Stratospheric Chemistry - Ozone

1. Ozone layer and Solar Spectrum

2. $\text{O}_3$ formation/destruction
   ➔ Chapman Reactions

3. Catalytic $\text{O}_3$ destruction

4. Null, ‘holding’ cycles & CFCs

5. Antarctic and Arctic ‘ozone hole’ formation
   ➔ Polar Stratospheric Clouds
Allotropes of Oxygen

**Oxygen atom (O)**

**Oxygen molecule (O₂)**

**Ozone molecule (O₃)**
UV Absorption in Atmosphere

- $O$ absorbs $\lambda < 100$ nm
- $O_2$ absorbs $\lambda < 200$ nm
- $O_3$ absorbs $\lambda < 320$ nm
Fig. 3.2 Absorption cross-section of oxygen (broken line) and ozone (dotted line) compared to the solar flux density (solid line) over the region of biologically harmful ultraviolet radiation (Data from Chamberlain, J. W. and D. M. Hunten, Theory of Planetary Atmospheres, Academic Press; 1987. Reprinted with permission.)
Ozone: UV-b (280-320 nm) ‘sunscreen’
Fig. 3.1 Concentration profile of ozone in the lower atmosphere, shown both as the mixing ratio (solid line) and as the log of number density (broken line). (Data from Wayne, R. P., *Chemistry of Atmospheres*, Clarenden Press; Oxford; 1991. Reprinted with permission.)
Fig. 10-1 The natural ozone layer: vertical and latitudinal distribution of the ozone number density ($10^{12}$ molecules cm$^{-3}$) at the equinox, based on measurements taken in the 1960s. From Wayne, R. P. *Chemistry of Atmospheres*. Oxford: Oxford University Press, 1991.
2. Ozone Formation/Destruction

O$_3$ Formation Chemistry

O$_2$ + $h\nu (\lambda << 240 \text{ nm}) \rightarrow 2$ O

O + O$_2$ + M $\rightarrow$ O$_3$ + M

Overall: $3$ O$_2$ $\leftrightarrow$ $2$ O$_3$
Ozone Destruction
Chemistry (oxygen only)

\[ \text{O}_3 + h\nu (\lambda \sim 240-320 \text{ nm}) \rightarrow \text{O}_2^* + \text{O}^* \]

\[ \text{O} + \text{O}_3 + \text{M} \rightarrow 2 \text{O}_2 + \text{M} \]

Overall: \( 2 \text{O}_3 \rightleftharpoons 3 \text{O}_2 \)
The Chapman Reactions

Synthesis

\[ \text{O}_2 + h\nu (\lambda << 240 \text{ nm}) \rightarrow \text{O} + \text{O} \quad (1) \quad \text{SLOW} \]

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (2) \quad \text{FAST} \]

Decomposition

\[ \text{O}_3 + h\nu (\lambda \sim 240-320 \text{ nm}) \rightarrow \text{O}_2^* + \text{O}^* \quad (3) \quad \text{FAST} \]

\[ \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 \quad (4) \quad \text{SLOW} \]
1. Oxygen molecules are photolyzed, yielding 2 oxygen atoms (SLOW)

2. Ozone and oxygen atoms are continuously being interconverted as solar UV breaks ozone and the oxygen atom reacts with another oxygen molecule (FAST)

3. Ozone is lost by a reaction of the oxygen atom or the ozone molecule with each other, or some other trace gas such as chlorine (SLOW)

This interconversion process converts UV radiation into thermal energy, heating the stratosphere.
Why does $O_3$ Concentration peak ~ 20-30 km altitude?

Recall the Chapman Reactions…

\[ O_2 + hv (\lambda < 240 \text{ nm}) \rightarrow O + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]

The upper stratosphere has plenty of high-energy photons which create enough O, but at higher altitudes, the concentration of $O_2$ is limited.

The lower stratosphere has plenty $O_2$, but has limited high-energy photons (to split $O_2$) and therefore, is limited in O.

At 20~30 km, there is enough high-energy photons to produce O and still plenty $O_2$
$3 \text{O}_2 \rightleftharpoons 2 \text{O}_3$

When,

$\text{O}_3$ formation rate $= \text{O}_3$ destruction rate

Then $[\text{O}_3]$ is at *steady-state*

Oxygen-only chemistry explains the appearance of the ozone layer, but over-estimates the peak ozone concentration by 2x.

