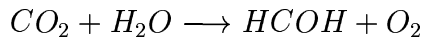


# Ozone Depletion

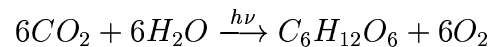
## Outline:

1.  $O_3$ ,  $O_2$  evolution
  2.  $O_3$  generation and depletion
  3. Antarctic ozone hole
  4. Biological effects of UV radiation
  5. Future outlook
1. Evolution of  $O_2$ ,  $O_3$  rich atmosphere (revisited)

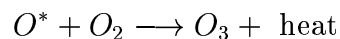
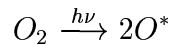
- Parallels evolution of life: nucleic acids  $\rightarrow$  bacteria



- Evolution of plants in pre-cambrian period: photosynthesis



- $O_2$  converted to ozone via:



- $O_3$  absorbs near  $\lambda = 250$  nm (UV range):  $O_3 \xrightarrow{h\nu} O_2 + O$
- Require 10% of atmosphere to be  $O_2$   $O_3$  for effective UV shield
- Shield allows evolution of eucaryotic cells: mitosis requires  $O_2$
- $O_2$  and  $O_3$  levels nearly constant until recently.

# Shielding of radiation

*Transmittance*  $T = I/I_0$  is the fraction of the intensity of incident radiation  $I_0$  that travels through medium.

- Well-described by Beer-Lambert Law

$$I(\lambda) = I_0(\lambda)e^{-\epsilon(\lambda)Cl}$$

- $\epsilon$  is the *absorbitivity*: depends on wavelength
- Suppose thickness changes:  $l' = l + \Delta l$ . Change in transmittance  $\Delta T$  is

$$T' = \frac{I'}{I_0} = e^{-\epsilon cl'}$$
$$\frac{\Delta T}{T} \approx -\epsilon \Delta l$$

- Decreasing  $l$  increases transmittance

Imagine all ozone in atmosphere forming a thin layer of pure ozone around the earth. Thickness of layer would normally be about 3 mm!

- Ozone is **not** distributed in this way: Ozone is distributed throughout atmosphere with highest concentration at around 25 Km above earth.
- Ozone levels measured in *Dobson units* (DU): 1 DU=0.01 mm of layer thickness at P=1 atm.
- Ozone layer is typically around 300 DU.
- For ozone, absorbitivity  $\epsilon$  depends on wavelength:

$$\epsilon(290nm) > \epsilon(300nm) > \epsilon(310nm)$$

- High energy rays absorbed more efficiently: different effects at different wavelengths.

$$\begin{aligned} & 1\% \text{ increase in } T \text{ at } 310nm \\ 1\% \text{ decrease in } l & \implies 3\% \text{ increase in } T \text{ at } 300nm \\ & 10\% \text{ increase in } T \text{ at } 290nm \end{aligned}$$

- Angle of sun important: direct sunlight (in tropics)  $\implies$  shorter path (smaller  $l$ )

**Conclusion:** Decreasing ozone layer increases transmittance of radiation  $T$  most at shortest wavelengths which are most harmful for biological molecules and tissue.

# Ozone Production and Destruction: Natural cycles

- Natural cycles kept steady state of concentration  $O_3$  for thousands of years

1. Source:

- Photolysis of molecular oxygen by UV light:  $\lambda < 242nm$



- Net reaction:  $3O_2 + h\nu \xrightarrow{M} 2O_3$ .

2. Sink:

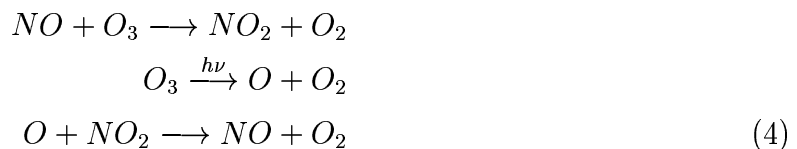


- Since  $O - O$  bonds are weaker in ozone, light is less energetic

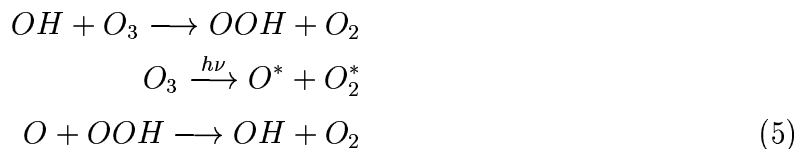
Reactions 1 and 3 together are known as the “Chapman Mechanism”

- Since  $O_3$  formation requires light absorption and concentration of  $O_2$  varies with altitude, mechanism predicts layering of ozone described by Chapman function
- Chapman function properties: Maximum of ozone concentration around  $35Km$  in tropics. As move away from tropics, maximum concentration occurs at higher altitudes and concentrations are smaller.
- Believed to be complete picture until mid 60's when accurate measurements of reaction rates carried out in lab. Found that predicted concentration of  $O_3$  was 2 times too high.
- Other natural sinks must be important

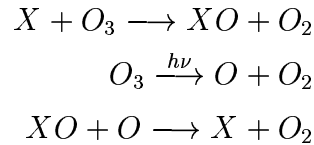
3. Other natural sinks:



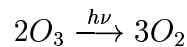
and



- These are *catalytic* processes.
- *NO* formed naturally from microbial processes in soil
- *OH* chemistry in troposphere and stratosphere: initiation step is  $H_2O + O^* \longrightarrow 2OH$
- Can represent both catalytic processes following the *initiation step* as:



- Net process: in presence of  $X = NO, OH$  or to minor extent,  $X = Cl, Br$ ,



- Catalytic destruction can continue until *termination* reaction. Example:



- These termination reactions become important when photolysis of  $O_3$  slows down.
- If product of radical+radical termination reaction is not removed, product can often be photolyzed again to release radicals to continue destruction of ozone.

## Construction of Mechanisms

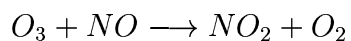
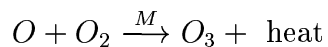
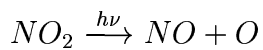
1. First step: detailed measurements of concentrations of reactants at different altitudes: Rockets, balloons and Mass Spectrometry
2. Hypothesis of mechanism based on chemical intuition and observations of concentrations
3. Determination of rates of reactions of all elementary steps: done in controlled laboratory conditions.
4. Solve kinetic equations for system to predict concentration of gases under a variety of conditions: computer simulations of non-linear, complex systems.
5. Verify predictions and refine model: perhaps proposed additional reactive channels or chemical interactions

## Example Complications

- Cycles interact: example  $NO + OOH \longrightarrow NO_2 + OH$  as in smog cycle

- $NO/NO_2$  and  $OH/HO_2$  concentrations correlated

- Null cycles:

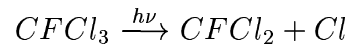


- No net reaction! Sunlight absorbed and converted to heat.
  - $NO/NO_2$  equilibrium affects  $O_3$  destruction.

# Stratospheric Ozone Depletion

**Problem:** Catalytic destruction of  $O_3$  in *stratosphere*.

- Hypothesis: Chlorine and Bromine atoms act as catalytic agents in stratosphere
- **Key Point:** Long-lived CFCs not reactive with  $OH$  and drift into stratosphere.
- Photo-initiation:



- Other source of Fluorine, Bromine and Chlorine atoms: Rocket and space shuttle travel release  $NO$ , ammonium perchlorate into stratosphere.
- Termination reaction of radical+radical yield long-lived *reservoir* gases in stratosphere.

