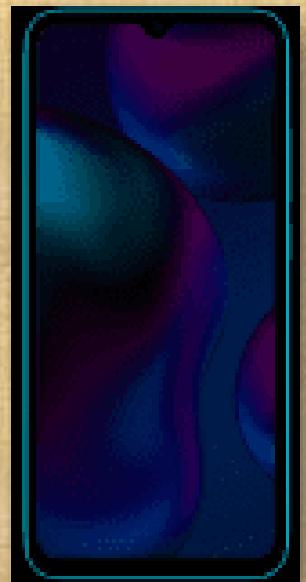
SEGMENT 1 (Nov 29 to Jan 3)		
QUIZ 1	10 Marks	
MID SEM	20 Marks	
SEGMENT 2 (Jan 5 to Feb 3)		
QUIZ 2	10 Marks	
MID SEM	20 Marks	
END EXAM	40 Marks	

Total 100 Marks

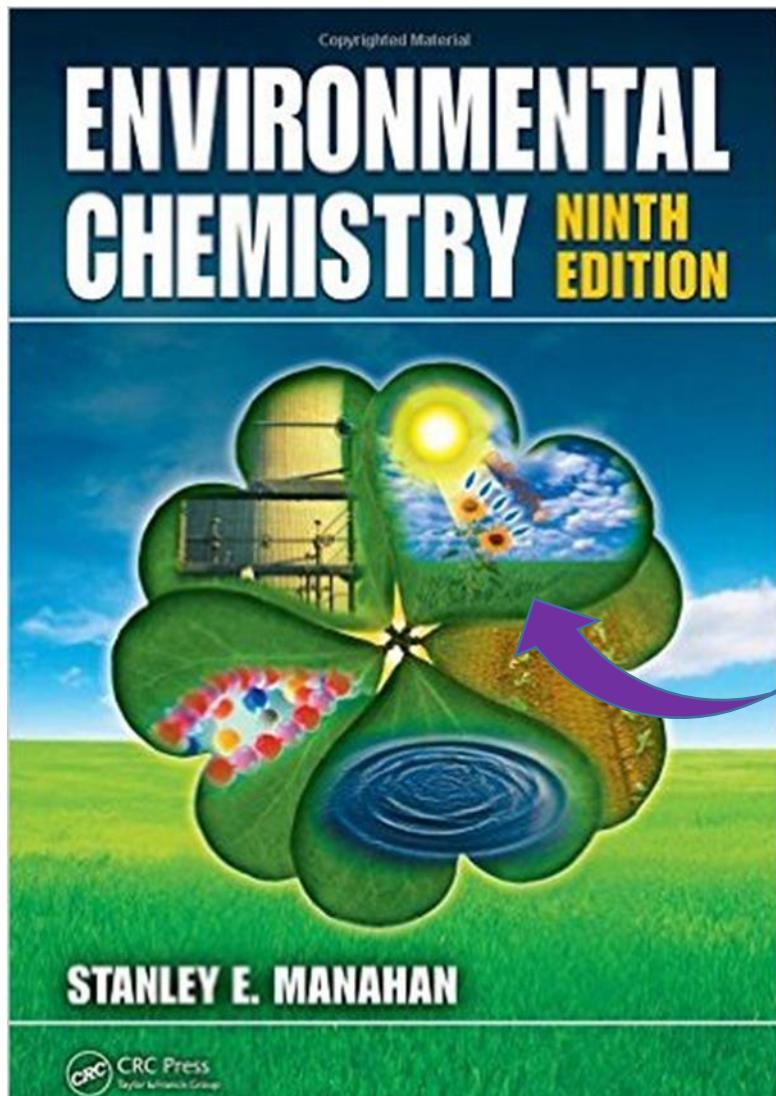
All should have smart phone
as all the exam will be via SAFE app

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Please download this app and get accustom with it



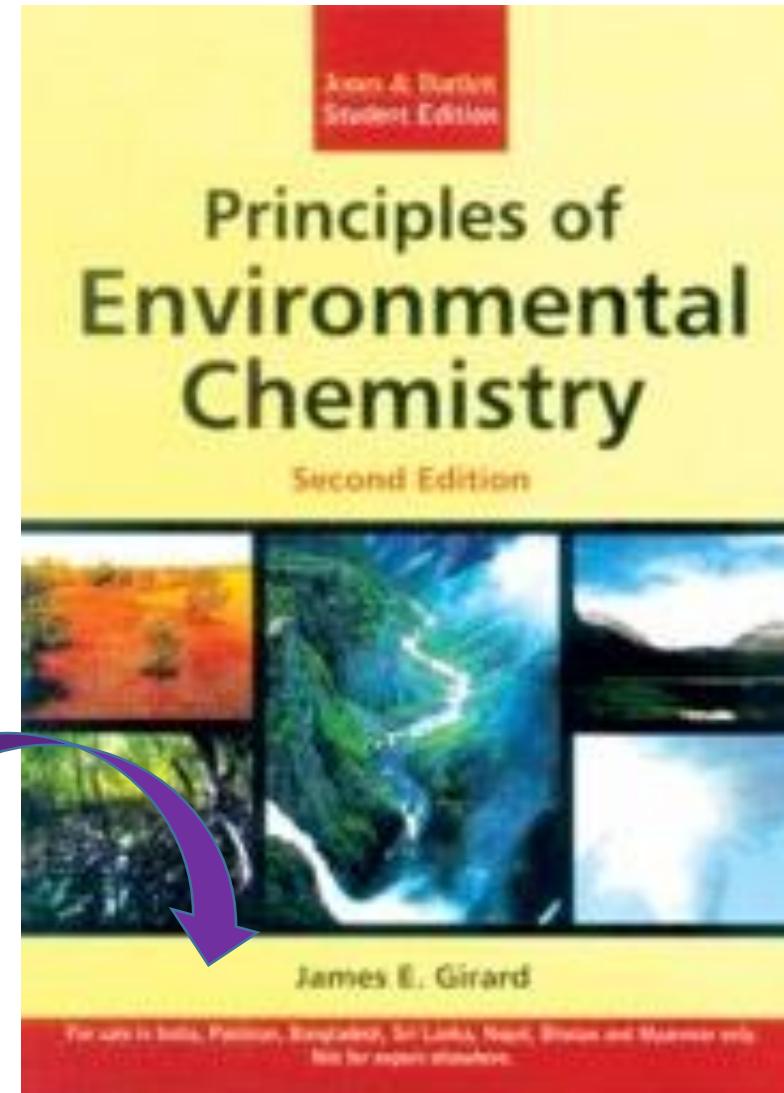
Reference books



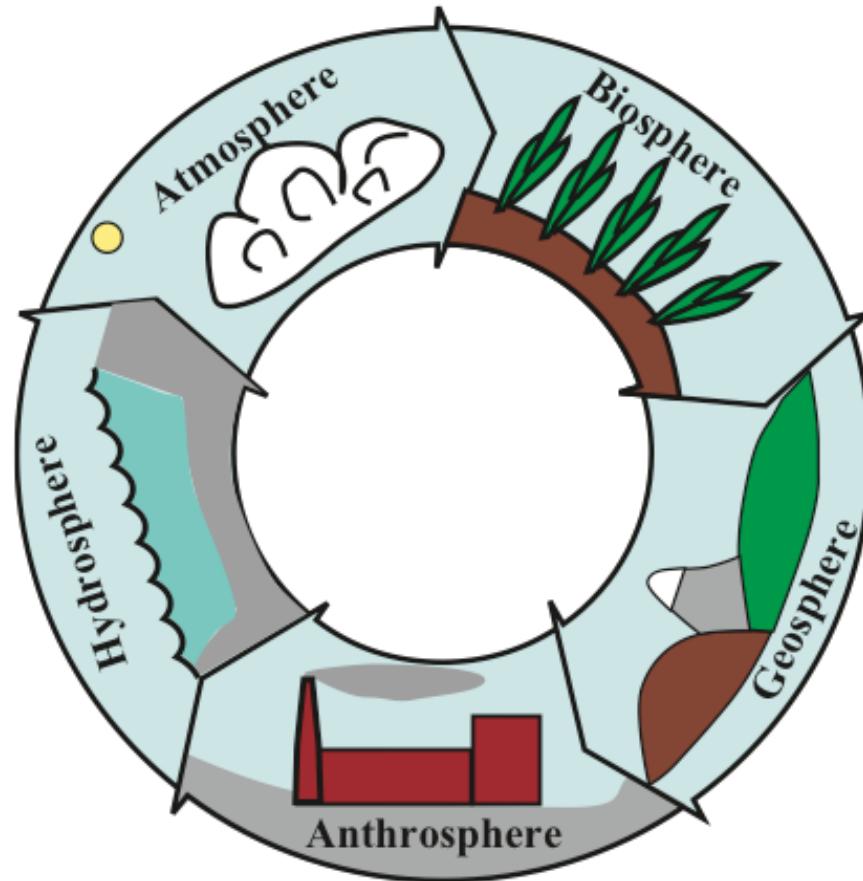
ENVIRONMENTAL CHEMISTRY
NINTH EDITION

STANLEY E. MANAHAN

Principles of
Environmental
Chemistry
By James E. Girard



The Five Spheres of the Environment

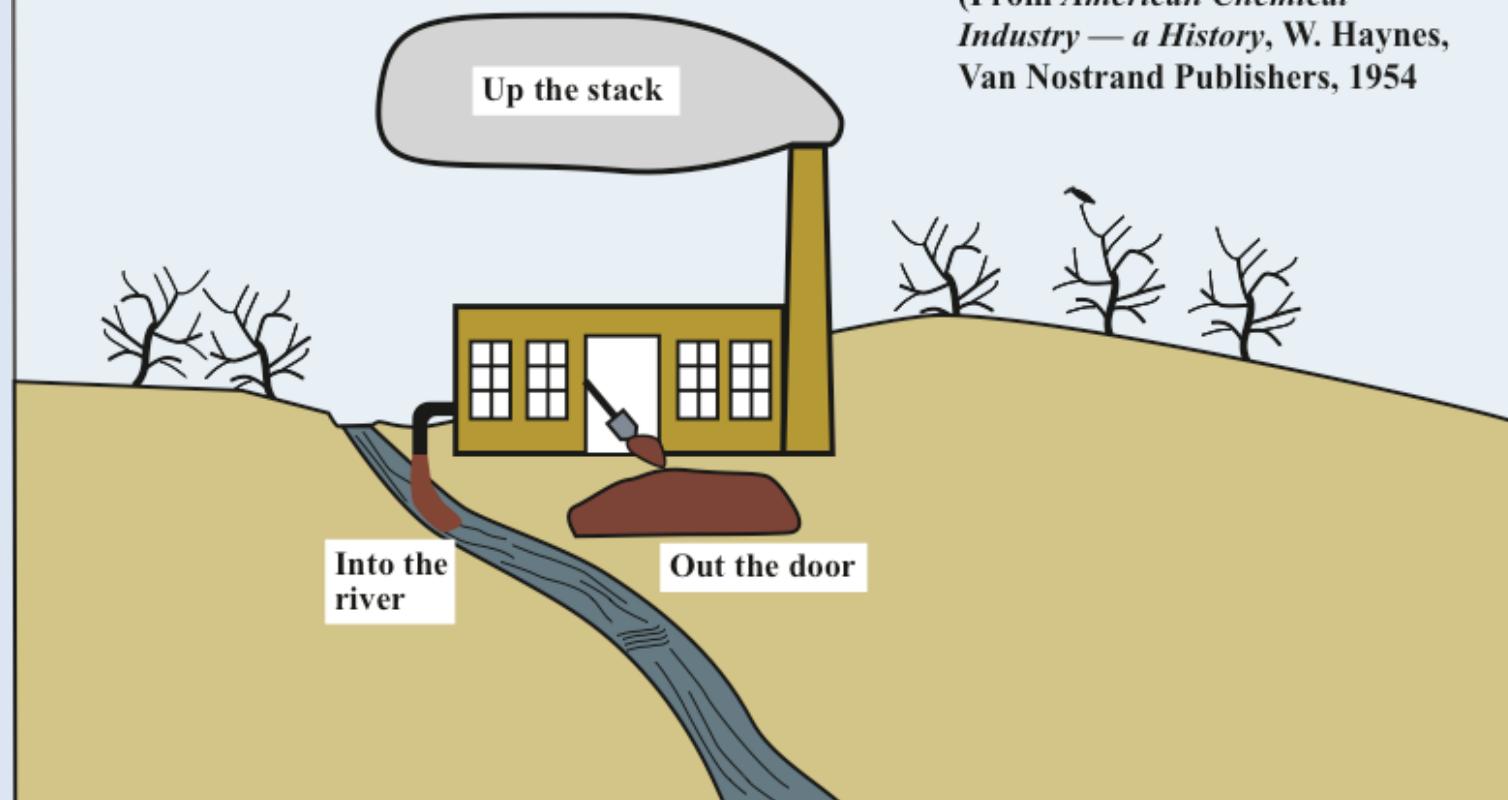


**Matter and Energy are Exchanged
Largely through Biogeochemical Cycles**

In the past many environmental problems were caused by practices that now seem to be totally unacceptable as expressed from the quote in this slide from what was regarded as a reputable book on the American chemical industry in 1954. The result was polluted air, polluted water, dangerous hazardous waste sites, and harm to living organisms.

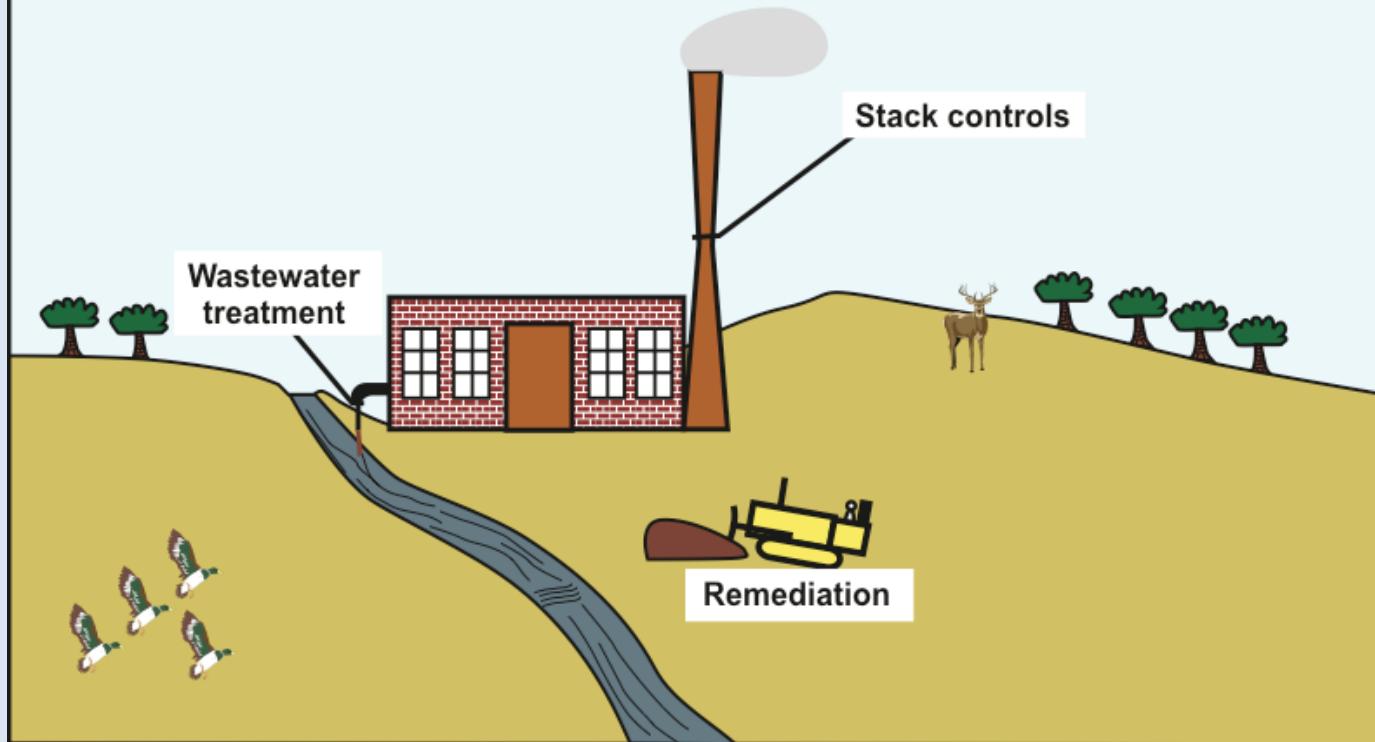
The Old Attitude: “By sensible definition any by-product of a chemical operation for which there is no profitable use is a waste. The most convenient, least expensive way of disposing of said waste — up the chimney or down the river — is best.”