Therefore, additional $\text{O}_3$ destruction processes are occurring.
3. Catalytic Ozone Destruction

General Mechanism:

\[ X + O_3 \rightarrow XO + O_2 \]
\[ XO + O \rightarrow X + O_2 \]

Net Reaction

\[ O + O_3 \rightarrow 2O_2 \]

Where X can be;

1. \( HO_x \) \((H\cdot, HO\cdot, HO_2\cdot)\)
2. \( NO_x \) \((NO, NO_2)\)
3. \( ClO_x \) \((Cl\cdot, ClO\cdot)\)
Hydroxyl Radical (HOx) Cycle

Photochemical production:

\[
\text{O} \,(^1\text{D}) \, + \, \text{H}_2\text{O} \, \rightarrow \, 2 \, \text{HO}^\cdot
\]

\[
\text{H}_2\text{O} \, + \, h\nu \, \rightarrow \, \text{H}^\cdot \, + \, \text{HO}^\cdot
\]

Note: O \,(^1\text{D}) = \text{singlet excited state oxygen aka } ^1\text{O}^* \\
\text{(generated photochemically from } \text{O}_3)\]

\[
\text{HO}^\cdot \, + \, \text{O}_3 \, \rightarrow \, \text{HO}_2^\cdot \, + \, \text{O}_2
\]

\[
\text{HO}_2^\cdot \, + \, \text{O} \, \rightarrow \, \text{HO}^\cdot \, + \, \text{O}_2
\]

Net Reaction

\[
\text{O} \, + \, \text{O}_3 \, \rightarrow \, 2 \, \text{O}_2
\]

Natural contribution to \text{O}_3 destruction. Increasing importance with altitude.
Nitric Oxide (NOx) cycle

\[
\begin{align*}
N_2O + O (^{1}D) & \rightarrow 2 \cdot NO \\
\text{Nitrous oxide tropospheric lifetime } & \sim 160 \text{ yr,} \\
\text{reaction occurs in stratosphere. Increasing} \\
\text{tropospheric concentrations due to fertilization.}
\end{align*}
\]

\[
\begin{align*}
\cdot NO + O_3 & \rightarrow \cdot NO_2 + O_2 \\
\cdot NO_2 + O & \rightarrow \cdot NO + O_2 \\
\hline
\text{Net Reaction} \\
O + O_3 & \rightarrow 2 O_2
\end{align*}
\]

Nitric oxide removal via reaction with hydroxyl
\[
\cdot NO + \text{HO}^{-} \rightarrow \text{HNO}_2
\]

‘Natural’ contribution to O\(_3\) destruction. Increasing importance at lower altitude.
Fig. 10-6 Sources and sinks of stratospheric NO$_x$ and NO$_y$. The direct conversion of N$_2$O$_5$ to HNO$_3$ takes place in aerosols and will be discussed in section 10.4.
Chlorine radical (ClOx) cycle

\[
\begin{align*}
\cdot \text{Cl} & + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2 \\
\text{ClO} \cdot + \text{O} & \rightarrow \cdot \text{Cl} + \text{O}_2 \\
\text{Net Reaction} & \\
\text{O} + \text{O}_3 & \rightarrow 2 \text{O}_2
\end{align*}
\]

Most \( \cdot \text{Cl} \) and \( \text{ClO} \cdot \) radicals in stratosphere are from anthropogenic sources.
Fig. 10-8 Sources and sinks of stratospheric ClO$_x$ and Cl$_y$. 
Sources of ClOx species

CH$_3$Cl (biogenic)
CH$_2$Cl$_2$, CHCl$_3$, CCl$_4$ – solvents
CFC’s – refrigerants, foaming agents and propellants (freons)
    CFC-xyz ($x =$ # C-1; $y=#H+1; z=#F$)
Long tropospheric lifetimes ($\lambda > 300$ nm)
Photo-dissociate in stratosphere ($\lambda < 300$ nm)
    e.g., CFC-11
    CFCl$_3$ + $hv$ $\rightarrow$ CFCl$_2$ + Cl (initiation step)
    Cl + O$_3$ $\rightarrow$ ClO + O$_2$ (ozone destruction)
    ClO + O $\rightarrow$ Cl + O$_2$ (propogation step)
Ozone Destruction Cycle 1

Oxygen molecule ($O_2$) → Chlorine atom (Cl) → Ozone ($O_3$) → Oxygen molecule ($O_2$)

- **ClO + O reaction**
- **Ozone catalytic cycle**
- **Cl + O$_3$ reaction**

- Oxygen atom (O)
- Chlorine monoxide (ClO)
- Ozone destruction

Chemical reactions:

1. $Cl + O_3 \rightarrow ClO + O_2$
2. $ClO + O \rightarrow Cl + O_2$
3. $Net: O + O_3 \rightarrow 2O_2$
1. UV causes a chlorine atom to break way from the CFC molecule.

