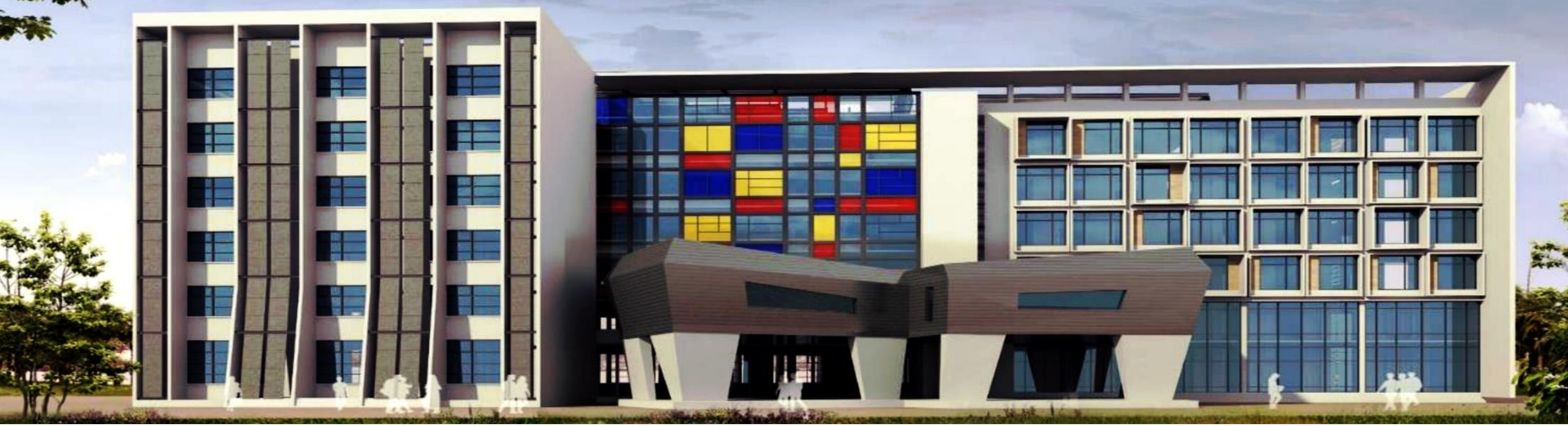


CY1018

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.

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

Reaction of Hydroxyl Radicals with HCs

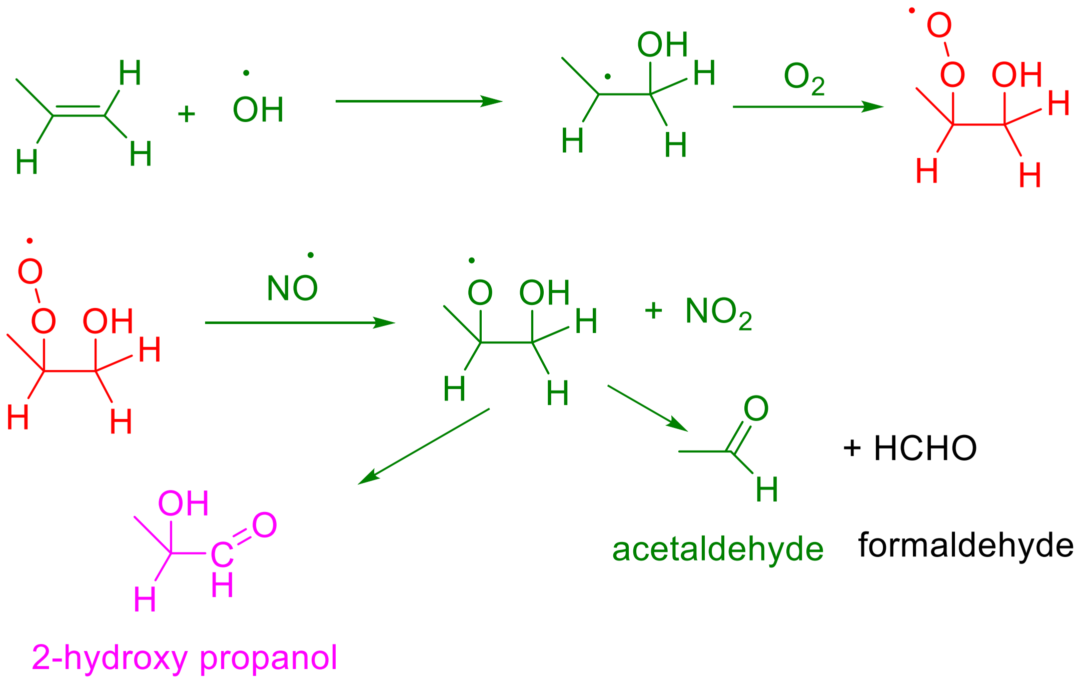
Compound	Bond	Energy KJ/mol
Methane	CH_3-H	427
Ethane	CH_3-CH_2-H	406
Propane	CH_3-CH_2-CH_2-H	393
Methanol	$HOCH_2$-H	393
Benzene	H_5C_5C-H	427
Toluene	$H_5C_6H_2C$-H	326