(From *American Chemical Industry — a History*, W. Haynes, Van Nostrand Publishers, 1954)

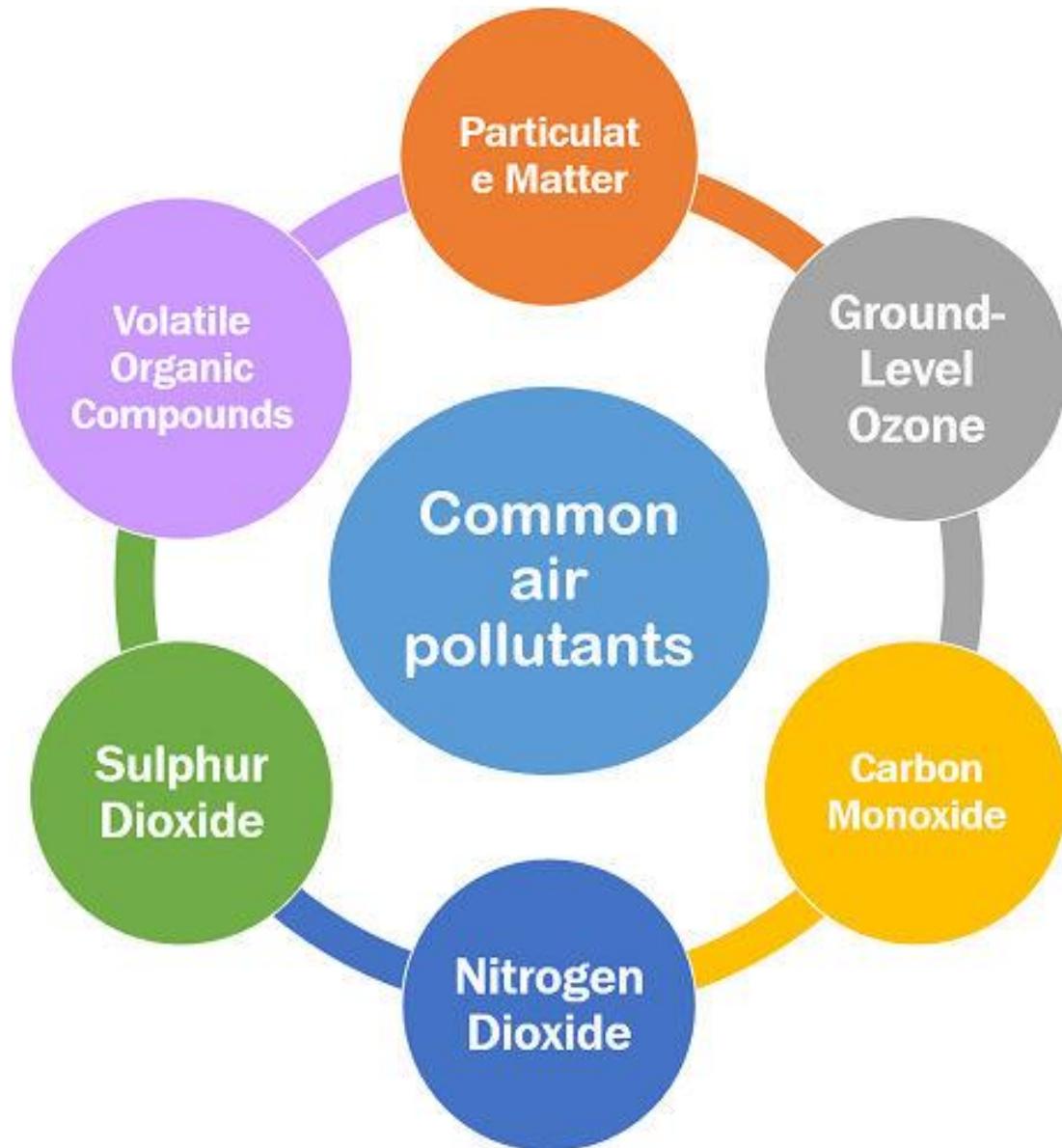


Dating from around 1970, laws and regulations were implemented to control air and water pollution and to clean up hazardous waste sites. These measures have relied largely upon "end of pipe" controls in which pollutants were generated but were removed before release to the environment. Although costly and requiring constant vigilance to make sure that standards have been met, these measures have been successful in reducing pollution and preventing increases in pollutant releases.

Currently: A "command-and-control approach using
"end-of-pipe" treatment measures and remediation of waste sites
has reduced major environmental problems



Deeper analysis of atmospheric pollution



Air quality measurement are commonly reported in terms of:

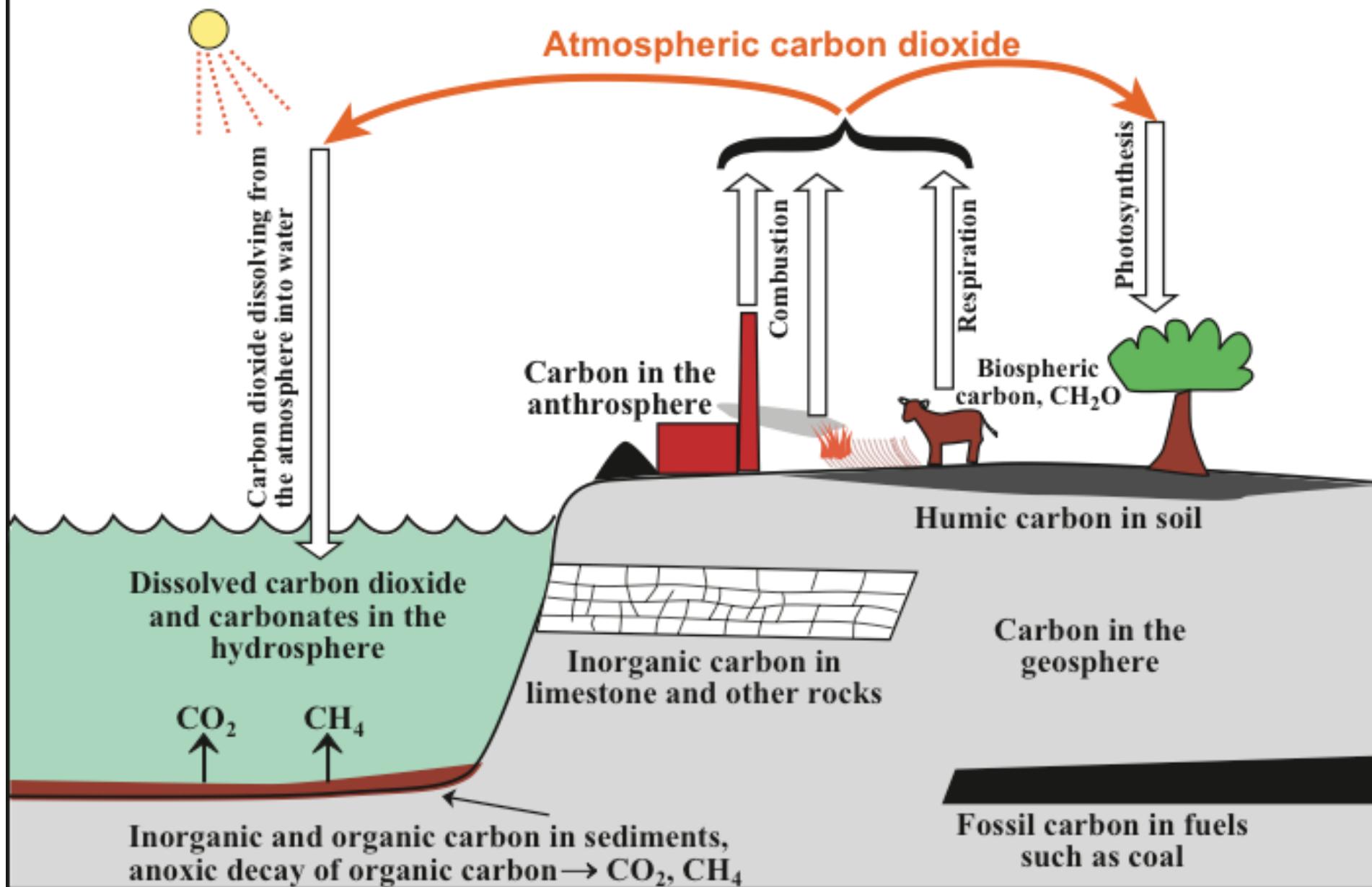
- micrograms per cubic meter ($\mu\text{g}/\text{m}^3$)
- parts per million (ppm) or parts per billion (ppb)
- For particulate matter, sizes are expressed in micron or micrometer.

Parts Per Million

$$\text{ppm} = \frac{\text{Mass of Solute (g)}}{\text{Mass of Solution (g)}} \times 10^6$$

Biogeochemical Cycles Are Important in Environmental Chemistry

The Carbon Cycle is Particularly Relevant to Climate Change



Analysis of air and air pollutant

- Analytical measurements from the foundation on which our understanding of the atmosphere is built
- In atmospheric chemistry one of the most fundamental measurement is the most difficult.
- What is composition of air?
- Nitrogen gas represents more than 78% of the atmosphere whereas reactive species such as ozone are present in ppm level. The range in concentration of atmospheric constituents is extremely wide as large as 10^4

Two different measurement Techniques:

In situ: It means the sample of the atmospheric gases must be placed inside the device (spectrometer) that is making

Remotely: (Remote sensing Technique): In this case by passing a beam of energy that originates on a satellite, an aircraft, the space shuttle or the ground through a portion of the atmosphere that is to be studied.

Although these measurement techniques involve different instrumentation, the underlying principles are same.

Analysis of air and air pollutant

- Automobile smoke stack emission are major sources of anthropogenic pollutants into the atmosphere, both of which are regulated by the Environmental Protection Agency (EPA). Measurement of these gases emitted from auto mobiles and smoke stacks are difficult to make because the exhaust gases are hot and travelling at a high velocity.

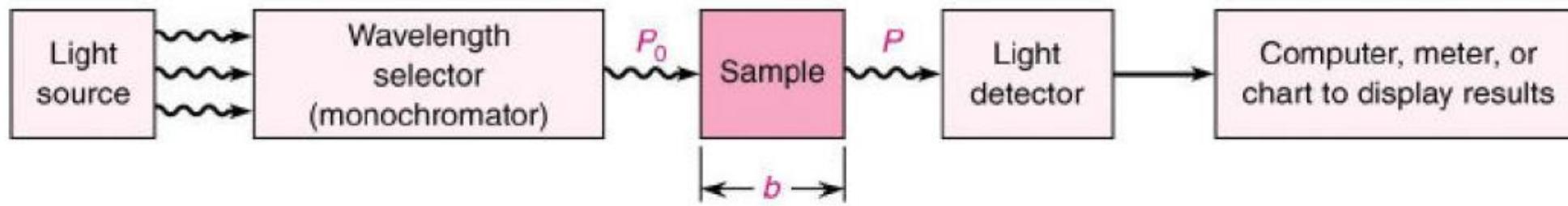
In situ Absorption Measurement

- **Spectroscopic Measurement:** This method rely on the fact that different chemical compounds absorbs electromagnetic radiation at different wave lengths. When a molecule absorbs a photon of electromagnetic radiation, the energy of the molecule increases.
- For example, when a molecule absorbs a microwave radiation, which is EMR of a relatively low energy, it only stimulate the rotational motion of the molecule.
- IR radiation which has higher energy than microwaves, stimulate vibrations of the molecules that absorbs it. UV radiation which has even higher energy than IR., causes electrons in the molecules absorbing it to be promoted into higher energy orbitals; the molecule is said to be in the excited state. The lowest energy state of the molecule is called ground state.

In situ Absorption Measurement

- Very high energy EMR such as X-ray has enough energy to break chemical bonds and ionize molecules.
- When the sample absorbs a beam of EMR radiation, the irradiance of the beam is decreased. The irradiance (P) which is some times intensity or radiant power is the energy per second per unit area of the light beam.
- EMR is passed through a monochromator (a prism) to select one wave length of EMR. The light of the single wave length is called monochromatic which means “one color”.
- The monochromatic light with irradiance P_0 passes into a sample b . The irradiance of the beam emerging from the other side of the sample is P . Some of the light may be absorbed by the sample and thus $P_0 \geq P$.

Instrumentation

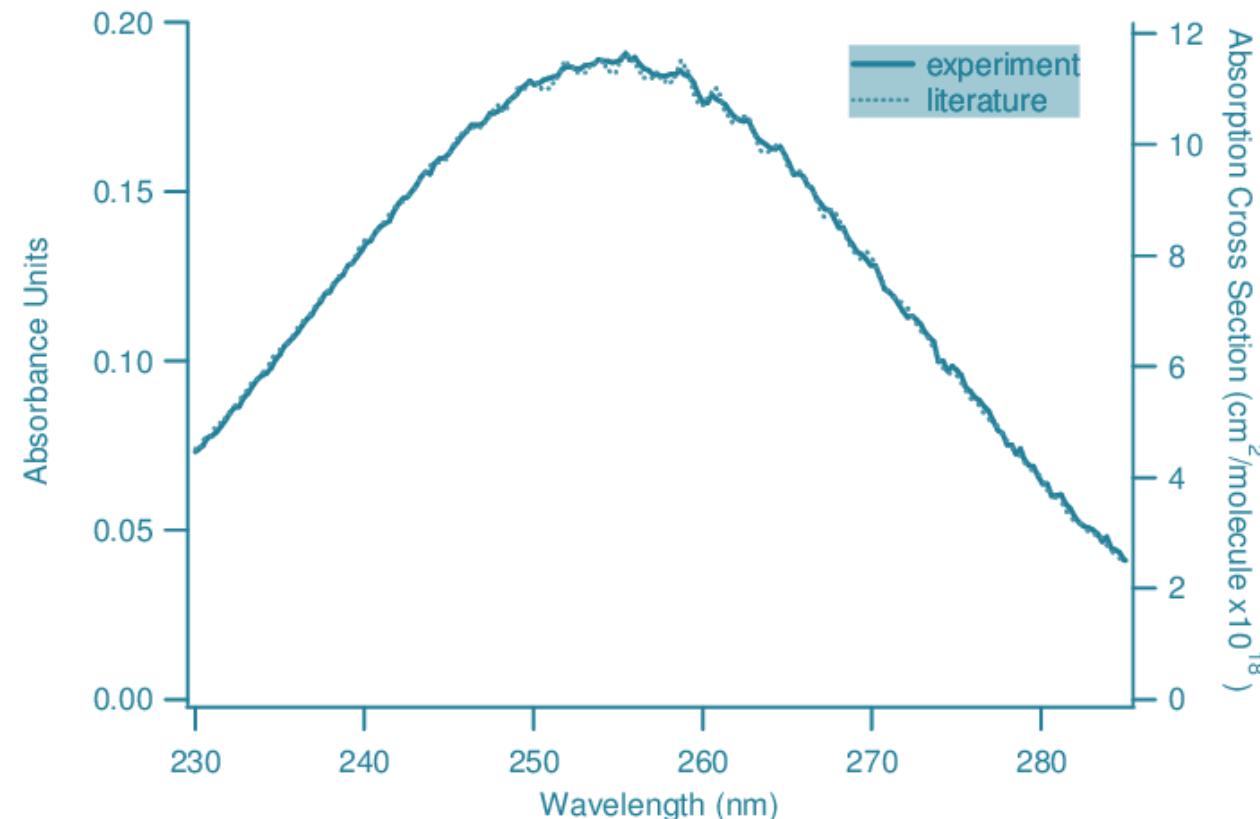


In situ Absorption Measurement

- **Transmittance (T):** it is defined as the fraction of the original light that has passed through the sample.
- $T = \frac{P}{P_0}$ T has the range of 0 to 1. The percentage of transmittance is $100 T$ and has a range from 0% to 100%. Absorbance (A) is defined as follows:
- $A = \log \left(\frac{P_0}{P} \right) = -\log T$; When no light is absorbed $P = P_0$ and $A = 0$
- Absorbance is important because it is directly proportional to concentration (C) of the absorbing molecules in the sample. A is dimensionless.
- The Beer-Lambert or simply Beer's Law:
- $A = \epsilon \cdot b \cdot C$ (b = path length cm or m etc, C = concentration moles/L, ppm, ppb etc)
- ϵ = molar absorptivity or extinction coefficient. It is the characteristics of the molecule that indicates how much light it will absorb at a particular wave length.

In situ Ozone measurement

- Ultraviolet absorption has been used to measure the condensation of ozone in stratospheric air. The figure shows that ozone has a strong absorption in the UV region. Other atmospheric gases such as O_2 , N_2 and H_2O do not absorb UV radiation and thus do not have to be removed from the air sample as they do not interfere with the ozone measurement.



In situ Ozone measurement

- The concentration of ozone in the stratosphere is less than 100 ppm, so the spectrophotometer that is used to make the measurement must be capable of measuring a small absorbance. This is most easily done by making the sample cell very long. Because Beer's law tells that absorbance is propositional to the sample path length and because we can get a lot of sample easily, a long sample path length will greatly improve our ability to measure ppm level of Ozone.

