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 atomosphere (revisited)

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

$$CO_2 + H_2O \longrightarrow HCOH + O_2$$

- Evolution of plants in pre-cambrian period: photosynthesis

$$6CO_2 + 6H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2$$

- O_2 converted to ozone via:

$$\begin{aligned} &O_2 \xrightarrow{h\nu} 2O^* \\ &O^* + O_2 \longrightarrow O_3 + \text{ heat} \end{aligned}$$

- 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

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

- ϵ is the *absorbtivity*: depends on wavelength
- Suppose thickness changes: $l' = l + \Delta l$. Change in transmittance ΔT is

$$\begin{aligned} T' = \frac{I'}{I_0} &= e^{-\epsilon c l'} \\ \frac{\Delta T}{T} &\approx -\epsilon \Delta l \end{aligned}$$

- 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, absorbtivity ϵ depends on wavelength:

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

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

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

- Angle of sun important: direct sunlight (in tropics) $\Longrightarrow$ 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: $\lambda < 242nm$

$$\begin{aligned} O_2 &\xrightarrow{h\nu} 2O \qquad (^3P) \\ 2\left[O(^3P) + O_2 \right. &\left.\xrightarrow{M} O_3\right] \end{aligned} \tag{1}$$

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

2. Sink:

$$O_3 \xrightarrow{h\nu, \lambda<300nm} O_2 + O \tag{2}$$

$$O + O_3 \longrightarrow 2O_2 \tag{3}$$

    - 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:

$$\begin{aligned} NO + O_3 &\longrightarrow NO_2 + O_2 \\ O_3 &\xrightarrow{h\nu} O + O_2 \\ O + NO_2 &\longrightarrow NO + O_2 \end{aligned} \tag{4}$$

    and

$$\begin{aligned} OH + O_3 &\longrightarrow OOH + O_2 \\ O_3 &\xrightarrow{h\nu} O^* + O_2^* \\ O + OOH &\longrightarrow OH + O_2 \end{aligned} \tag{5}$$

- 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:

$$\begin{aligned} X + O_3 &\longrightarrow XO + O_2 \\ O_3 &\xrightarrow{h\nu} O + O_2 \\ XO + O &\longrightarrow X + O_2 \end{aligned}$$

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

$$2O_3 \xrightarrow{h\nu} 3O_2$$

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

$$OH + NO_2 \longrightarrow HNO_3 \xrightarrow{H_2O} \text{acid rain}$$

- 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:

$$\begin{aligned} NO_2 &\xrightarrow{h\nu} NO + O \\ O + O_2 &\xrightarrow{M} O_3 + \text{ heat} \\ O_3 + NO &\longrightarrow NO_2 + O_2 \end{aligned}$$

  - 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:

$$CFCl_3 \xrightarrow{h\nu} CFCl_2 + Cl$$

- Other source of Flourine, 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.

$$Cl + OOH \longrightarrow HCl + O_2$$
$$Cl + CH_4 \longrightarrow HCl + CH_3$$
$$ClO + NO \longrightarrow ClONO_2 \text{ (Chlorine Nitrate)}$$