Stratospheric Ozone (con’t): Production, Destruction, & Trends

Antarctic Ozone Hole: Sept. 12, 2012

http://ozonewatch.gsfc.nasa.gov/

Thermal Structure of the Atmosphere

Why are the Thermosphere and Stratosphere so “hot”?

Thermosphere:
Photodissociation of $O_2$

$O_2 \rightarrow h\nu + O + O$ (ionization)

$\lambda \approx 120-210 \text{ nm}$

Stratosphere:
Ozone production and destruction in ultraviolet radiation:

$O_3 + O \rightarrow O_2$ (production)

$\lambda < 310 \text{ nm}$

produces heat
Photodissociation of Oxygen

\[ \text{O}_2 + \text{UV light (120-210 nm)} \rightarrow \text{O} + \text{O} \]

Makes "free O" for making ozone (O\(_3\))

Occurs above 50 km in atmosphere
(Upper Stratosphere)

“Good” and “Bad” Ozone

Now

Natural Ozone Production

The Chapman Profile: balancing density and photon flux
Factors controlling the rate of photodissociation

1. The wavelength of light.
   The wavelength must be short enough so the wave has sufficient energy to break the bond between the two atoms in the oxygen molecule. The most efficient wavelengths for photodissociation occur in the ultraviolet (0.15µm).

2. Variation of oxygen density.
   As altitude increases oxygen density decreases (Chapman Profile). The higher the oxygen density the greater the likelihood of having an interaction between an oxygen molecule and a photon.

3. Variation of photon flux.
   Photon flux decreases with decreasing altitude because of photon absorption by the atmosphere. Rate of photodissociation of oxygen is greatest at an altitude of about 100 km.

The Chapman Cycle

1930s, Sydney Chapman proposed a series of reactions to account for the ozone layer: the Chapman Cycle

The Chapman Cycle explains how the ozone layer is formed and maintained. Describe this process in some detail.

Four chemical reactions:

- **Initiation**
  \[ \text{O}_2 + \text{light} \rightarrow 2\text{O} \quad (120 – 210 \text{ nm}) \]

- **Propagation** (cycling)
  \[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}^* \quad \text{(exothermic)} \]
  \[ \text{O}_3 + \text{light} \rightarrow \text{O}_2 + \text{O} \quad (220 – 320 \text{ nm}) \]

- **Termination**
  \[ \text{O}_3 + \text{O} \rightarrow 2\text{O}_2 \quad \text{(exothermic)} \]

The Chapman Cycle

**Oxygen-only Chemistry**

"Odd-oxygen" species (O₃) are rapidly interconverted

\[ \text{O}_x = \text{O} + \text{O}_2 \]
Ozone Production
(>50 km)

Ozone Destruction
(50-15 km)

O₃ production & destruction

DU: Ozone measurement unit

Dobson Unit (100 DU = 1 mm O₃ at STP)
Rowland & Molina & Crutzen (1974)

Discovered that CFCs can last 10-100s of years in atmosphere.
CFCs susceptible to break down by UV
Predicted that CFCs will reduce ozone inventories.
Proof that this was occurring came in 1985.
Montreal Protocol 1987

Nobel Prize (1995)

A Brief History

- June 28, 1974, Drs. Sherry Rowland and Mario Molina published the first study warning that CFCs could harm the ozone layer (Molina and Rowland, 1974).
- They calculated that if CFC production continued to increase it would cause a global ozone loss of 30-50% loss by 2050. (current number is 70%).
- They warned that the loss of ozone would significantly increase the amount of UV-B light reaching the surface, increasing incidences of skin cancer.
- Although no stratospheric ozone loss had been observed yet, CFCs should be banned.
- At the time, the CFC industry was worth about $8 billion in the U.S., employed over 600,000 people directly, and 1.4 million people indirectly (Roan, 1989).

Key ingredients to make an Ozone Hole:

- Chlorine: supplied by manmade CFCs
- Cold: Antarctic Polar Vortex
- Seasons: Dark and Light seasons
- Clouds: Polar Stratospheric Clouds
- UV radiation: Springtime sunlight
CFCs: Chlorofluorocarbons

CFCs introduced 1950s

“Miracle compounds”: inert, cheap, many applications.

Uses:
- Foam & Insulation
- Propellants
- Air conditioning
- Electronics

CFC Compounds

<table>
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<tr>
<th>Compound</th>
<th>Formula</th>
<th>ODP</th>
<th>Atmospheric lifetime (years)</th>
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<tbody>
<tr>
<td>CFC-11</td>
<td>CF₂Cl₂</td>
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<td>60</td>
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<tr>
<td>CFC-12</td>
<td>CF₂Br₂</td>
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<tr>
<td>CFC-113</td>
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<td>Halon 1211</td>
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<tr>
<td>Halon 1301</td>
<td>CBr₃</td>
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<td>Halon-2402</td>
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<td>HFC-22</td>
<td>CH₂F₂</td>
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<tr>
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<tr>
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<tr>
<td>HCFC-124</td>
<td>CF₂CHCl₂</td>
<td>0.018-0.824</td>
<td>5-10</td>
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</tbody>
</table>

Antarctic Polar Vortex

Large polar land mass
- Ice covered, large temperature gradients
- Circular airflow around Antarctica
- APV effectively creates an atmospheric “fence” impeding air exchange with other regions

(This is arctic polar vortex)
Polar Stratospheric Clouds (PSCs)

Ice clouds during Austral winter (no light, very cold)
PSCs concentrate, activate Cl (as Cl- and CLO)
Ice crystals act as reaction sites for O₃ destruction
CFCs accumulate in stratosphere

O₃ loss by UV photolysis

Austral spring: sunlight appears, UV
1. UV radiation splits off Cl atom from CFC molecule
2. Ozone destroying reactions:
   Cl + O₃ → ClO + O₂
   ClO + O → Cl + O₂
   (Cl is free to react with another O₃ again)
   Net: O₃ + O → O₂ + O₂

UV radiation and CFCs
CFC and $O_3$

**Discovery of the Ozone Hole**
British Antarctic Survey (Farman et al 1985)

Figure 1. Mean October atmospheric ozone levels over Antarctica. Open boxes: British Antarctic Survey data; filled boxes: NASA data (adapted from Farman 1990).
Antarctic Ozone Hole in Dobson Units

Area of the Ozone Hole

The Ozone Hole right now
The Ozone Hole in 2007

Current Status (2012)

Ozone Hole Area

SH Dobson units

Future projections
Full recovery takes a long time (50 years)

The world avoided...

By 2020, an Arctic “ozone hole” is apparent
As over Antarctica, the ozone losses are extreme, and spread to mid-latitudes.