2. The free chlorine atom hits an ozone molecule.

3. The chlorine atom pulls one oxygen atom away.

4. A free oxygen atom hits the chlorine monoxide molecule.

5. The result is another free chlorine atom.

6. Free chlorine will continue to deplete ozone in the stratosphere.
# Ozone Depleting Potential (ODP)

## Common CFCs

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>$\tau$ (troposphere)</th>
<th>ODP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC-11</td>
<td>CFCl$_3$</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>CFC-12</td>
<td>CF$_2$Cl$_2$</td>
<td>195</td>
<td>1</td>
</tr>
<tr>
<td>CFC-113</td>
<td>CF$_2$CICFCl$_2$</td>
<td>101</td>
<td>0.8</td>
</tr>
<tr>
<td>CFC-115</td>
<td>CF$_2$CICF$_3$</td>
<td>522</td>
<td>0.6</td>
</tr>
</tbody>
</table>

## CFC alternatives

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>ODP</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCFC-22</td>
<td>CHClF$_2$</td>
<td>0.06</td>
</tr>
<tr>
<td>HCFC-123</td>
<td>CHCl$_2$CF$_3$</td>
<td>0.02</td>
</tr>
<tr>
<td>HCFC-124</td>
<td>CHClFCF$_3$</td>
<td>0.02</td>
</tr>
<tr>
<td>HFC-125</td>
<td>CHF$_2$CF$_3$</td>
<td>0.00</td>
</tr>
</tbody>
</table>
4. ‘Null’ and ‘Holding’ cycles

Null (do nothing) cycles interconvert odd oxygen species

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}
\end{align*}
\]

Net: \( \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \)

Other important reservoir species (bold)

\[
\begin{align*}
\text{NO}_2 + \text{HO} & \rightarrow \text{HNO}_3 \\
\text{Cl} + \text{CH}_4 & \rightarrow \text{HCl} + \text{CH}_3
\end{align*}
\]

Holding cycles store reactive species in stable forms that act as a temporary reservoir

\[
\text{NO}_3 + \text{NO}_2 \quad \text{====} \quad \text{N}_2\text{O}_5
\]
Other reservoir species

\[
\text{ClO}^\bullet + \text{HO}_2^\bullet \rightarrow \text{HOCl} + \text{O}_2
\]

\[
\text{ClO}^\bullet + \cdot\text{NO}_2 + \text{M} \rightarrow \text{ClONO}_2 + \text{M}
\]

Reservoir species are non-reactive and store the reactive radicals until they are later released and re-enter the catalytic cycle to destroy ozone.
5. Antarctic and Arctic Ozone Hole

- Occurs during polar SPRING
- After very cold and dark conditions
- Polar stratospheric clouds
- Reservoir species release Cl

Antarctic Ozone Hole

17 September 2009

Total ozone (Dobson units)
Why does the ozone hole form at the poles?

During the dark winter, it is very cold and due to the Earth’s rotation, a polar vortex is created as air is drawn towards the South Pole.

Due to the low temperatures, you get polar stratospheric clouds (PSCs).

- **Type I**: ~193 K, particles 1 \( \mu \text{m} \) of \( \text{HNO}_3 \cdot 3\text{H}_2\text{O}(s) \)
- **Type II**: 187 K, particles 10 \( \mu \text{m} \) \( \text{H}_2\text{O}(s) \)

Accumulated reservoir species are also present in the vortex. The reservoir species react on the PSCs, releasing \( \text{Cl}_2 \) and \( \text{HOCl} \).

\[
\begin{align*}
\text{HCl} + \text{ClONO}_2 & \rightarrow \text{Cl}_2 + \text{HNO}_3 \\
\text{H}_2\text{O} + \text{ClONO}_2 & \rightarrow \text{HOCl} + \text{HNO}_3
\end{align*}
\]
Here comes the sun!

\[ \text{Cl}_2 + h\nu \rightarrow 2 \cdot \text{Cl} \]

\[ \text{HOCl} + h\nu \rightarrow \cdot \text{Cl} + \cdot \text{OH} \]

The chlorine radical can now enter the catalytic cycles and destroy ozone.