- The dissociation reaction is $R\text{–}H \longrightarrow R^\bullet + H^\bullet$
- The bond dissociation energy depends how the R radical is stabilized $3^o > 2^o > 1^o$ 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 sp^2 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 $C_6H_5CH_2\bullet$ 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 NO_2 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

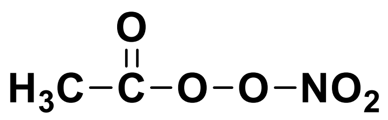
Secondary Smog Forming Reactions

- 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

$$CH_3CHO + {}^{\bullet}OH \longrightarrow CH_3CO^{\bullet} + H_2O$$

$$CH_3CO^{\bullet} + O_2 \longrightarrow CH_3COOO^{\bullet}$$

$$CH_3COOO^{\bullet} + {}^{\bullet}NO_2 \longrightarrow \underset{\text{PAN}}{CH_3COOONO_2}$$



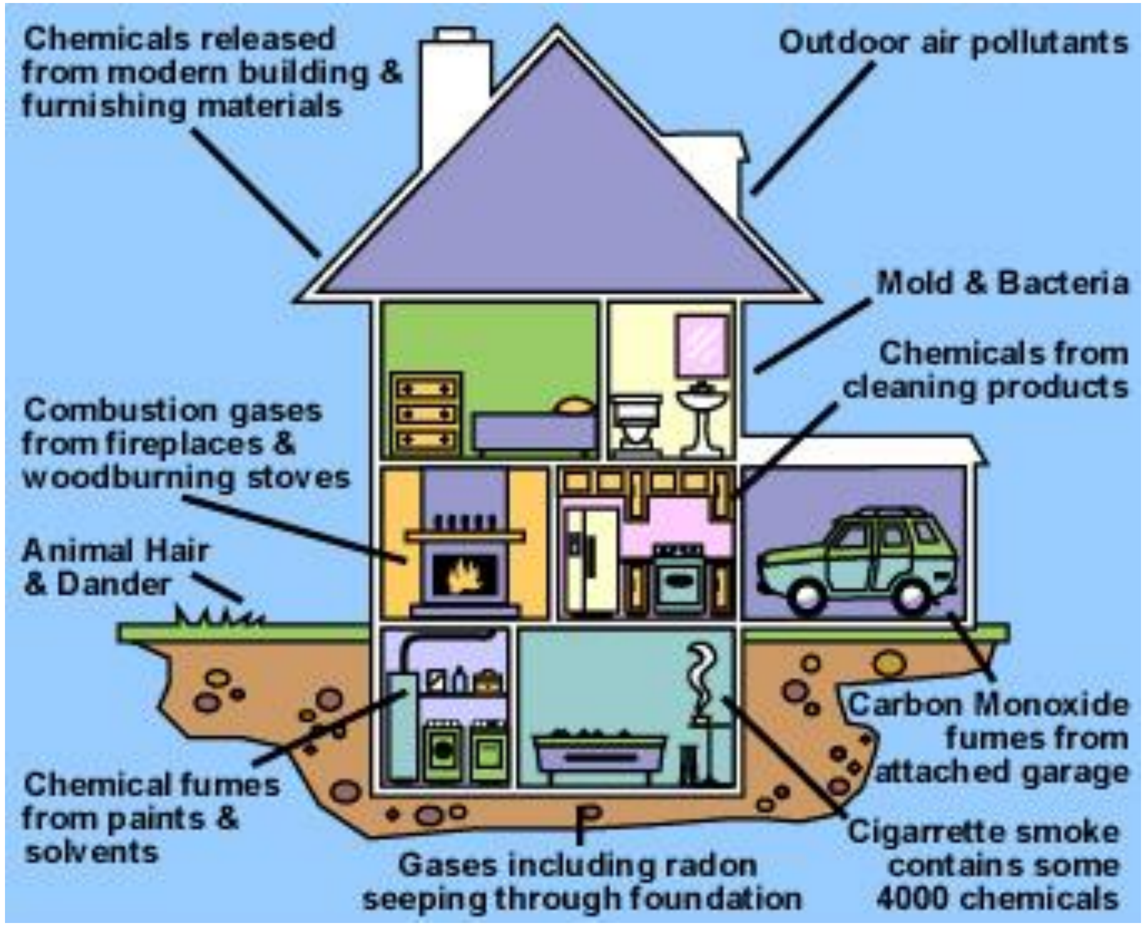
Peroxyacetyl nitrate

- 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 intodays 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