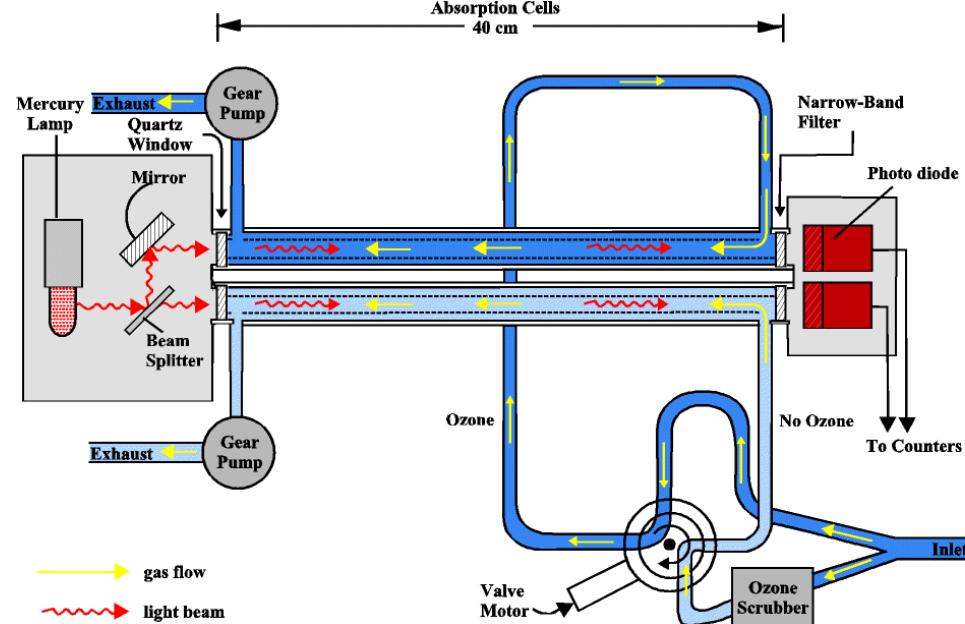
Ozone:Dual Beam UV-Photometer

[Proffitt, M.H., and R.J. McLaughlin,, Rev. Sci. Instrum., 54, 1719-1728, 1983]

[Proffitt, M.H., and R.J. McLaughlin, Rev. Sci. Instrum., 54, 1719-1728, 1983]

Absorption Cells

40 cm



Basic Pollutants

Basic Pollutants

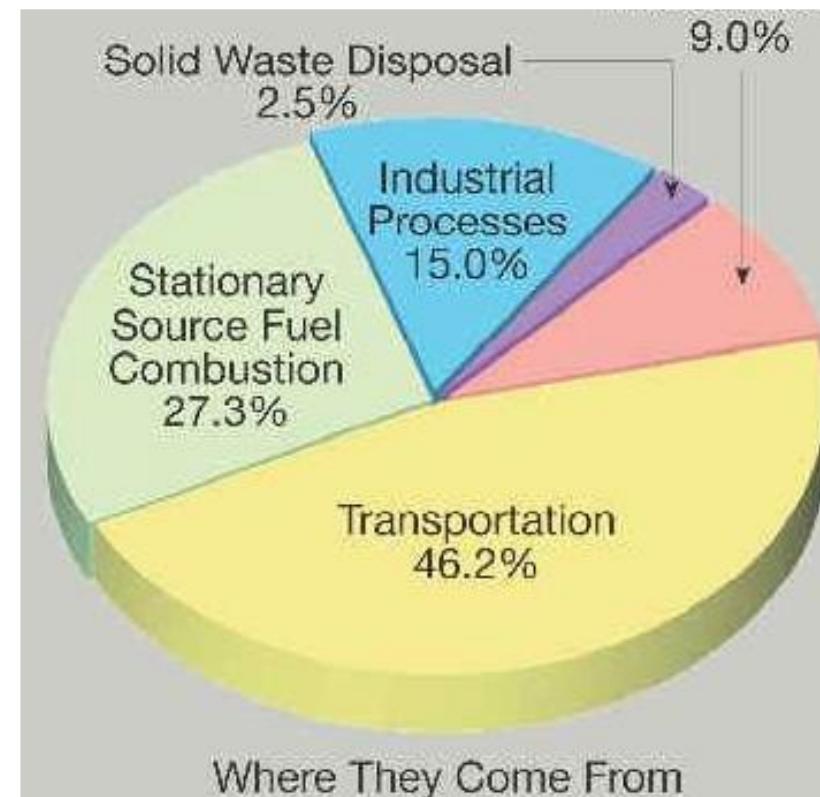
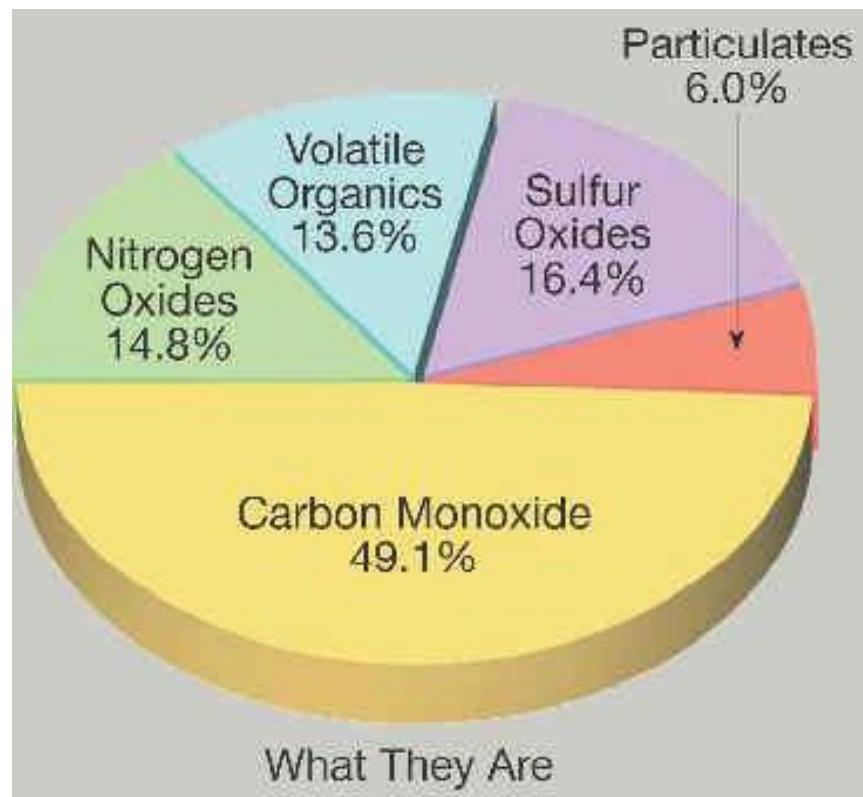
<u>Pollutant</u>	<u>Abbreviation</u>	<u>Type</u>
Carbon Monoxide	CO	Primary
Sulfur Dioxide	SO ₂	Primary
Ozone	O ₃	Secondary
Nitrogen Dioxide	NO ₂	Secondary
Hydrocarbon Compounds (also called VOCs – volatile organic compounds)	HC	Primary & Secondary
Particulate Matter	PM	Primary & Secondary
Lead	Pb	Primary & Secondary

Types of Pollutants

Primary pollutants are those gases or particles that are pumped into the air to make it unclean. They include carbon monoxide from automobile (cars) exhausts and sulfur dioxide from the combustion of coal. Primarily air pollutants can be caused by primary sources or secondary sources.

The pollutants that are a direct result of the process can be called primary pollutants.

A classic example of a primary pollutant would be the sulfur-dioxide emitted from factories.



Chemistry of Troposphere

❖ Air Pollutant

- An air pollutant is defined as the substance that is present in the atmosphere at a concentration that is sufficient to cause harm to human, other animals, vegetations or materials
- Approx 90% of all air pollution is caused by these primary air pollutant

1. Carbon monoxide (CO)

2. Sulfur dioxide (SO_2)

3. Nitrogen Oxides (NO_x)

4. Volatile Organic Compounds (VOCs)

5. Mostly Hydrocarbons (HCs)

6. Suspended particles

➤ In addition, Secondary pollutants are also present

➤ Harmful substances produced by chemical reactions between primary pollutant and other constituent of the atmosphere. e.g. H_2SO_4 , HNO_3 ; SO_4^{2-} and NO_3^- contribute to the acid rain

Ozone and other photochemical oxidants contribute to photochemical smog

Chemistry of Troposphere

❖ Carbon Monoxide

➤ Source of Carbon monoxide

➤ Main anthropogenic source of CO is the combustion of gasoline in automobile engines

1. Gasoline is a complex mixture of hydrocarbons (HCs)

2. If this is ignited in an adequate supply of oxygen; the products are CO_2 and H_2O



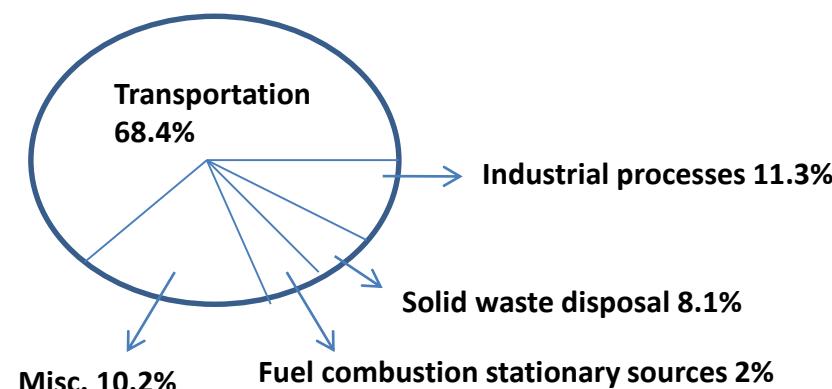
1. In the confined space of the internal combustion of engine O_2 supply is limited and combustion is incomplete. Thus CO is formed and released to the atmosphere in auto mobile exhaust



❖ However, the introduction of catalyst converter

reduce the CO emissions

❖ Natural source of CO into the atmosphere is CH_4 gas



Methane is also produced in the stomach in the cattle and sheep and finally released into the atmosphere

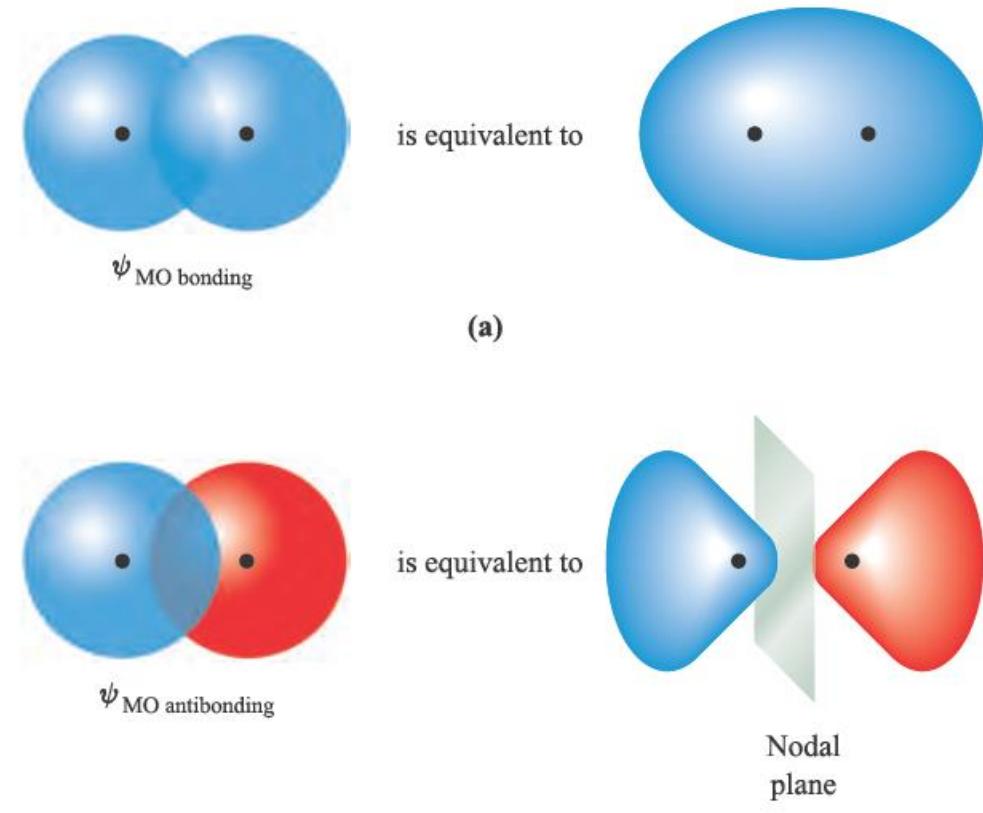
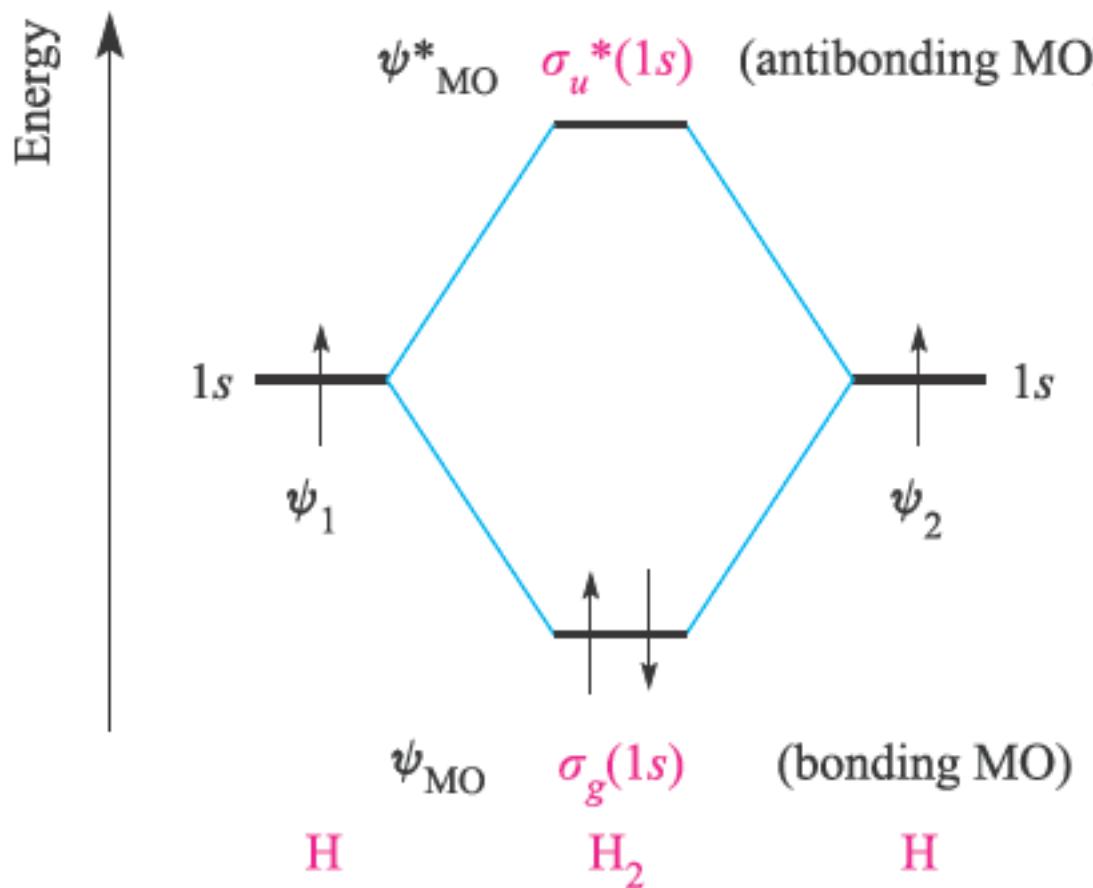
Carbon Monoxide

- ❖ Effect of CO on Human Health
 - Even though CO is the most abundant air pollutant, it is not very toxic at the levels usually found in the atmosphere, however if allowed to build up in a confined space, it can cause serious health problems
 - CO interferes with the oxygen carrying capacity of blood; normally hemoglobin (Hb) in red blood cells combine with oxygen in the lungs to oxyhemoglobin (HbO_2). The HbO_2 is carried in the blood stream to various parts of the body, where oxygen is released to the tissues
 - Carbon monoxide binds much more strongly to Hb than oxygen - Why?
 - If CO is present in the lungs, it displaces oxygen from Hb and thus reduces the amount of oxygen that can be delivered to the tissues

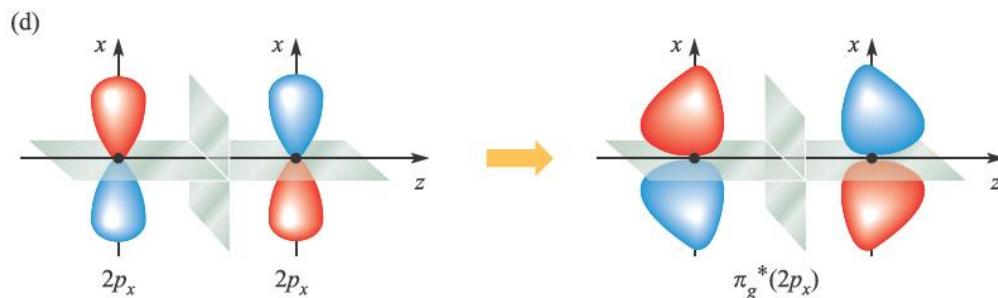
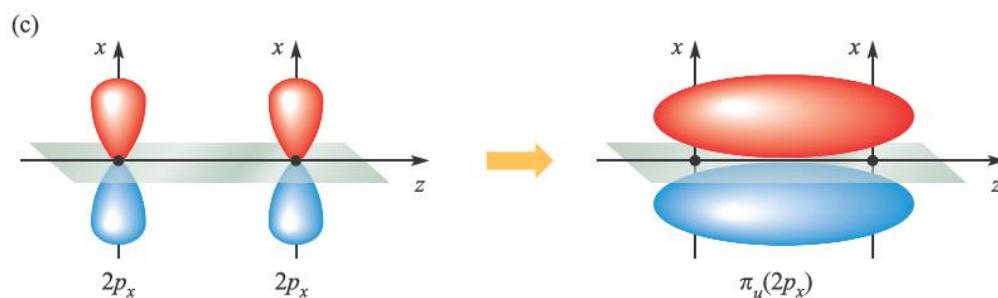
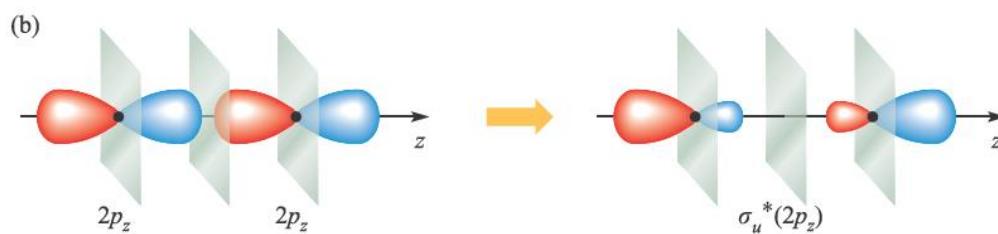
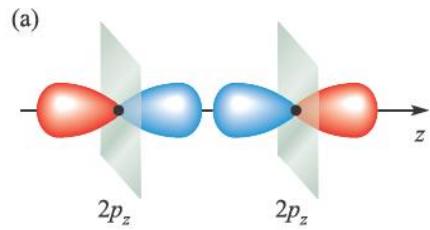


- ❖ Treatment of CO poisoning:
- ❖ Symptoms of CO poisoning: headache, dizziness, impaired judgment, drowsiness, slowed reflexes, respiratory failure and death

