Ozone formation and destruction in the stratosphere

• The composition of the stratosphere is similar to that of the troposphere, but $T \sim 220$ K and $p$(total) $\sim 0.1$ atm

• The “ozone layer” is not really a layer

“Chapman Mechanism”

Ozone formation:

$$O_2(g) + h\nu \rightarrow 2 O(g) \quad \lambda < 240 \text{ nm}$$
not in troposphere

$$O(g) + O_2(g) \rightarrow O_3(g)$$

Ozone destruction:

$$O_3(g) + h\nu \rightarrow O(g) + O_2(g) \quad \lambda < 325 \text{ nm}$$
stratosphere and troposphere

$$O(g) + O_3(g) \rightarrow 2O_2(g)$$

• Steady state does not correspond to equilibrium (solar driven): note energetics of these reactions

• Over 300,000 t of ozone are made and destroyed each day in the atmosphere

• Experimental concentration of ozone is less than the Chapman mechanism predicts

  $\therefore \rightarrow$ Other sinks for ozone loss
The other sinks are **chain reactions** involving radical species X, where X can be any of NO, Cl, Br, OH, H

\[
\begin{align*}
X(g) + O_3(g) & \rightarrow XO(g) + O_2(g) \\
XO(g) + O(g) & \rightarrow X(g) + O_2(g)
\end{align*}
\]

Net reaction is:

\[
O(g) + O_3(g) \rightarrow 2O_2(g)
\]

X is a catalyst that is re-formed in each cycle

The upper atmosphere contains small concentrations of these “X” substances, and these reactions proceed naturally – they do not necessarily represent pollution

**What is the significance of stratospheric ozone?**

- the conversion of solar radiation into heat makes the stratosphere warmer than the upper troposphere

*Generalization* the warm parts of the atmosphere all have energy deposited in them

- the absorption of solar radiation < 300 nm in the stratosphere prevents this damaging radiation from reaching the Earth’s surface

- in the wavelength range 300-325 nm (UV-B) just a little radiation does leak through, and this is enough to dissociate **tropospheric** ozone
The CFC (chlorofluorocarbon) story

- CFCs do not absorb radiation < 250 nm (not present in troposphere)
- Chemically unreactive: no tropospheric sinks
- Slow migration to stratosphere, $t_{1/2} \approx 5$ yr; globally well mixed
- In stratosphere, slow reaction with $t_{1/2}$ many decades:

  \[
  \text{e.g. } \text{CF}_2\text{Cl}_2 + h\nu \rightarrow \text{CF}_2\text{Cl} + \text{Cl} \quad \text{weakest bond breaks}
  \]

- Hence CFCs are a source of stratospheric chlorine atoms which are catalysts for destroying stratospheric ozone: “X” in the chain sequence on the previous page
- Photolysis initiates the chain reactions; up to $10^4$ cycles per chlorine atom
- CFCs increase an existing “sink strength”, thereby lowering the steady state concentration of ozone. [originally, it was thought that this was a new sink]

CFC Numbering System

- Add 90 to the number; the three digits represent the numbers of C, H, F atoms; make up the rest of the “unused bonds” with Cl. Example: CFC-112 is C$_2$F$_2$Cl$_4$

What were/are CFCs used for?

- Refrigerants
- Propellants for foams
- Propellants for aerosols
The Road to the Montreal Protocol

- CFCs first discovered in the atmosphere 1974
- Many were increasing at 6%/year in the late 1970s
- Travel to the stratosphere takes 5-10 years
- N. American and European ban on aerosol use 1978
- Montreal Protocol 1987 with a ban on “hard” CFCs + CH₃CCl₃ + CCl₄ to take place January 1, 1996
- 10 year extension for developing countries (originally by 2010)
- Halons (e.g., CF₃Br) phased out January 1, 1994

The Montreal Protocol is historic because it is the first instance of international action on the basis of a future anticipated environmental threat

Mario Molina and Sherwood Rowland received the 1995 Nobel Prize in Chemistry for their seminal work on stratospheric ozone depletion: Nature, 1974, 249, 810
Why have CFCs been banned?