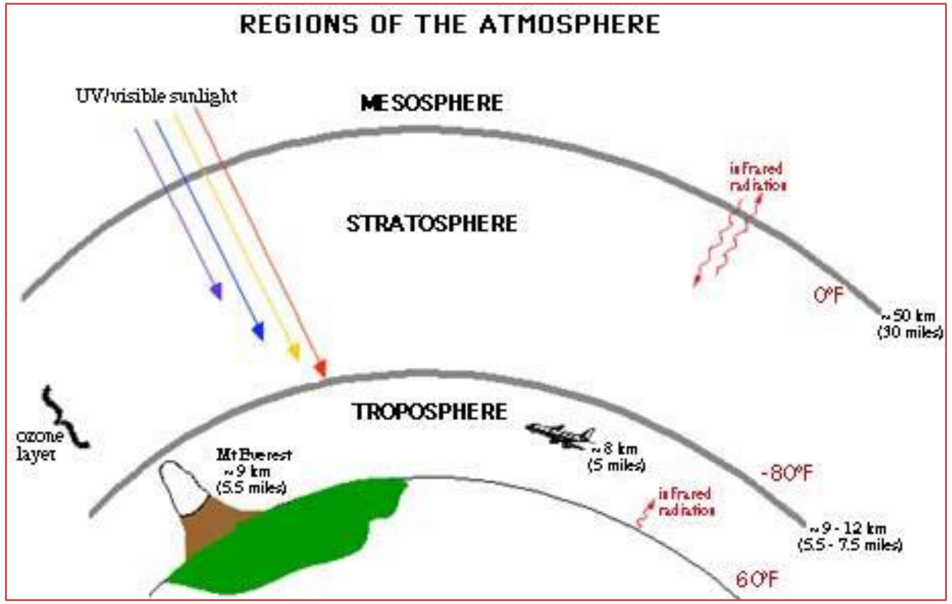
Chemistry of the Stratosphere

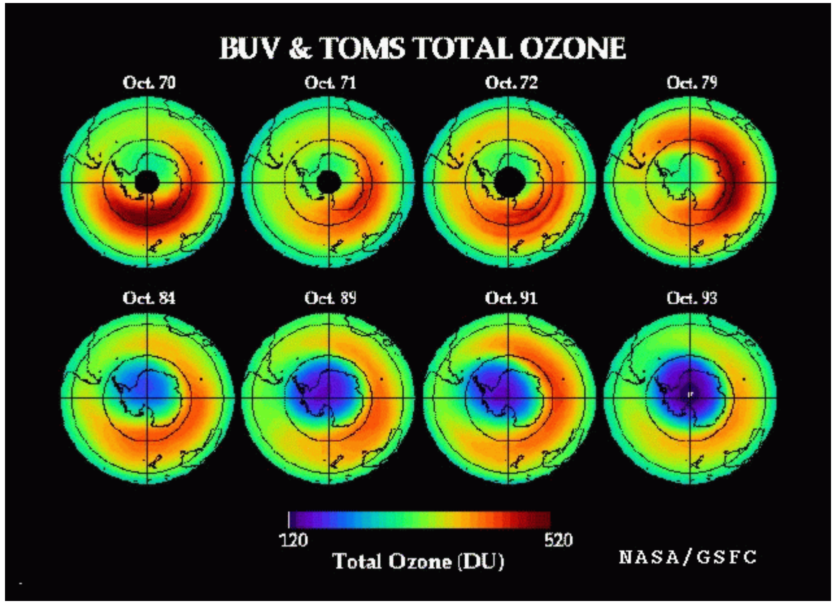
- Today the ozone layer is considered the Earth's natural sun screen because it filtered harmful UV radiation before it can reach the surface of the Earth
- A substantial reduction in the amount of ozone in the ozone layer could threaten all life on Earth

Dobson Unit

- The Dobson Unit (DU) is used to describe the amount of ozone in the stratosphere
- It is named under after G.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 refer to the ozone hole