Molecular Orbital Theory



Molecular Orbital Theory



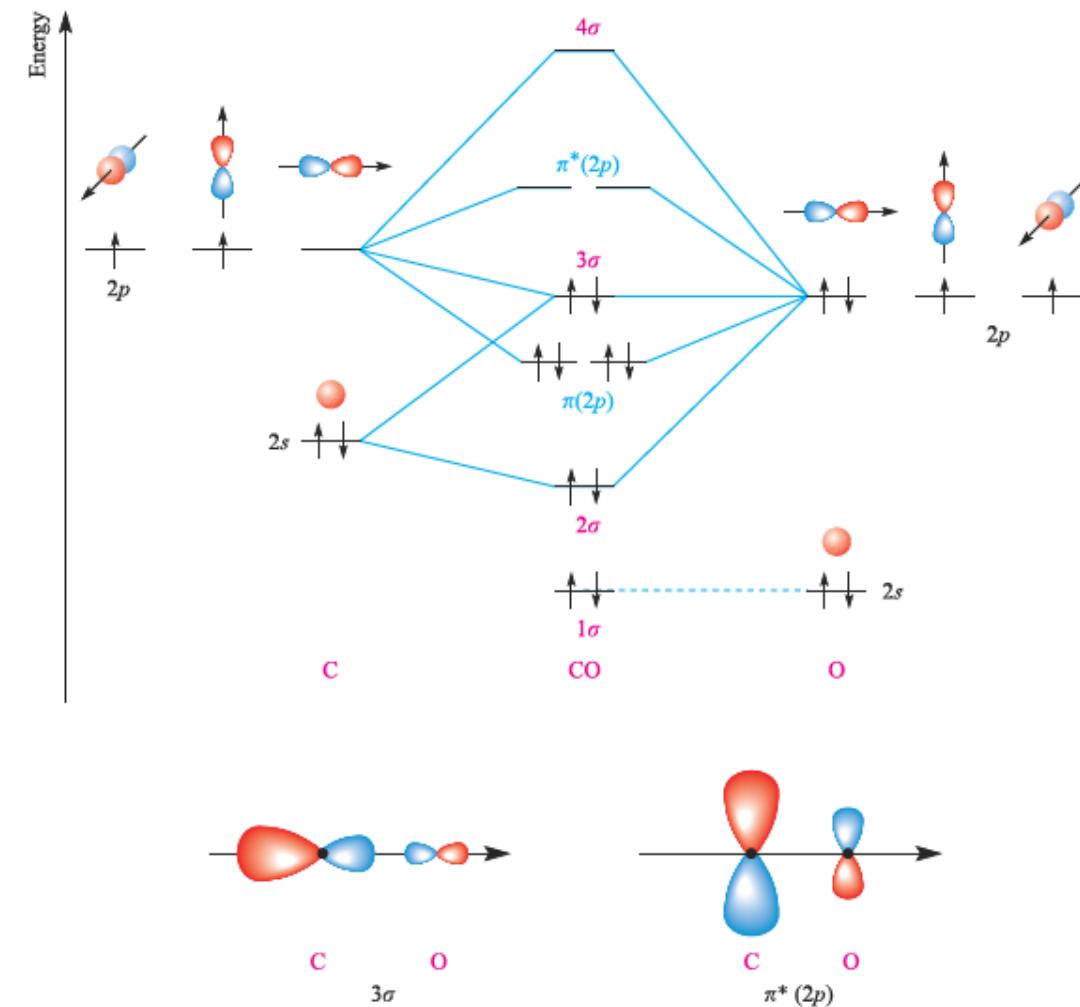
- ❖ Carbon monoxide binds much more strongly to Hb than oxygen – Why?

Molecular Orbital Theory

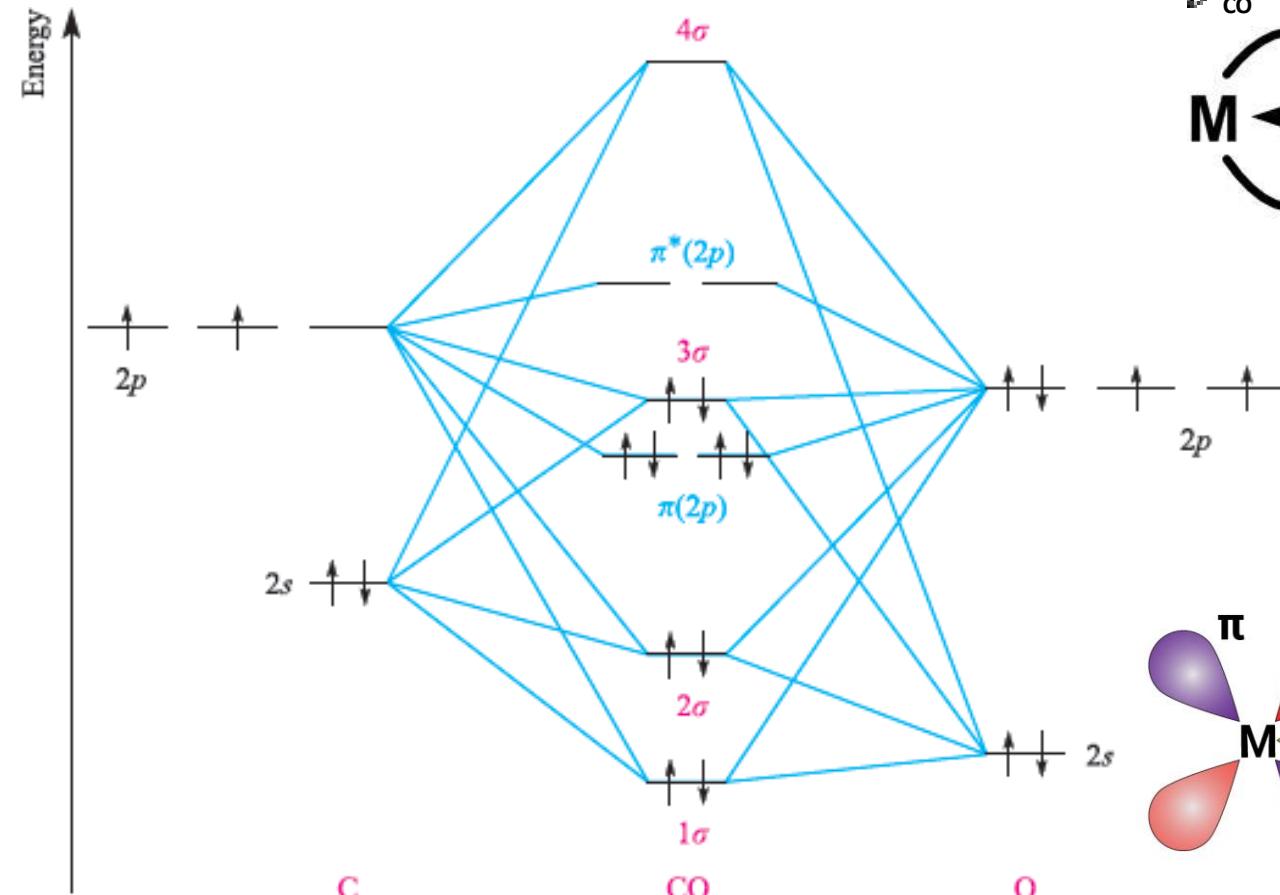
In order to investigate the way in which CO bonds to metals, we must appreciate the electronic structure of the CO molecule.

Before constructing an orbital interaction diagram for CO, we must take note of the following:

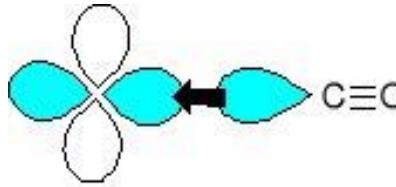
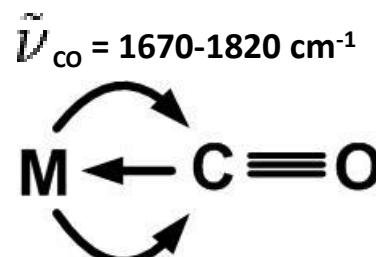
- ❖ $Z_{\text{eff}}(\text{O}) > Z_{\text{eff}}(\text{C})$;
- ❖ the energy of the O 2s atomic orbital is lower than that of the C 2s atomic orbital;
- ❖ the 2p level in O is at lower energy than that in C;
- ❖ the 2s–2p energy separation in O is greater than that in C



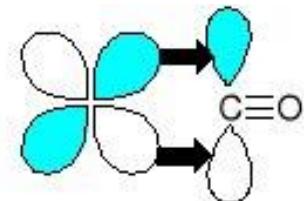
Molecular Orbital Theory



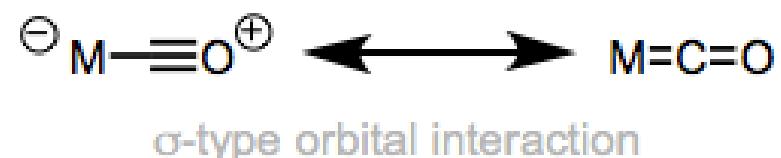
MO diagram



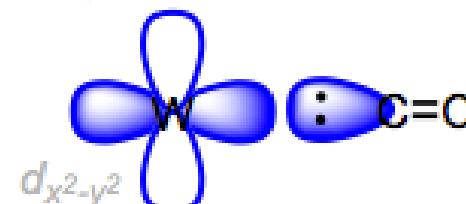
sigma bond



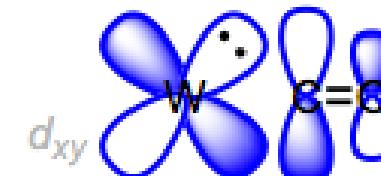
pi back-bond



σ-type orbital interaction



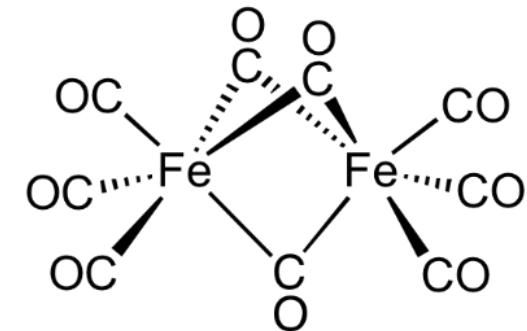
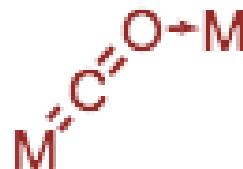
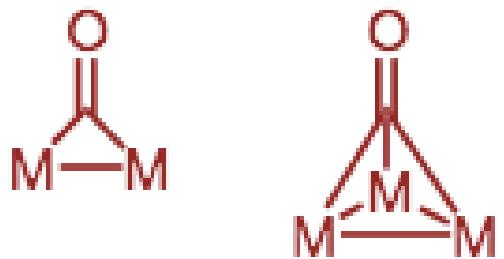
π-type orbital interaction



Electron donor! Electron acceptor!

Carbon Monoxide

Bridging modes of CO



❖ How the wave number of CO will change in metal carbonyl complexes

✓ Free CO

2143 cm^{-1}

$\text{V}(\text{CO})_6$

1976 cm^{-1}

$\text{Cr}(\text{CO})_6$

2000 cm^{-1}

$\text{Mn}_2(\text{CO})_{10}$

2013 cm^{-1}

$\text{Fe}(\text{CO})_5$

2023 cm^{-1}

$\text{Co}_2(\text{CO})_8$

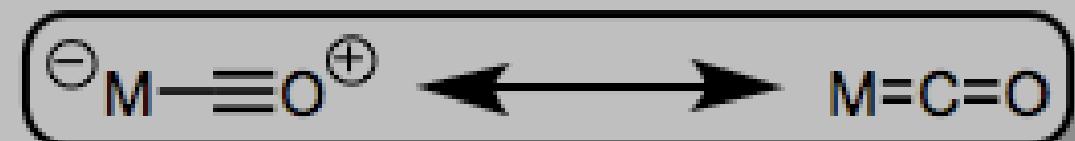
2044 cm^{-1}

$\text{Ni}(\text{CO})_4$

2057 cm^{-1}

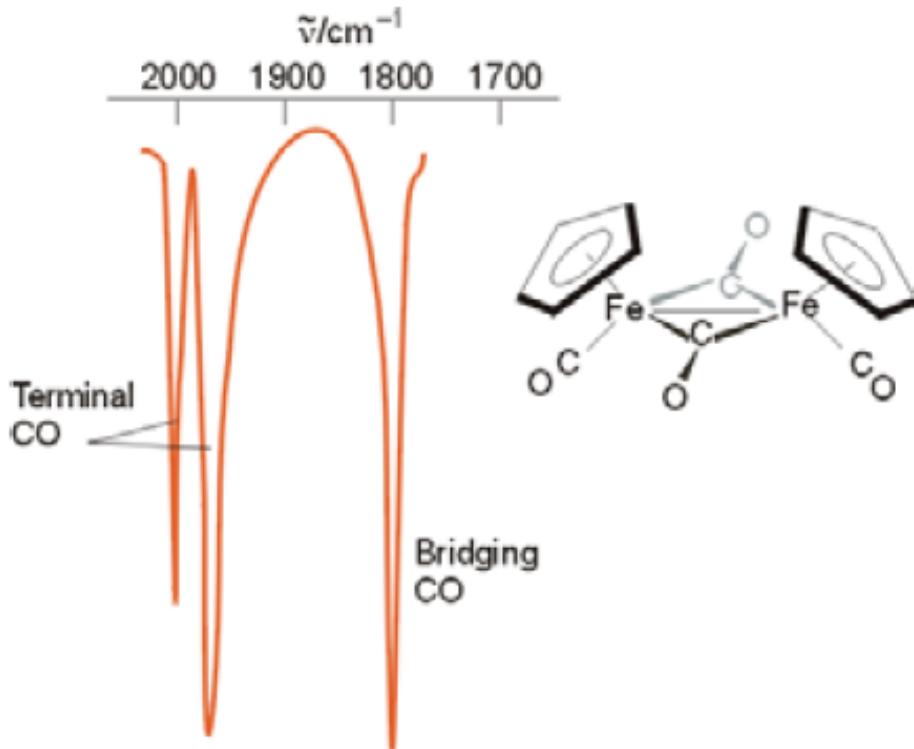
$[\text{Ti}(\text{CO})_6]^{2-}$

1747 cm^{-1}



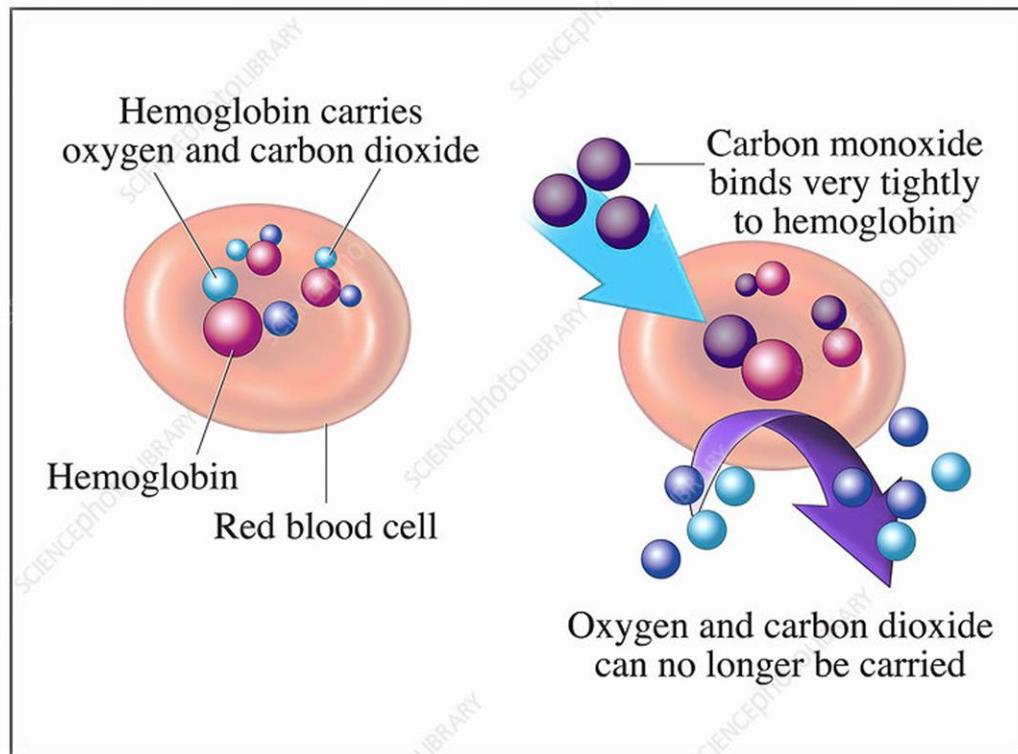
Example

- ◆ IR spectrum shows bands in the bridging and terminal regions
- ◆ Bridging IR band is single implying that the two COs are almost co-linear
- ◆ Two terminal IR stretch bands implying that the two COs are not co-linear

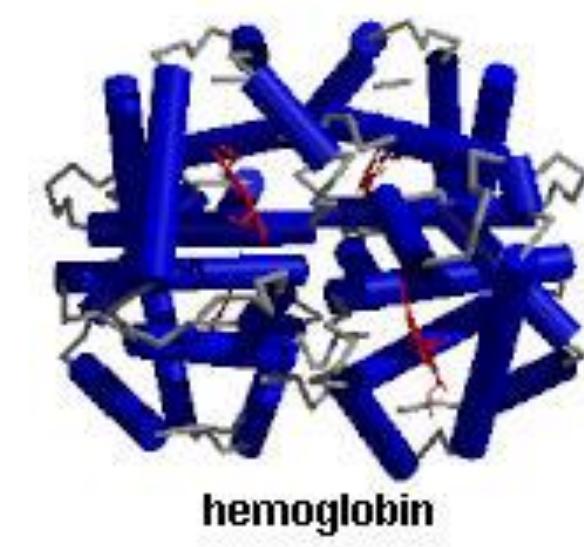
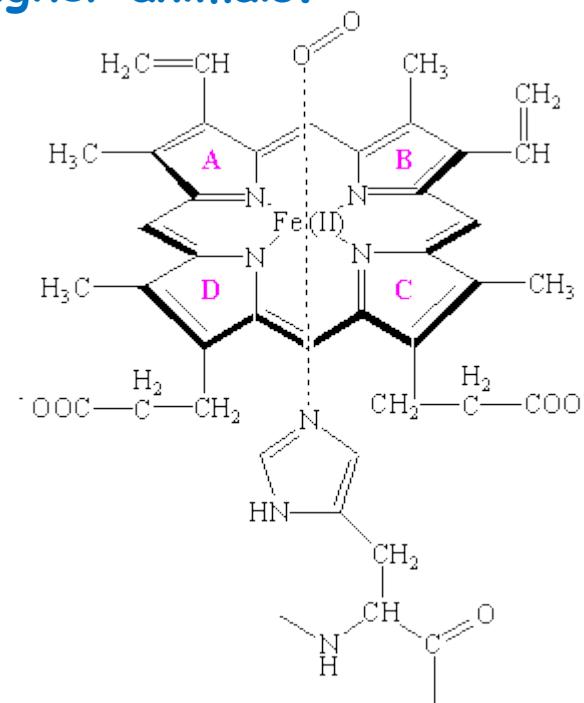


Carbon Monoxide

- Carbon monoxide binds much more strongly to Hb than oxygen - Why?