Occurs very quickly (within days), the ozone levels drop to less than half their winter value.

As the temperature increases, the polar vortex breaks up and the PSCs begin to disappear.

Chlorine radicals become reservoir species (HCl and ClONO\(_2\)) once again.
Global Satellite Maps of Total Ozone in 2009

- Early spring
  - 16 – 30 March
- Early winter
  - 16 – 30 December
- Early fall
  - 16 – 30 September
- Early summer
  - 16 – 30 June

Legend:
- Total ozone (Dobson units)
  - 600
  - 500
  - 400
  - 300
  - 200
  - 100

Maps show the distribution of total ozone over the globe for different time periods.
Polar Vortex

- extreme cold (minus 80-90 °C)
- descending air
- PSCs

Reservoir species?

HCl & ClONO\textsubscript{2} react on PSCs to form Cl\textsubscript{2} & HOCl

Cl\textsubscript{2} + hv $\rightarrow$ BOOM

HOCl + hv $\rightarrow$ BOOM

Fig. 4.29. The winter vortex over Antarctica. The cold core is almost isolated from the rest of the atmosphere, and acts as a reaction vessel in which the constituents may become chemically 'preconditioned' during the long polar night.
Fig. 4.34 Schematic diagram of chemical conversions in the ClO$_x$-catalysed decomposition of ozone in the presence of PSCs. Source: European research in the stratosphere, European Communities, Luxembourg, 1997.
Why South pole?

Colder temps $\rightarrow$ more PSCs
Antarctic Total Ozone
(October monthly averages)

1970
1971
1972
1979
2006
2007
2008
2009

Total ozone (Dobson units)

100 200 300 400 500
Antarctic Ozone 1979-94

**O$_3$ Concentration**

**O$_3$ Hole Size**

Source: National Aeronautics and Space Administration (NASA).
Fig. 10-9 Historical trend in the total ozone column measured spectroscopically over Halley Bay, Antarctica in October, 1957–1992. One Dobson unit (DU) represents a 0.01-mm-thick layer of ozone under standard conditions of temperature and pressure; 1 DU = $2.69 \times 10^{16}$ molecules cm$^{-2}$. From *Scientific Assessment of Ozone Depletion: 1994*. Geneva: WMO, 1995.
Figure 1. Diagram showing the effect of polar stratospheric clouds on ozone loss. The upper panel shows the situation when there are no polar stratospheric clouds. Ozone depletion takes place only in the gas phase (homogeneous chemistry). The lower panel shows the situation when there are polar stratospheric clouds present. The reservoir gases hydrochloric acid and chlorine nitrate react with each other on the surface of the PSC particles through a red-ox reaction and liberate elementary chlorine (Cl₂). Elementary chlorine is easily photolysed by sunlight and forms atomic chlorine, which reacts fast with ozone to form chlorine monoxide (ClO, active chlorine) and oxygen (O₂). ClO dimerises and forms Cl₂O₂ which is easily photolysed, liberating atomic chlorine again. Due to this catalytic cycle, one atom of Cl can destroy thousands of ozone molecules before it is passivated through reaction with NO₂, methane or other substances. This explains why a few ppb of chlorine can destroy several ppm of ozone. In addition, PSC particles can grow large enough to sediment, thereby removing HNO₃ from the stratosphere. This means that there will be limited amounts of NO₂ present to quench the active chlorine, and the ozone depleting process can continue for several weeks. The diagram has been made by Finn Bjerkli, Norwegian Institute for Air Research (NILU).
Air in the upper atmosphere and lower mesosphere descends into the polar vortex.

Strong circulating winds isolate the air in the middle and lower atmosphere over Antarctica.

Circumpolar vortex

Ice crystals contaminated with $\text{NO}_3\text{Cl}$ within the stratosphere:

- $E = hf$
- $\text{Cl}_2$
- $\text{Cl}^-$

Ozone depletion facilitated by the polar vortex.