Chemistry of the Stratosphere



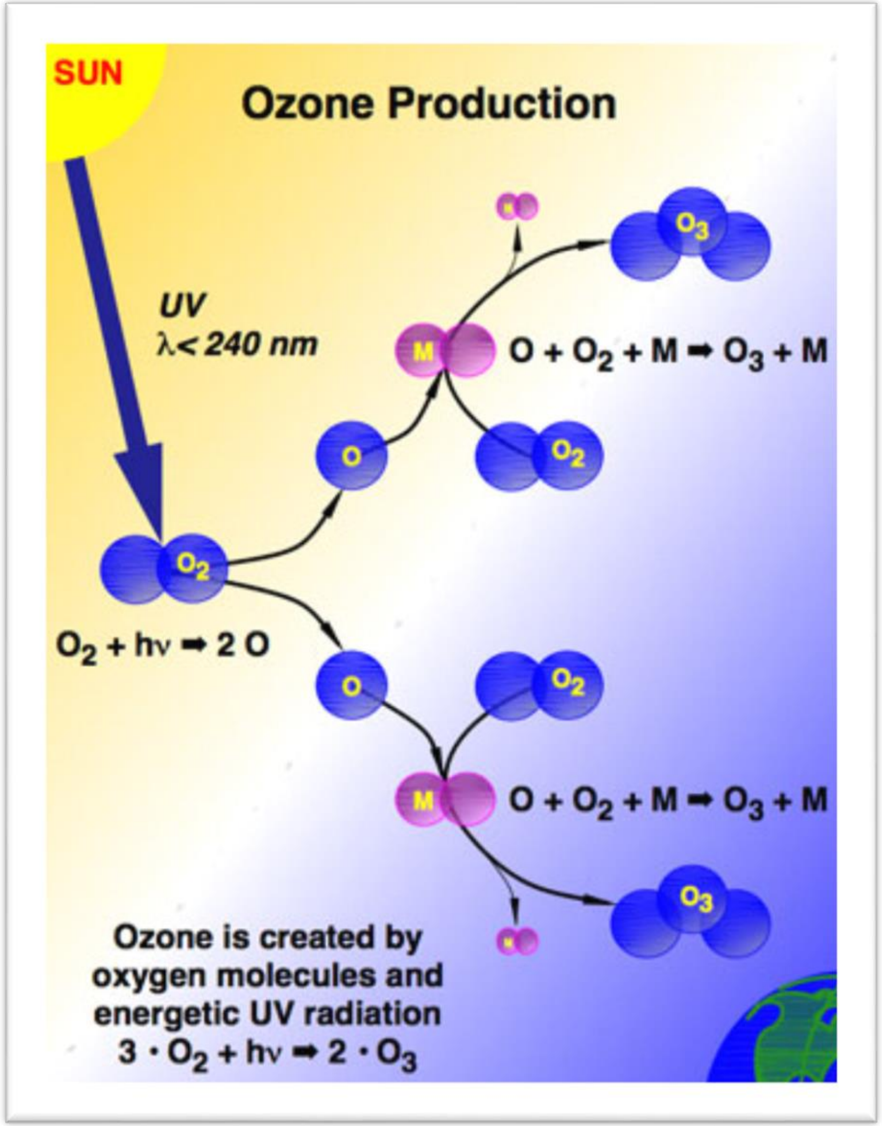


The production of Ozone the Stratosphere

- 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 an ordinary molecules of oxygen gas (**O_2**) in the stratosphere absorbs UV radiation from the sun wave length less than 240 nm and this dissociate O_2 to single oxygen atom (**O**)

$$O_2 + h\nu\ (\lambda < 240) \longrightarrow O + O \qquad \text{(slow)} \qquad \Delta H = 498\ \text{KJ/mol}$$

The production of Ozone the Stratosphere



- Single oxygen atoms are very reactive and immediately combine with O_2 to form O_3

$$O + O_2 + M \longrightarrow O_3 + M + \text{Heat} \qquad \text{(fast)}$$

- 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 wave lengths of 220-320 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

- **Calculate the wavelength required to dissociate oxygen molecule for the following?**

$$O_2 + h\nu \longrightarrow O + O \qquad \Delta H = 498\ KJ/mol$$

Common names for the UV spectrum			
λ(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 Surface

Determining the steady state concentration of Ozone

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) $X + O_3 \longrightarrow XO + O_2$; ii) $XO + O \longrightarrow X + O_2$

- These are the additional steps for ozone destruction compare to the steps discussed earlier
- 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 (NO), iii) Chlorine, and iv) bromine atoms