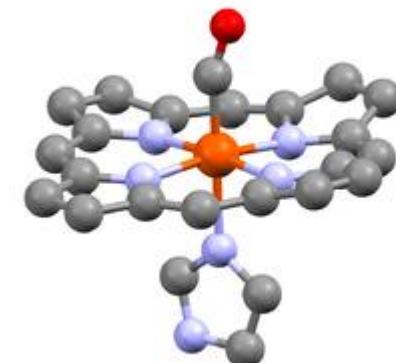
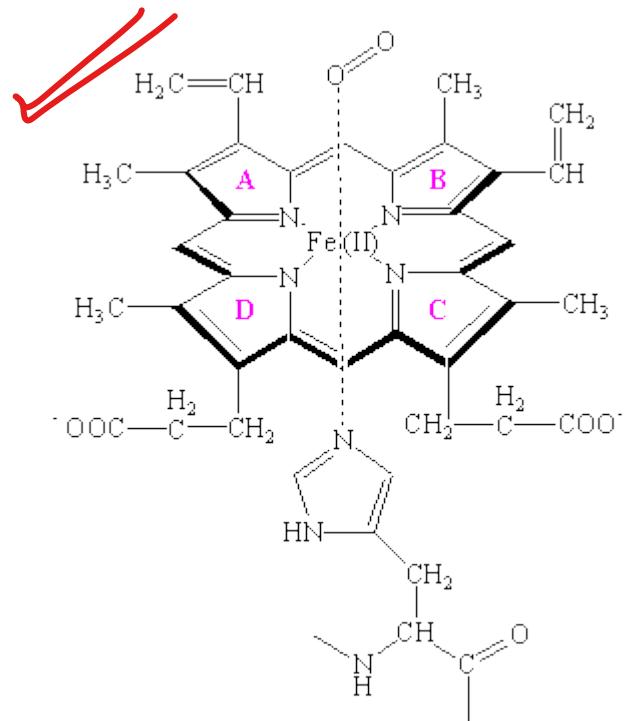


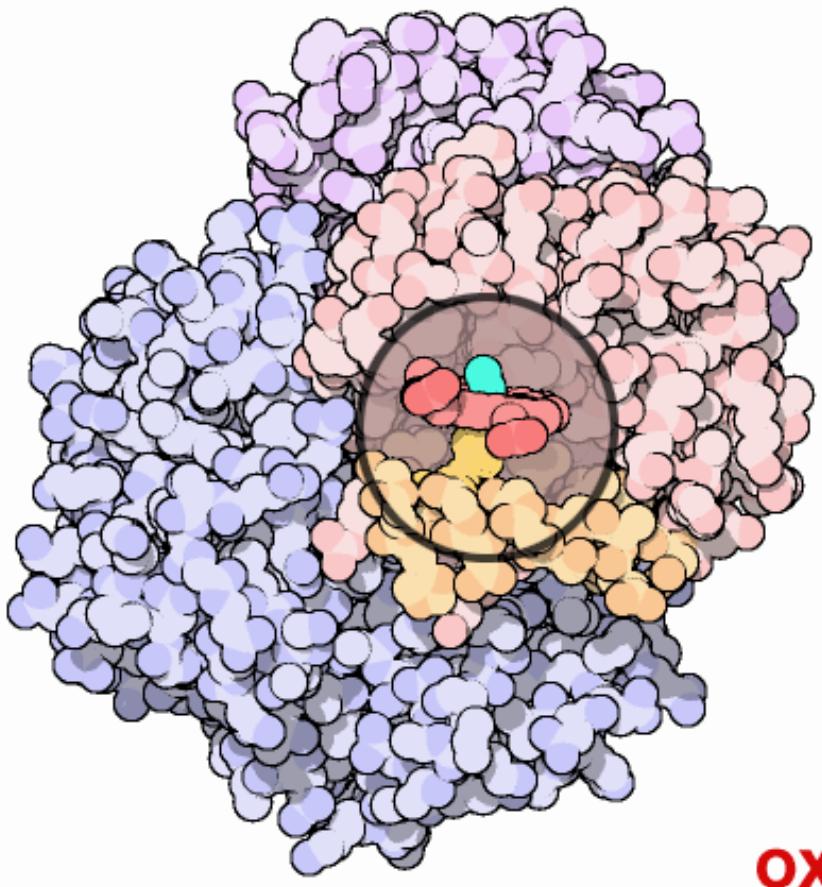
Myoglobin is a hemoprotein, isolated from the cells of vertebrate skeletal muscle that is both a structural and functional relative of hemoglobin, the oxygen-transport protein of the blood of higher animals.

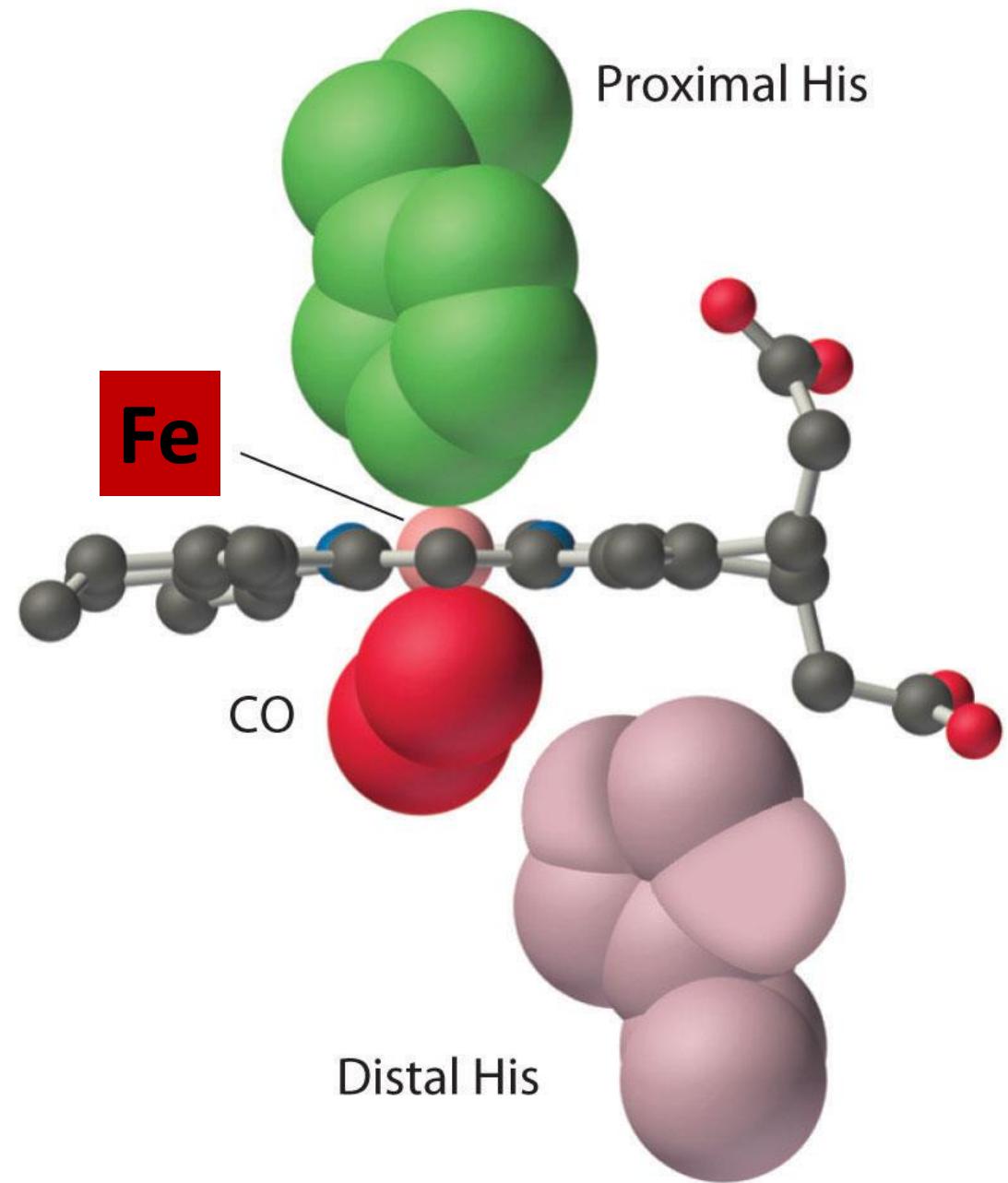
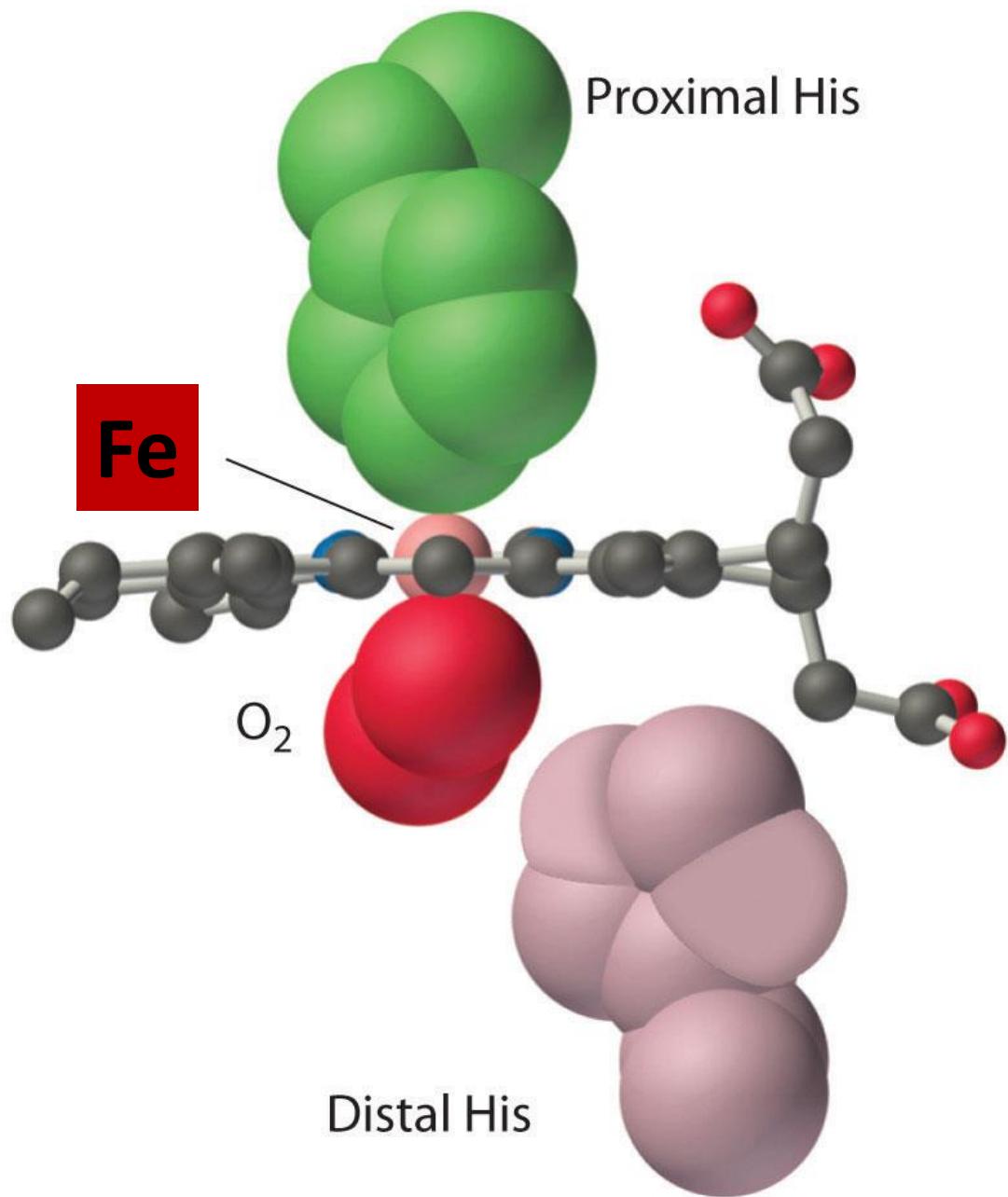


Carbon Monoxide

- At the center of the heme is an Fe(II) atom. Four of the six coordination sites around this atom are occupied by nitrogen atoms from a planar porphyrin ring
- The fifth coordination site is occupied by a nitrogen atom from a histidine side chain on one of the amino acids in the protein
- The last coordination site is available to bind an O₂ molecule
- The heme is therefore the oxygen-carrying portion of the hemoglobin and myoglobin molecules
- The structure of myoglobin suggests that the oxygen-carrying heme group is buried inside the protein portion of this molecule, which keeps pairs of hemes from coming too close together
- This is important, because these proteins need to bind O₂ reversibly and the Fe(II) heme, by itself, cannot do this. When there is no globin to protect the heme, it reacts with oxygen to form an oxidized Fe(III) atom instead of an Fe(II)-O₂ complex







Carbon Monoxide

Fate of Atmospheric CO

It is generally believed that CO is removed from atmosphere by reaction with hydroxyl radical.

Oxidized by reaction with hydroxyl radical



Production of hydroperoxyl radical



Additional reactions



Soil microorganisms metabolize CO

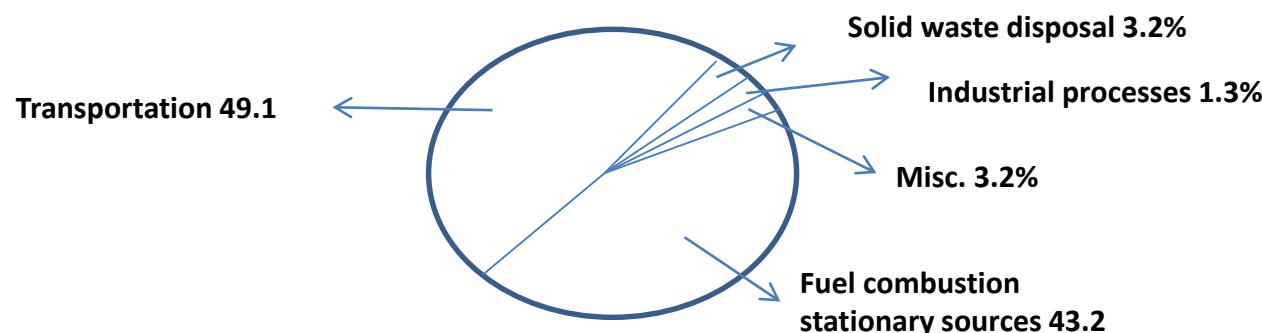
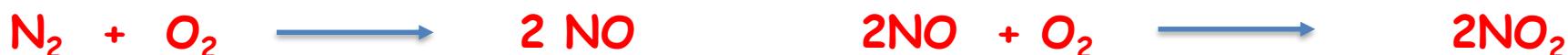
- Soil is a sink for CO

Nitrogen Oxides (NO_x)

- ❖ Nitrogen dioxide (NO_2) is the major pollutant in the atmosphere and is formed from nitric oxide (NO). Collectively nitrogen oxides are designated as NO_x

- Source of NO_x

- Anthropogenic NO_x enter the atmosphere from the combustion of fossil fuels by automobiles, aircraft and power plants
- At normal atmospheric temp. N_2 and O_2 does not react. However, at very high temp. atmospheric N_2 reacts with oxygen to give a series of complex reactions. Two gases combine to give NO



Nitrogen Oxides (NO_x)

- When NO is released, it combines rapidly with atmospheric oxygen to form NO_2 .
NO has an unpaired electron and can be written as NO^\bullet .

Bacterial decomposition of nitrogen containing organic matter in soil is another natural source of NO_x

❖ Fate of Atmospheric NOx

1. Regardless of its source, NO_2 ultimately removed from the atmosphere as nitric acid and nitrates in dust and rain fall. In a series of complex reactions involving hydroxyl radicals, NO_2 combines with water vapor to form nitric acid. The simplified overall reaction is



2. Much of the nitric acid in the atmosphere is formed within aqueous aerosols. If the weather conditions are right, the aerosols coalesce into larger droplets in clouds and the result is acid rain.

