Lecture 6

• Recap on where ozone comes from

• Catalytic destruction of ozone

(We’re following Chapter 17 of the textbook)

Coming up:
• Antarctic ozone hole (Weds)

• Stopping ozone depletion (international agreement) & ozone depletion in the scientific versus anti-scientific debate (Thurs)
Calculate the NET reaction…

(1) \( \text{O}_2 + \text{UV} \rightarrow \text{O} + \text{O} \)
(2) \( 2\text{O}_2 + 2\text{O} \rightarrow 2\text{O}_3 \)
(3) \( \text{O}_3 + \text{UV} \rightarrow \text{O}_2 + \text{O} \)
(4) \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \)

\[\text{UV} + \text{UV} \rightarrow \text{heat}!\]

• There is no net production or destruction of any chemical species.
• This cycle of reactions produces:
  - heat (warming the stratosphere)
  - an equilibrium concentration of \( \text{O}_3 \) (also of \( \text{O} \))
  - "dynamic equilibrium"

Given solar energy (UV flux) and \( \text{O}_2 \) concentration…
• equilibrium concentration of \( \text{O}_3 \) depends on rate of reaction (4).
#1: Strictly speaking, the production reaction should be written:

\[
\begin{align*}
(2) \quad & \text{O}_2 + \text{O} + \text{M} \quad \rightarrow \quad \text{O}_3 + \text{M} \\
\end{align*}
\]

The “M” is any molecules but most likely nitrogen, N\textsubscript{2}, which is the most abundant component of air (78%) We skipped the "M" for simplicity

#2: Note also that photons are sometimes represented in chemical reactions by the symbol “\(h\Box\)”. This is because the energy of a photon is equal to the product of h (Planck’s constant) and frequency, \(\Box\). i.e. photon energy, \(E = h\Box\)
Stratospheric Ozone
catalyst

A substance that accelerates the rate of a reaction without itself being consumed
Example catalytic reaction.

Calculate the NET reaction…

(a) \( \text{O}_3 + \text{X} \rightarrow \text{XO} + \text{O}_2 \)

(b) \( \text{XO} + \text{O} \rightarrow \text{X} + \text{O}_2 \)

\[\text{-----------------------------}\]

(\text{net}) \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 + \text{O}_2 \)

• Species X is facilitates the destruction of ozone (and atomic oxygen) but is not itself consumed.

• Do you recognize the net reaction? Have you seen it before?
A catalyst accelerates the rate of a reaction without itself being consumed.

(a) \( O_3 + X \rightarrow XO + O_2 \)

(b) \( XO + O \rightarrow X + O_2 \)

\[
\text{(net)} \quad O_3 + O \rightarrow O_2 + O_2
\]

A new model of ozone equilibrium...

(1) \( O_2 + UV \rightarrow O + O \)
(2) \( O_2 + O \rightarrow O_3 \)
(3) \( O_3 + UV \rightarrow O_2 + O \)
(4*) \( O_3 + O \rightarrow O_2 + O_2 \)

*the 4th reaction from the oxygen-only cycle is catalyzed by species X.

Result will be a lower equilibrium concentration of \( O_3 \) (due to more efficient removal).
Catalytic Destruction

Species X can be:  
- NO (odd-nitrogen)
- Cl (chlorine)
- Br (bromine)

Reactions when X = chlorine…

(a) \( O_3 + Cl \rightarrow ClO + O_2 \)

(b) \( ClO + O \rightarrow Cl + O_2 \)

--------------------------------------

(Net) \( O_3 + O \rightarrow O_2 + O_2 \)

NO, Cl, and Br have all been greatly enhanced in the stratosphere due to human activities.
Recap on the history of CFCs

1929: 100 people are killed in a hospital in Cleveland due to a leak in the refrigeration system.

Refrigeration systems require a "working gas" to transfer heat via compression and expansion cycle. Traditional working gases were toxic - sulfur dioxide and ammonia.

The invention of chlororfluorocarbons (CFCs) in the 1930s was a great step forward for public safety. CFCs are "inert" and totally non-toxic.

Soon, many other uses were found for CFCs and related bromine compounds known as halons (carbon-fluorine-bromine compounds).

Slowly but surely, CFCs accumulated in the atmosphere.

Initially no one knew of CFCs’ potential danger.

"The presence of these compounds constitutes no conceivable hazard" (Jim Lovelock, 1973, in Nature magazine).

“This sentence has turned out to be one of my greatest blunders” (Jim Lovelock (1988) “The Ages of Gaia: A biography of our living Earth”, p.165)
CFC cycle in atmos:
- source in tropo; well-mixed
- photolyzed in strato; decreases with height

Three categories:
- source gases (CFCs, etc)
- unreactive forms in strato: HCl and ClONO₂
- reactive form in strato: ClO

Only the reactive form is a catalyst and a danger to stratospheric ozone

[Figure source: WMO, Scientific Assessment of Ozone Depletion 2002]
Atmospheric lifetimes of CFCs

Atmospheric lifetime (or "residence time"): The average length of time a substance spends in the atmosphere.

<table>
<thead>
<tr>
<th>name</th>
<th>trade name</th>
<th>chemical formula</th>
<th>atmospheric lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-12</td>
<td>Freon-12</td>
<td>CCl₂F₂</td>
<td>100 yrs</td>
</tr>
<tr>
<td>CFC-11</td>
<td>Freon-11</td>
<td>CCl₃F</td>
<td>45 yrs</td>
</tr>
</tbody>
</table>
Observed changes in CFCs: in-class activity

Emissions of all these compounds were greatly reduced in about 1990. Which compound has the longest atmospheric lifetime? Explain.
CFC’s & Stratospheric Ozone
Ozone level governed by dynamic equilibrium. Loss rate via step (4) is key.

Understanding in 1970s:
- Cl can catalyze reaction (4)
- Cl in stratosphere is increasing due to CFCs but
- Cl is slowly removed as HCl (relatively unreactive):
  Cl + CH₄ = HCl + CH₃
- and most Cl is stratosphere is locked up in unreactive forms
thus,
- CFCs should cause only modest loss of ozone (predicted 7% loss by 2100)

BUT then came the OZONE HOLE DISCOVERY (1985)