- CFC lifetimes 100+ years: photolysis is inefficient

- Loss of stratospheric ozone allows more UV-B radiation to reach the earth’s surface

- Relationship between UV radiation and skin cancer (melanoma deaths among white US males)

- High UV at noon, in summer, high altitude, in the tropics
CFC Replacement Compounds

- HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons): desired properties are chemical stability, low toxicity, appropriate boiling point

- CFC replacements must undergo tropospheric oxidation

- Since CFCs deplete stratospheric ozone replacements should avoid or minimize Cl atoms

- Because hydrocarbons oxidize in the troposphere replacement compounds should include H atoms. As will be discussed in Chapter 3, HCFCs and HFCs can react with tropospheric OH radicals.

  e.g. \( \text{CH}_3\text{CHF}_2 + \text{OH} \rightarrow \text{CH}_3\text{CF}_2 + \text{H}_2\text{O} \)
  followed by further reactions of \( \text{CH}_3\text{CF}_2 \)

- CFCs and their replacements are also greenhouse gases: polar C-F and C-Cl bonds. Fully fluorinated compounds must be avoided (no hydrogen atoms to react with OH) and high global warming potential
Ozone Depleting Potential (ODP)

Relative areas are ODPs based on equal masses. CFC-11 is $\text{CFCl}_3$, HCFC-22 is $\text{CHF}_2\text{Cl}$, HCFC-123 is $\text{C}_2\text{HF}_3\text{Cl}_2$
CFCs, HFCs, HCFCs: ODP vs Global Warming Potential

<table>
<thead>
<tr>
<th>Compound</th>
<th>ODP (CFCl₃ = 1)</th>
<th>GWP (CO₂ = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC-22</td>
<td>CHF₂Cl</td>
<td>0.05</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>CF₃CHCl₂</td>
<td>0.02</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>CF₃CHFCl</td>
<td>0.02</td>
</tr>
<tr>
<td>HFC-125</td>
<td>CF₃CHF₂</td>
<td>0.0</td>
</tr>
<tr>
<td>HFC-134a</td>
<td>CF₃CH₂F</td>
<td>0.0</td>
</tr>
<tr>
<td>HCFC-141b</td>
<td>CH₃CFCl₂</td>
<td>0.1</td>
</tr>
<tr>
<td>HCFC-142b</td>
<td>CH₃CF₂Cl</td>
<td>0.06</td>
</tr>
<tr>
<td>HFC-152a</td>
<td>CH₃CHF₂</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Note:* HFCs have ODP = zero; GWPs taken from the IPCC Report and http://216.239.33.100/search?q=cache:4ApslDfh9poC:tis.eh.doe.gov/oepa/rules/60/60fr52357.pdf+global+warming+potential+HCFC&hl=en (20 year horizon). They are much larger than the values in the text.

Response of industry to CFC phase-out

- aerosol propellants: CO₂; CH₃OCH₃-H₂O; C₄H₁₀-CH₂Cl₂
- foam blowing agents: [HCFC-22]; HCFC-141b; cyclopentane
- refrigerants: HFC-134a; hydrocarbons (in Europe)
- Note concern about CF₃CO₂H as a highly stable breakdown product of several HFCs, including HFC-134a
FIG. 18. Trends of various controlled ozone-depleting chlorine species. [Analysis provided by the Climate Monitoring and Diagnostics Laboratory (CMDL).]
Polar Ozone Holes (the precipitating event for the Montreal Protocol)


- "Polar Sunrise" experiments have shown that this effect is seen (but not every year) in the Arctic also

The other cycles for ozone depletion: $X = \text{Cl, NO, OH, H}$

- CH$_3$Cl: a natural source of atmospheric chlorine; marine origin; long tropospheric $t_{1/2}$
- NO: not much transport from the troposphere (short $t_{1/2}$); mostly made in the upper atmosphere, but injection into stratosphere from e.g., volcanic eruptions, supersonic aircraft
- Another route is photolysis of N$_2$O

\[
\text{N}_2\text{O} + \text{hv} \rightarrow \text{N}_2 + \text{O}^* \text{ (excited oxygen atom)}
\]
\[
\text{O}^* + \text{N}_2\text{O} \rightarrow 2\text{NO}
\]

Note: O* also comes from high energy dissociation of ozone

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}^* + \text{O}_2^*
\]

- OH arises from photolytic cleavage of H$_2$O in the stratosphere (not troposphere) and from reaction of excited state oxygen atoms with water vapour

\[
\text{O}^* + \text{H}_2\text{O} \rightarrow 2\text{OH}
\]

- H atom chemistry is most important in the upper stratosphere, where $p(\text{O}_2)$ is less: $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$ competes in the troposphere
A Final Thought

• Why do you think that the Montreal Protocol received international acceptance but the Kyoto Agreement has not?