❖ Fate of Atmospheric NO_x

- ❖ Some of the nitric acid formed reacts with ammonia and metallic particles in the atmosphere to form nitrates



- ✓ Nitrates dissolve in rain and snow or settle as particle. The combine fallout contribute to acid deposition

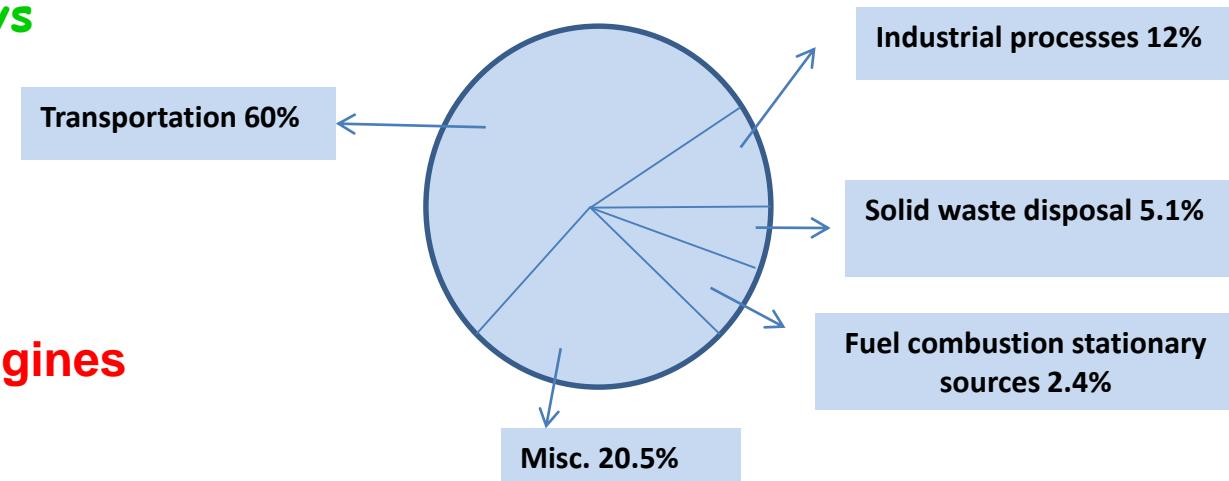
Effect of NO_x on Human Health and Environment

- NO₂ is red brown toxic gas and has unpleasant acrid odor. It can cause irritation of the eyes, inflammation of lung tissue, and emphysema.
- NO_x is a serious health problem because of its role in the formation of secondary pollutants associated with photochemical smog.
- ❖ Most of the research has concentrated on reducing automobile emission by means of the catalytic converter

Volatile Organic Compounds (VOCs)

- A great variety of VOCs, including many HCs enter the atmosphere from both natural and anthropogenic sources
- The petroleum industry is the main anthropogenic source of HCs in the atmosphere
- Gasoline is a complex mixture of many volatile HCs and in urban areas, gasoline vapors can escape into the atmosphere in several ways

1. When gas is pumped at gas stations
2. During filling of storage tanks
3. Unburned gasoline in exhaust
from automobiles and small combustion engines

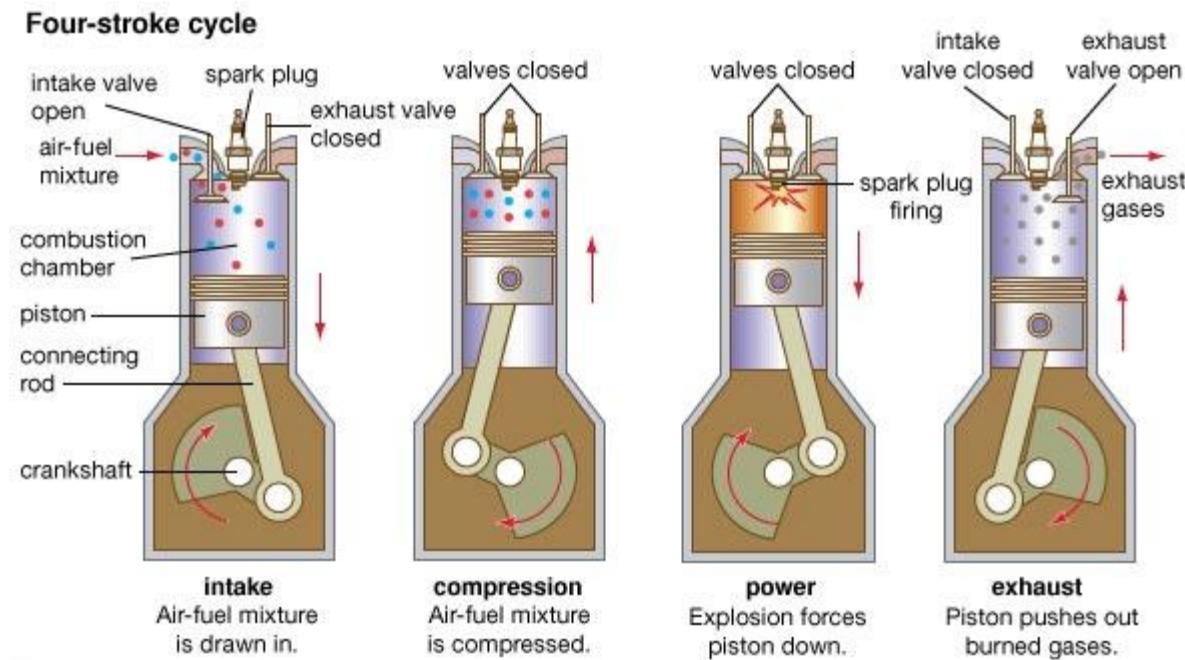


- ❖ In the natural world, the pleasant aroma of pine, eucalyptus and sandal wood trees are caused by the evaporation of VOCs called terpenes from their leaves
- ❖ Natural sources account for 85% of total emission; anthropogenic source contributes 15%

Volatile Organic Compounds (VOCs)

❖ Automobile Four-Cycle Internal Combustion Engine

- Gasoline powered four cycle internal combustion engine is predominant in more developed countries
- To know how NO_x, CO and HCs are produced through this we have to know how this engine works
- There are four steps in one complete cycle of the gasoline engine
- In the confined space of the internal combustion engine, oxygen is in limited supply and CO is formed and released to the atmosphere



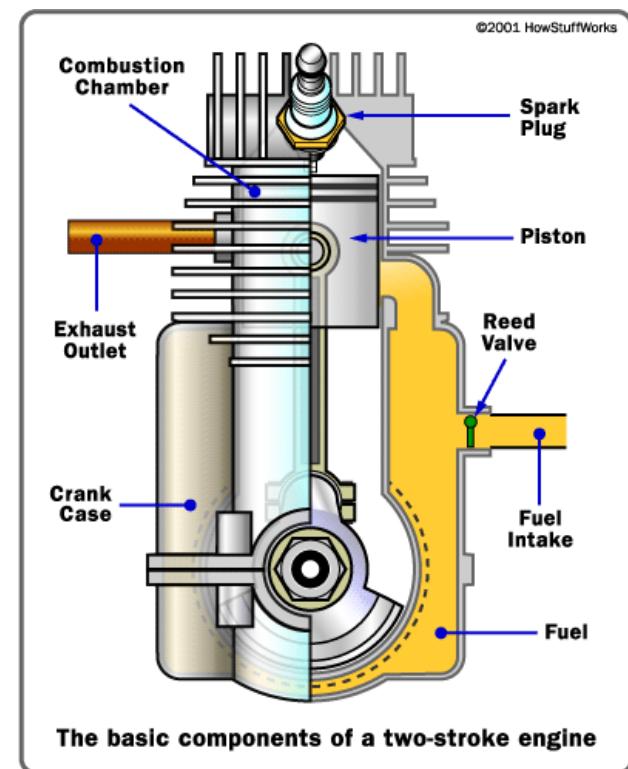
Volatile Organic Compounds (VOCs)

❖ Automobile Four Cycle Internal Combustion Engine

- In the internal combustion engine, temp and pressure is very high and NO is formed from N₂ and O₂. The unburned HCs are emitted with the burned gas as pollutant VOCs
- The air/fuel ratio has a dramatic effect on the emission of pollutants from the four cycle engine
- During the engine tune up, adjustment of the carburetor or the fuel injection system can greatly reduce emission of pollutant
- The ideal stoichiometric air/fuel ratio is 14.5
- Adjustment to a more fuel rich (lower air/fuel) ratio makes the car easier to start and decrease the emission of Nox and HCs; unfortunately it also decreases the fuel efficiency and the car will get fewer Km per liter. The emission of CO is also increased as air is less available
- Adjustment to a more air rich (higher air/fuel) ratio will make the car harder to start, although it increases fuel efficiency, the emission of Nox is increased
- The ideal ratio is a compromise between fuel efficiency and the emission of the lowest collective amount of pollutant

Volatile Organic Compounds (VOCs)

- ❖ Gasoline Powered Two Cycle Engine
 - ❖ Two cycle engine is used to power motor scooter, mopeds, snowmobiles. It is less complicated than the four cycle engine and also less expensive
 - ❖ It takes fuel, releases exhaust in the same stroke and emits from 25% to 30% of the fuel consumed as unburned HCs
 - ❖ The two cycle engine has no valves and that power is produced in one of two steps rather than one in four steps; this means the two cycle engine runs faster and hotter than the four cycle engine
1. In two cycle engine motor oil ; gasoline 1: 40 ratio
 2. Motor oil has C₁₈ to C₂₅ HCs i.e. higher molecular weight
 3. In two cycle engine, combustion takes place at a lower temperature than the four cycle engine
 4. Due to higher molecular weight motor oil is not vaporized and burned efficiently like gasoline
 5. Two step cycle requires that the exhaust gases from combustion are leaving the cylinder through the exhaust port while the fresh air/fuel mixture for the next power stroke is simultaneously entering the cylinder from the side arm



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 than 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			



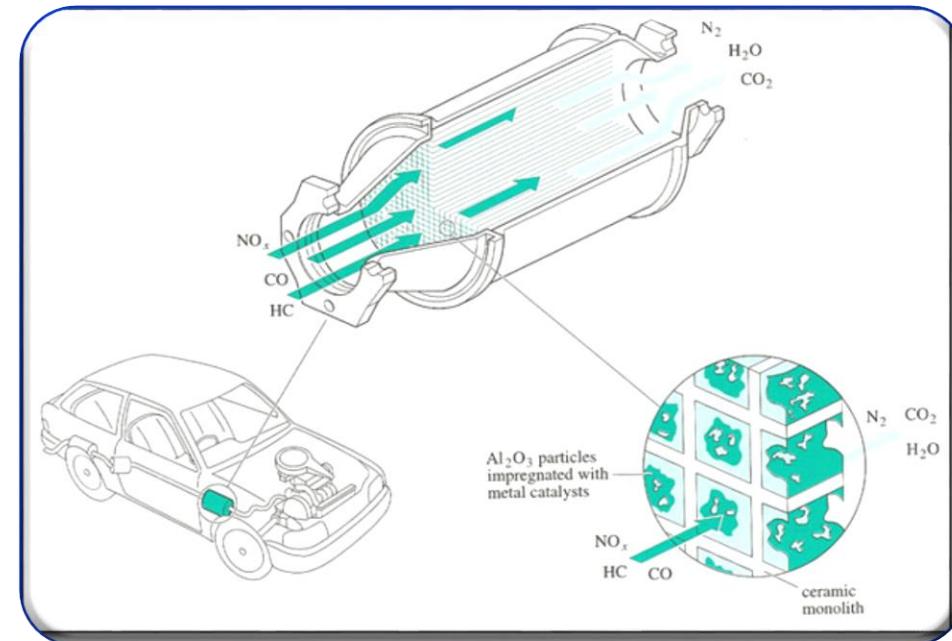
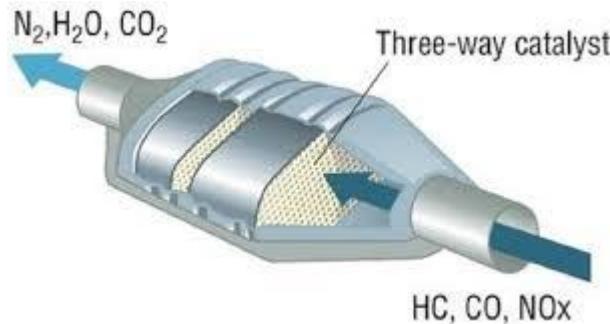
Automobile Pollutants

- 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 HC	HCs	CO	NOx	Evaporative HC	
<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 HC 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 NO_x to nitrogen gas by hydrogen generated at the surface of the Rh catalyst by the reaction of H₂O and unburned HCs



- Then air is injected into the exhaust stream to produce oxygen and CO oxidized to CO₂ in the presence of Pt and Pd catalyst



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

Rh, Pt, Pd Cat



- Oxidation of a typical gasoline HC, Octane occurs as

Pt, Pd Cat

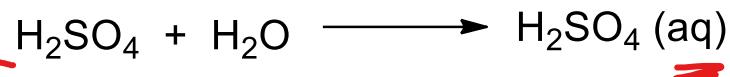
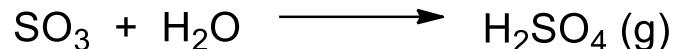
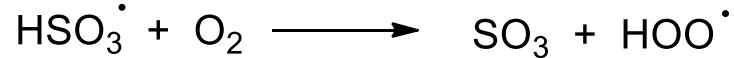
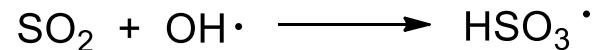


- Automobiles using catalytic converters must have their air/fuel ratio set as 14.8:1 to get optimum result. At room temp, the efficiency of the catalytic converter is nearly zero .

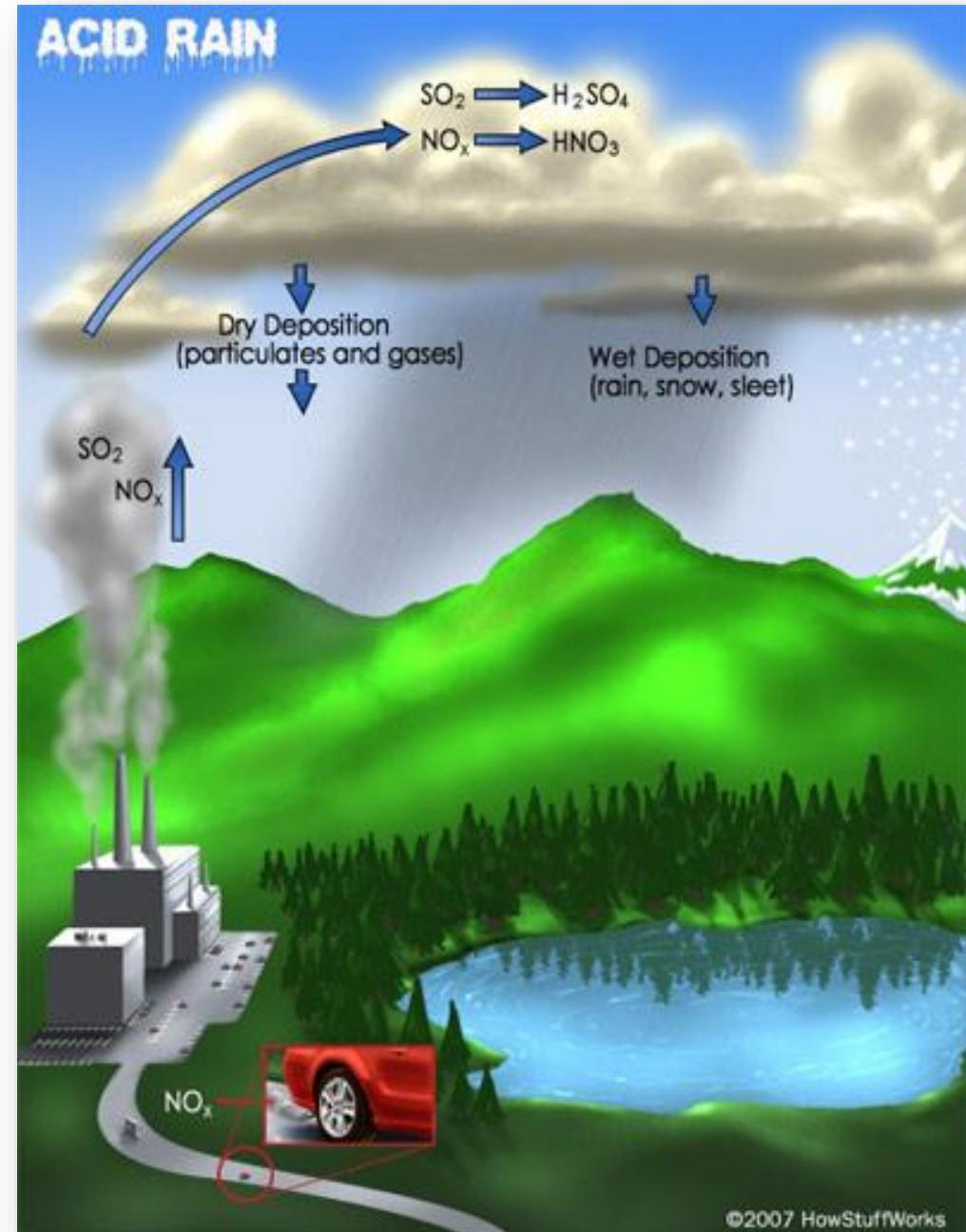
Sulfur Dioxide

- 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 : $\text{S} + \text{O}_2 \longrightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$
- H_2S (produced an end product of anaerobic decomposition of sulfur containing organic matter by microorganism) enter to the atmosphere to form SO_2
$$2\text{H}_2\text{S} + 3\text{O}_2 \longrightarrow 2\text{SO}_2 + 2\text{H}_2\text{O}$$
- 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 $\text{H}_2\text{SO}_4(\text{g})$. The mechanism involves hydroxyl radicals and the eqns.

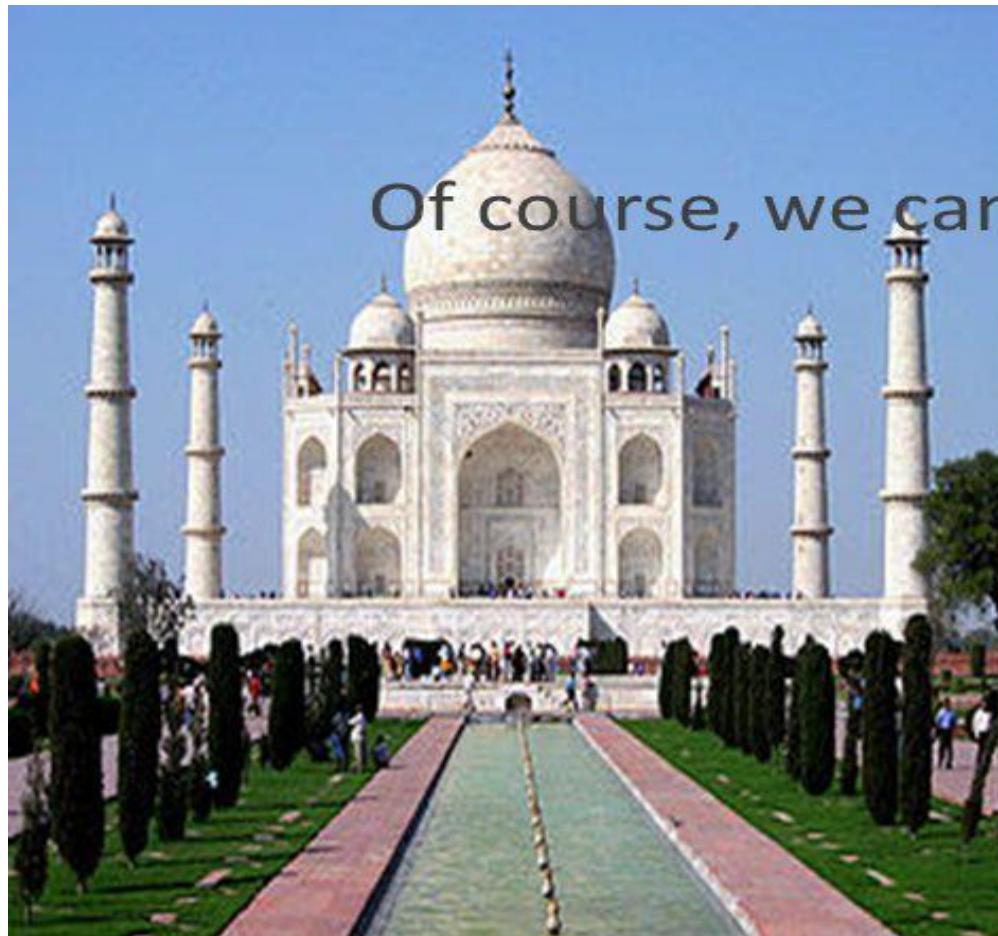
Fate of atmospheric SO₂: Acid Rain



- 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 SO₂ dissolves if there is a significant water in the air to form sulfurous acid
$$\text{SO}_2(\text{g}) + \text{H}_2\text{O} (\text{aq}) \longrightarrow \text{H}_2\text{SO}_3(\text{aq})$$
- The dissolved SO₂ is oxidized by trace amount of H₂O₂ and Ozone that are also present in the aerosol droplets to sulfate ions (SO₄²⁻)
- $\text{HSO}_3^- + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{HSO}_4^-$
 $\text{HSO}_3^- + \text{O}_3 \longrightarrow \text{O}_2 + \text{HSO}_4^- \quad \}$



Effect of Acid Rain



Original color of Taj Mahal



Taj Mahal after the
constant effect of acid rain

Effect of SO₂ on Human Health and Environment

- SO₂ 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
- SO₂ also harmful to plants. Crops such as barley, alfalfa, cotton and wheat are particularly adversely affected

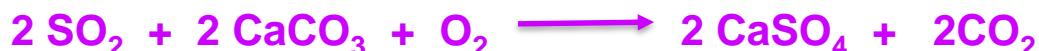
❖ How to control SO₂ emissions

1. Sulfur can be removed from coal before combustion.

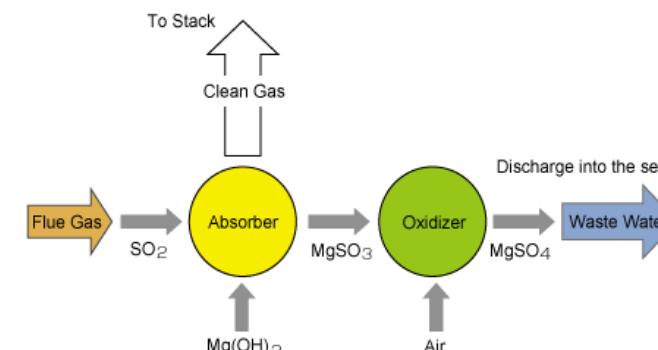
2. SO₂ can be removed from the smoke stack after combustion but before it reaches to atmosphere

❖ 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 (CaCO₃) or dolomite [Ca•Mg(CO₃)₂] or both. On heating the basic CaCO₃ with acidic SO₂ in presence of O₂ to form CaSO₄



IMP.



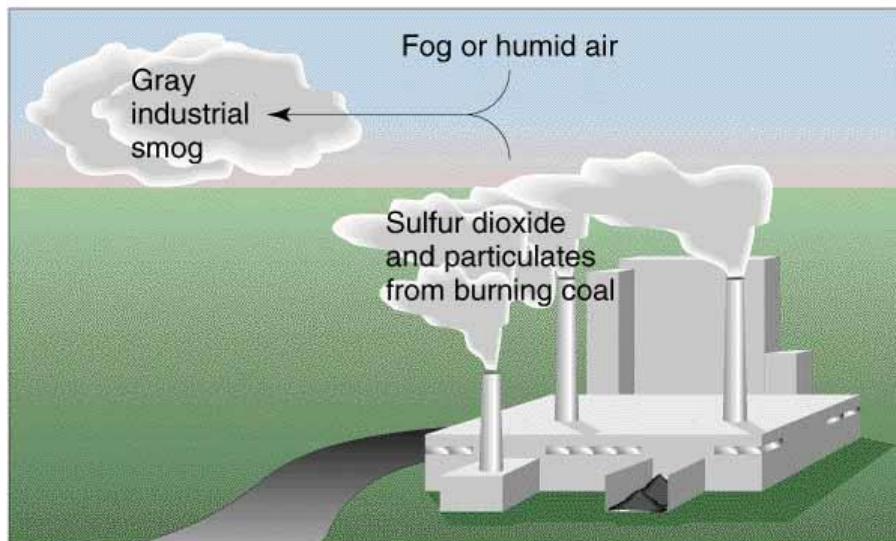
Industrial Smog

- 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

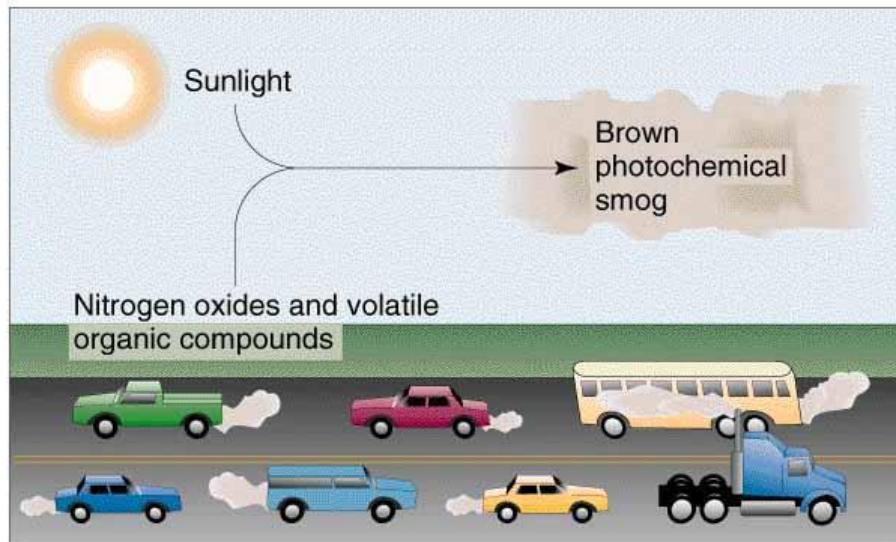
❖ Photochemical Smog

- ❖ 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



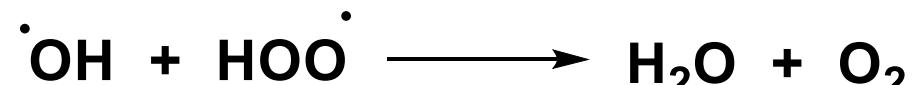
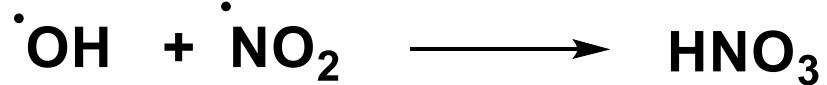
(b) Photochemical smog



Production of Hydroxyl Radicals

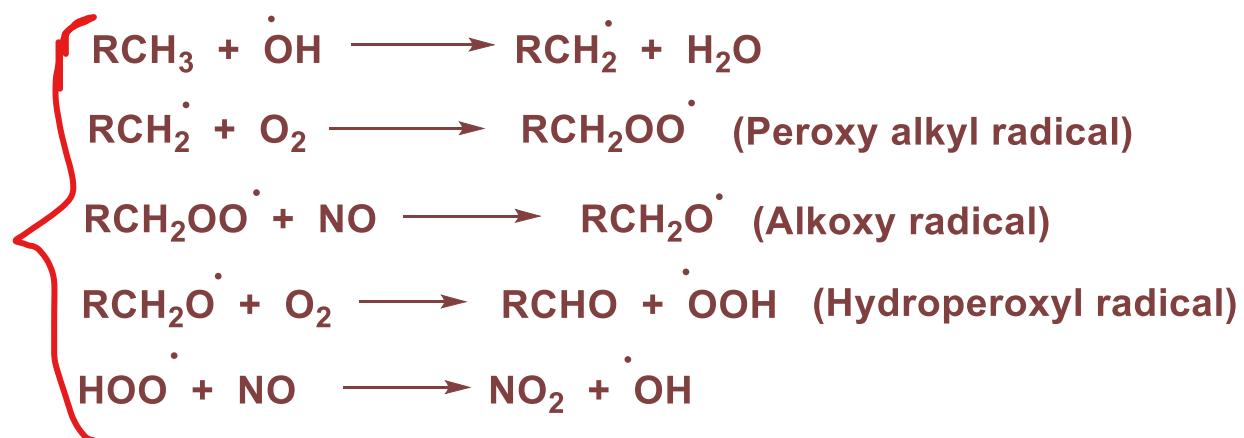
- By the time sunlight reaches the surface of the Earth, all of the light energy UV light has been absorbed in the stratosphere
 - NO_2 is the only automobile emission that is capable of absorbing visible light that reaches the Earth surface
- $$\left\{ \begin{array}{l} \text{➤ } \text{NO}_2 + \text{sunlight} (< 320 \text{ nm}) \longrightarrow \text{NO} + \text{O} ; \quad \text{O} + \text{O}_2 \longrightarrow \text{O}_3 \\ \text{➤ } \text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2 \end{array} \right.$$
- The ozone produced absorbs light in the blue region of the visible spectrum ($< 320 \text{ nm}$) and photo dissociates:
 - 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)
 - $\text{O} + \text{H}_2\text{O} \longrightarrow 2\text{OH}^\bullet$ 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



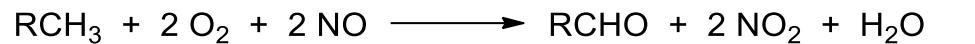
❖ The products are very soluble in water and are removed from troposphere during precipitation

- Unburned HCs in automobile exhausts (RCH_3) react with hydroxyl radical to form a number of secondary pollutants including HC radicals $\text{RO}_2\cdot$. This radical then reacts with NO to form aldehydes and the hydro peroxide radical $\text{HO}_2\cdot$



Production of Hydroxyl Radicals

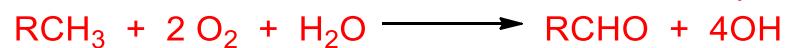
- ❖ Each step in this reaction produces a radical. The overall reaction is can be summarized as



(1)



(2)



- ❖ 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

Reaction of Hydroxyl Radicals with HCs

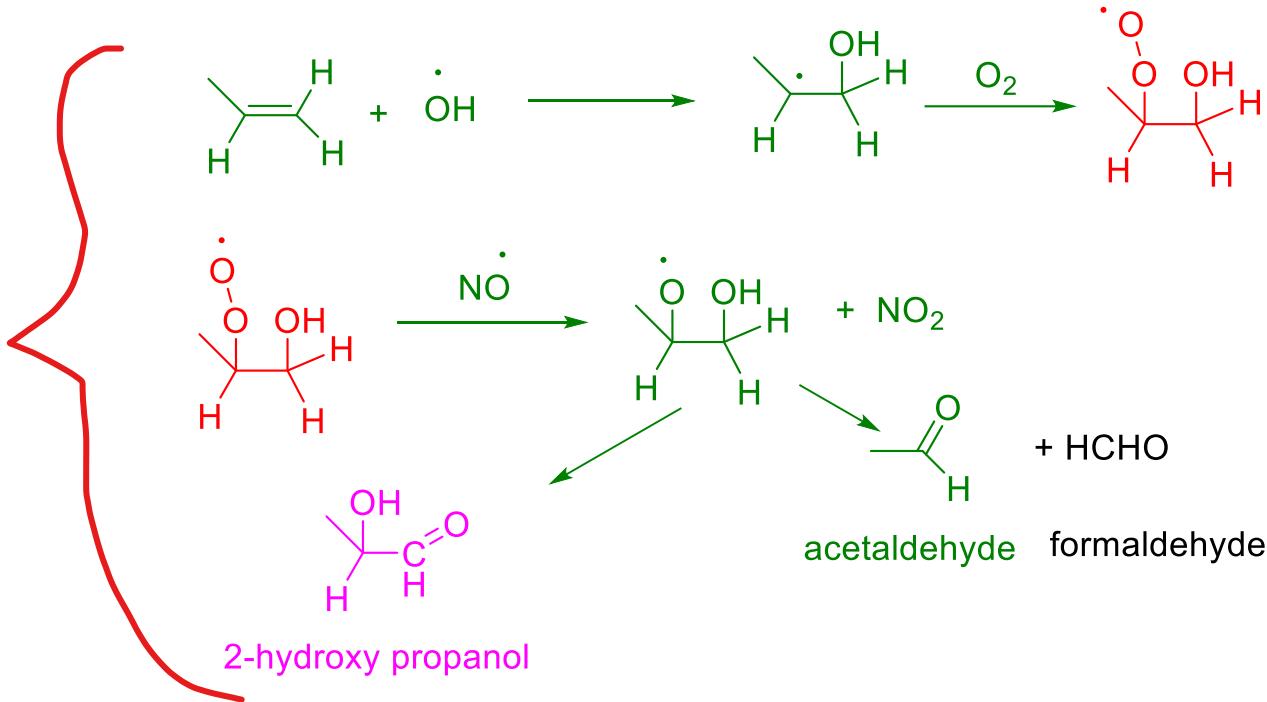
Compound	Bond	Energy KJ/mol
Methane	CH ₃ -H	427
Ethane	CH ₃ -CH ₂ -H	406
Propane	CH ₃ -CH ₂ -CH ₂ -H	393
Methanol	HOCH ₂ -H	393
Benzene	H ₅ C ₅ C-H	427
Toluene	H ₅ C ₆ H ₂ C-H	326

- The dissociation reaction is $\text{R}-\text{H} \longrightarrow \text{R}^\bullet + \text{H}^\bullet$
- The bond dissociation energy depends how the R radical is stabilized $3^\circ > 2^\circ > 1^\circ$ i.e., a tertiary C-H bond more easily dissociate than secondary C-H bond
- For benzene, the C-H has high dissociation energy as the aromatic carbon is sp² which mean sp² C-H bonds are much stronger than aliphatic C-H bond due to higher s character
- Higher reaction rate (low dissociation energy) are observed for toluene or xylene as the C₆H₅CH₂• can be stabilized by adjacent aromatic ring

Reaction of Hydroxyl Radicals with HCs

❖ Addition to the double bond

- The reaction of hydroxyl radicals with alkenes proceeds at even a faster rate than the hydrogen abstraction for HCs
- This reaction is not a hydrogen atom extraction but rather an addition of the hydroxyl radical to the double bond

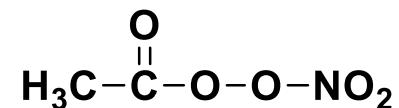
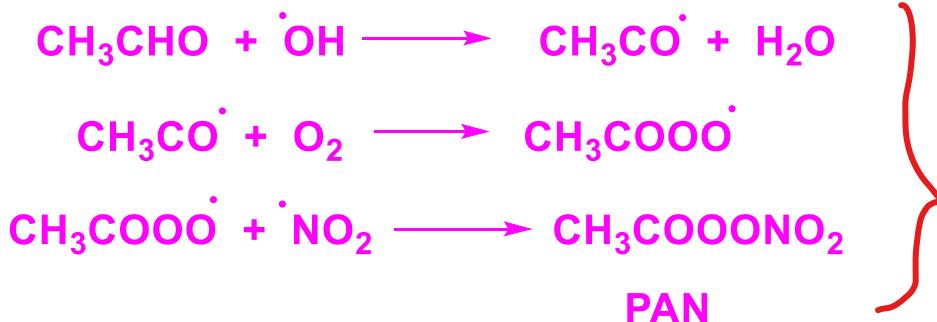


- The NO₂ produced in this reaction can go on to make more ozone and the products of this addition reaction i.e., acetaldehyde, formaldehyde, 2-hydroxypropanol all go on to form other pollutant in secondary smog forming reactions



Secondary Smog Forming Reactions

- The products formed in the previous reactions can undergo further reactions to the troposphere. The following reaction sequence takes place for all aldehydes formed. Acetaldehyde is used as example



Peroxyacetyl nitrate

PAN

- PAN is the component of smog that causes major eye irritation. PANs are relatively stable molecules and have long lifetimes in cooler air

- Ozone, aldehyde and PANs all contribute to the harmful effects of photochemical smog, but ozone the pollutant produced in greatest quantity causes the most serious problems in the troposphere

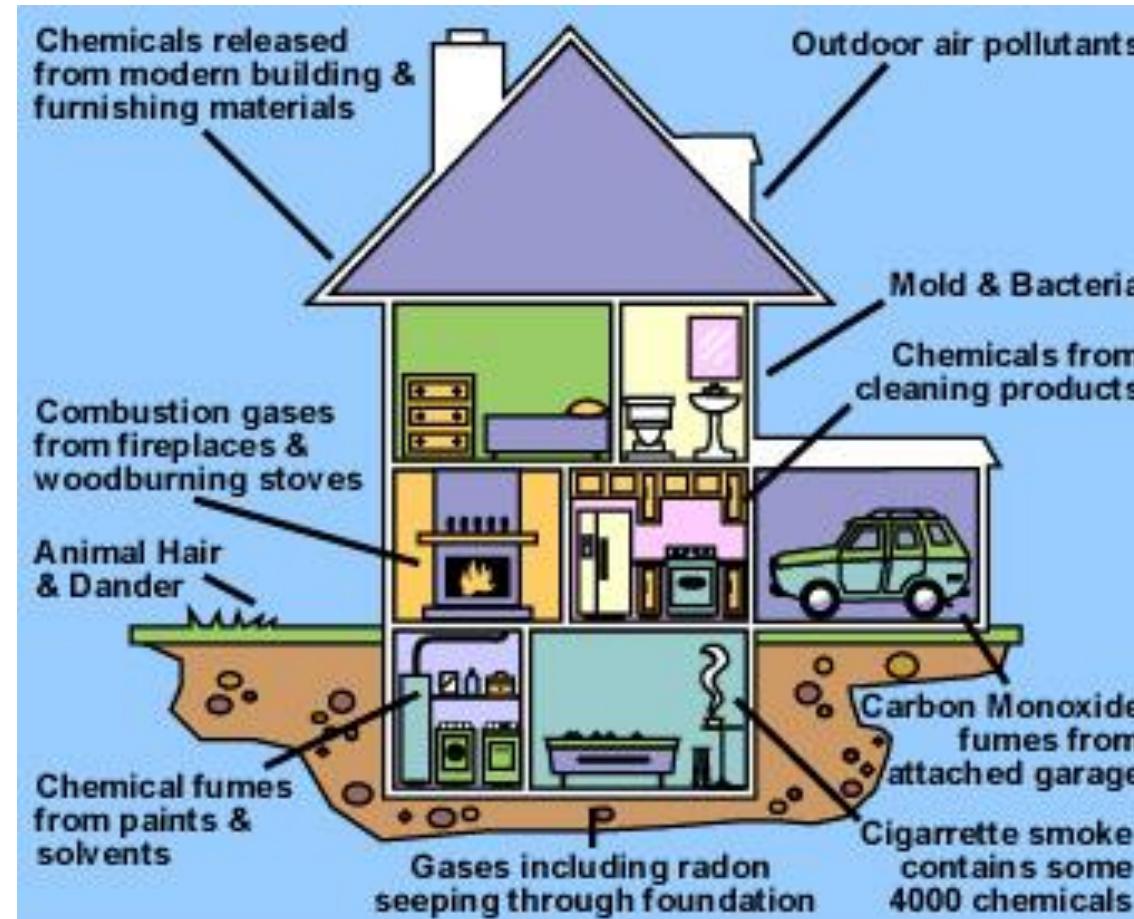
- Ozone in the stratosphere protect us from damaging UV radiation from Sun

- Ozone is powerful oxidizing agent and cause irritation in eyes and nasal passages

- Ozone is also very toxic to plants

Indoor Pollution

- One can expect to be safer from air pollutant indoors, but in todays well sealed homes and offices, this is often not the case
- In buildings where there is little or no circulation or fresh air, pollutants may accumulate to dangerous level

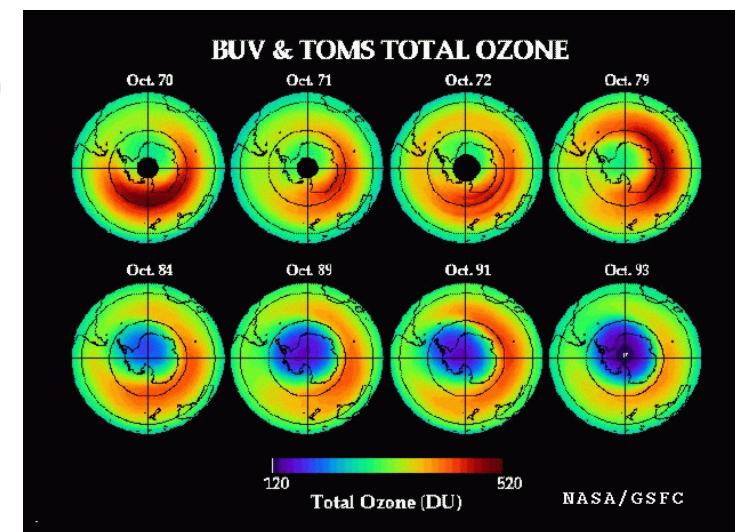
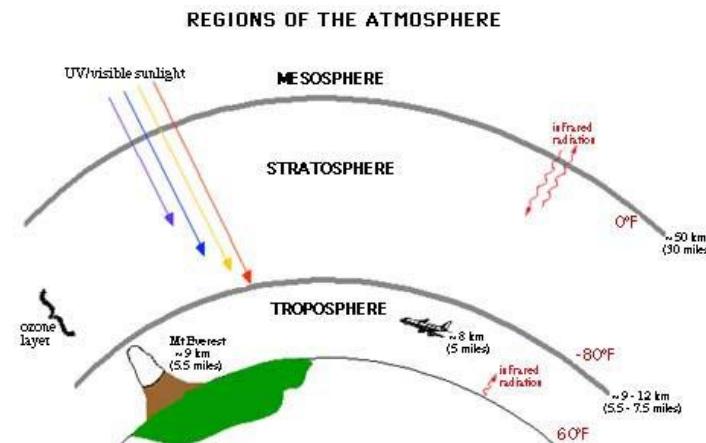


Chemistry of the Stratosphere

- Today the ozone layer is considered the Earth's natural sun-screen because it filtered harmful UV radiation before it can reach the surface of the Earth
- A substantial reduction in the amount of ozone in the ozone layer could threaten all life on Earth

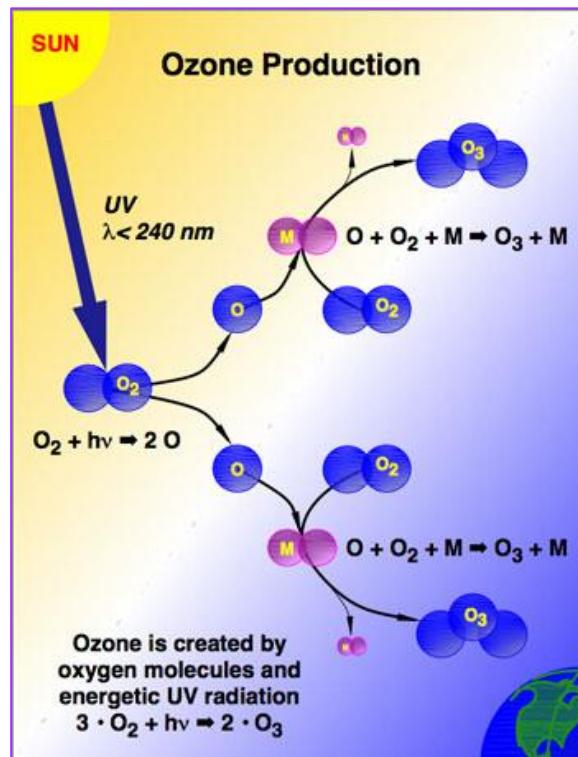
Dobson Unit

- The Dobson Unit (DU) is used to describe the amount of ozone in the stratosphere
- It is named under after Gordon M. B. Dobson who built the first instrument to measure the total abundance of ozone from the ground
- **1 DU = 2.7×10^{16} ozone/sq centimeter**
- In the past, the average amount of ozone covering the Earth was more than 270 DU
- In 2000, the average abundance of ozone from 90° N to 90° S was 293.4 DU
- However, the amount of ozone over the Antarctic is 220 DU which is referred to the **ozone hole**



The production of Ozone the Stratosphere

- In the absence of pollution, ozone (O_3), is not present to any appreciable amount in troposphere but occurs naturally in the stratosphere
- Ozone's concentration is greatest an altitude of 20 to 30 km from the Earth's surface
- The ozone layer is formed when ordinary molecules of oxygen gas (O_2) in the stratosphere absorbs UV radiation from the sun wavelength less than 240 nm and this dissociate O_2 to single oxygen atom (O)



- Single oxygen atoms are very reactive and immediately combine with O_2 to form O_3 : $O + O_2 + M \longrightarrow O_3 + M + \text{Heat}$ (fast)
- M can be a third molecule (N_2) present in the atmosphere
- The heat generated by this reaction is carried away by the third molecule
- At the same time the ozone formed is absorbing UV radiation very strongly with wavelengths of 220-330 nm to be broken down to an oxygen molecule and oxygen atom
- Also, when O_3 encounters an oxygen atom, two can combine to form two O_2 molecules
- A dynamic equilibrium is established

The production of Ozone the Stratosphere

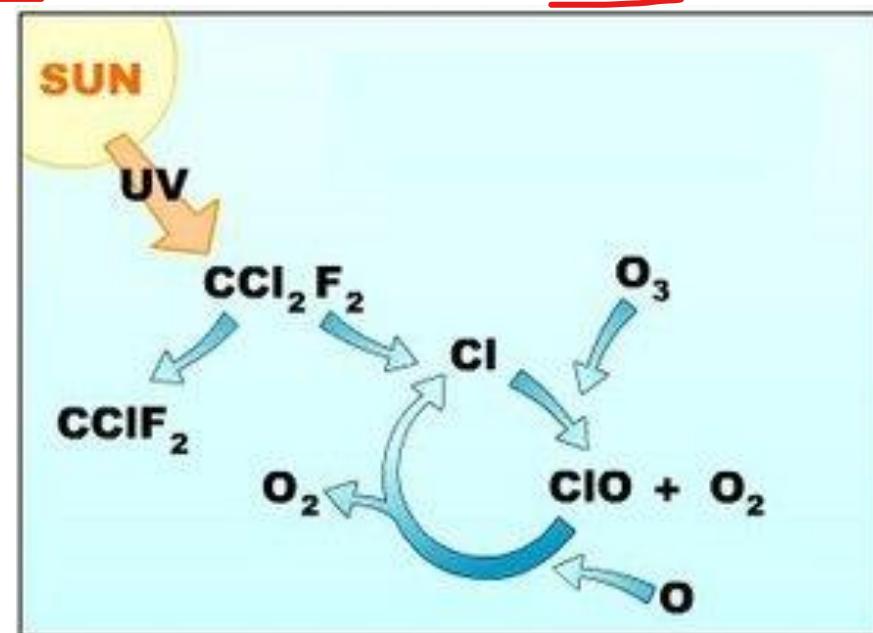
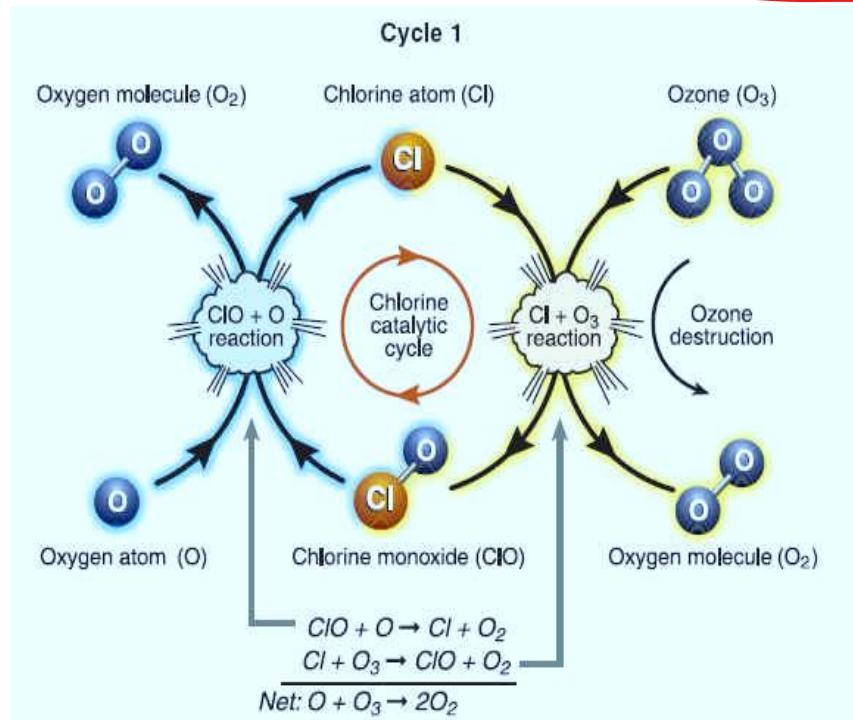
Common names for the UV spectrum			
$\lambda(\text{nm})$	Name	Species absorbing	Location
10-240	Far UV	O_2, N_2	Thermosphere
250-290	UV-C	O_3	Stratosphere
290-320	UV-B	O_3	Stratosphere, troposphere
320-380	UV-A	NO_2	Polluted troposphere
400-750	Visible	Many	Earth's Surface

Catalytic destruction of Ozone

- Ozone is very reactive molecule and is termed a **meta-stable** molecule i.e. it **decomposes slowly in contact with a molecule of another gas**
- There are number of number of species react efficiently by abstracting an oxygen atom from the ozone molecule. Say "X" designates the reactive species. Thus, the reaction steps are
 - i) $\text{X} + \text{O}_3 \longrightarrow \text{XO} + \text{O}_2;$
 - ii) $\text{XO} + \text{O} \longrightarrow \text{X} + \text{O}_2$
- These are the additional steps for ozone destruction compare to the steps discussed earlier

The production of Ozone the Stratosphere

- So, the sum of above two reactions is $O_3 + O \longrightarrow 2O_2$
- The overall reaction does not contain the X species, because X is not consumed in the reaction. It acts as a catalyst for the destruction of ozone
- "X" lowers the activation energy and atomic oxygen is required to regenerate X
- The catalytic species "X" can be i) Hydroxyl radical, ii) nitric oxide, iii) Chlorine , and iv) bromine atoms



DESTRUCTION OF OZONE BY CFC

Catalytic destruction of Ozone

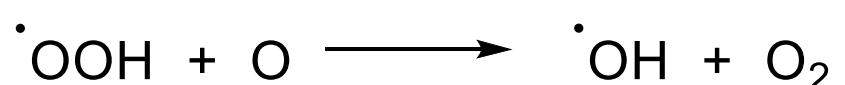
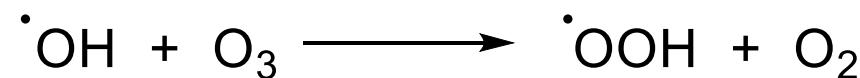
Hydroxyl Radical Cycle

- Hydroxyl radical ($\cdot\text{OH}$) can be produced by two different photochemical process. The first is hydrogen abstraction with either water or methane

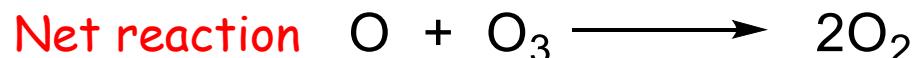


- The second is photolysis of water $\text{H}_2\text{O} + h\nu \longrightarrow \text{H}\cdot + \cdot\text{OH}$

- Hydroxyl radical is responsible for nearly one half of the total ozone destruction in the lower stratosphere



One $\cdot\text{OH}$ radical can have as many as 40 cycles i.e., 40 ozone molecule can decompose



Catalytic destruction of Ozone

Nitric Oxide Cycle

- Auto mobiles and truck engines releases large quantities of nitric oxide (NO) into the troposphere
- Nitric oxide is converted to NO_2 and eventually to HNO_3 which fall down as rain fall before reaching to stratosphere
- N_2O is much less reactive than NO and reaches to stratosphere .
- Above 30 km the N_2O can absorb high energy photons to produce molecular nitrogen and an excited oxygen atom (O^*)

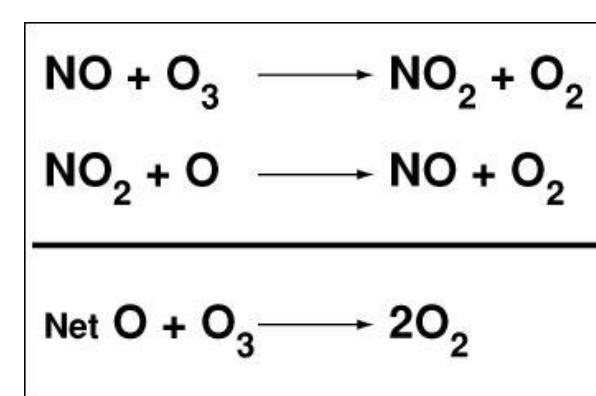


- Below 30 km in the stratosphere, the excited state oxygen reacts with the N_2O to produce NO .



- NO can act as X in the catalytic process

1 NO_x radical can catalyze the destruction of 10,000 ozone molecules



Catalytic destruction of Ozone

The Chlorine Cycle

- The major sources of stratospheric chlorine and bromine have been the anthropogenic **chlorofluoro carbons (CFCs)** and bromine containing halons (haloalkanes)
- CFCs used as refrigerants, propellant for aerosol spray and solvents for cleaning electric circuit
- Halons are used in commercial fire extinguisher system
- CFCs and halons are nontoxic and nonflammable which make them superior to other gases that were used for the same application
- CFCs are so unreactive they don't break down when released and can persist in the troposphere for more than 100 years. Over time, air currents carry them into stratosphere
- In 1974, two chemists F. S. Rowland and Mario Molina predicted that when exposed to UV radiation in stratosphere, CFCs would break down to form chlorine radical ($\text{Cl}\cdot$)
- Each chlorine radical involved in a chain reaction has the potential to destroy 100,000 molecules of ozone before winds carry it back to the troposphere
- **Bromine containing compounds are more efficient to destroy the ozone**