Stratospheric Ozone Depletion

Ozone

Allotrope of oxygen

Ordinary oxygen is a diatomic molecule, $\text{O}_2$

\[
\begin{array}{c}
\text{O} \\
\text{O}
\end{array}
\]

Another form of elemental oxygen is $\text{O}_3$

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{O}
\end{array}
\]

O$_3$ associated with thunderstorms, electric discharges.

O$_3$ very reactive, strong oxidizing agent.

Presence in atmosphere

O$_3$ is a trace gas in atmosphere. Ozone “layer” in stratosphere, if brought to ground level $\approx$ 3 mm thick

[Image of ozone concentration graph showing peaks at 7 ppm and 0.1 ppm]
Expanded scales, etc
Chemistry of Ozone Layer

Light Absorption by Molecules

\[ \text{O}_2 \text{ above stratosphere filters UV light from 120 - 220 nm, rest is filtered in stratosphere.} \]

\[ \text{O}_3 \text{ filters UV light from 220 - 370 nm in stratosphere} \]
O$_3$ very effective from 220 - 290 nm.
   (incl. UV-C)
Not so effective for UVB (290 - 320 nm)
Principles of Photochemistry

Basic equations

\[ E = h\nu = \frac{hc}{\lambda} \]

\( hc = 119,627 \text{ kJ/mol/nm} \)

(one molecule absorbs 1 photon, 6.02 x 10^{23} molecules)

\[ E = \frac{119,627}{\lambda(\text{nm})} \text{ kJ/mol} \]

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>E (kJ mol^{-1})</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>544</td>
<td>Strong O_2 absorption limit</td>
</tr>
<tr>
<td>190</td>
<td>413</td>
<td>Limit of UV-B at surface</td>
</tr>
<tr>
<td>320</td>
<td>374</td>
<td>Limit of UV-A region</td>
</tr>
<tr>
<td>400</td>
<td>299</td>
<td>Violet limit of visible</td>
</tr>
<tr>
<td>750</td>
<td>160</td>
<td>Red limit of visible</td>
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</table>
Energies are $-\Delta H$ for chemical rxns.

$$\text{O}_2 \rightarrow 2 \text{O} \quad \Delta H^\circ = 495 \text{ kJ/mol}$$

To make this rxn go:

$$\lambda = \frac{119,627}{495} = 241 \text{ nm}$$

So if $\lambda < 241$ nm, the above rxn can occur

Non catalytic creation + development of $\text{O}_3$

Above stratosphere, get mostly O

$$\text{O}_2 + h\nu \rightarrow 2 \text{O}$$

then

$$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} + \text{heat}$$

(gives rise to T profile of stratosphere)

Also, then can get

$$\text{O}_3 + \text{UV photon}(\lambda < 320 \text{ nm}) \rightarrow \text{O}_2 + \text{O}^*$$

($\Delta H^\circ_{gs} = 105 \text{ kJ/mol}$)

Also get

$$\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$$
Catalytic Processes of \( \text{O}_3 \) Destruction

\[
\begin{align*}
\text{X} + \text{O}_3 & \rightarrow \text{XO} + \text{O}_2 \\
\text{XO} + \text{O} & \rightarrow \text{X} + \text{O}_2
\end{align*}
\]

Overall rxn: \( \text{O}_3 + \text{O} \rightarrow \text{O}_2 \)

\( \text{X} \) is a catalyst. All \( \text{X} \) are free radicals (odd # of electrons)

Choices for \( \text{X} \)
(a) \( \text{HO} \cdot \) \( \frac{1}{2} \text{O}_3 \) destruction
   (produced in \( \text{O}^* + \text{CH}_4 \rightarrow \cdot \text{OH} + \cdot \text{CH}_3 \)
   \( \text{H}_2\text{O} \rightarrow 2\cdot \text{OH} \)

(b) Atomic Cl or Br (not natural due to reactivity)
   \( \text{Cl} \cdot + \text{O}_3 \rightarrow \text{ClO} \cdot + \text{O}_2 \)
   \( \text{ClO} \cdot + \text{O} \rightarrow \text{Cl} \cdot + \text{O}_2 \)
O₃ + O → O₂
each Cl atom can destroy tens of thousands of O₃
Source of Cl•
RX + hν → R• + X•
or RX + •OH

(c) NO
N₂O + hν → N₂ + O*
N₂O + O* → 2 NO•
NO• + O₃ → NO₂• + O₂
NO₂• + O → NO• + O₂
O₃ + O → O₂

Most Cl is “stored” as inactive molecules, HCl, ClONO₂
Cl• + CH₄ → HCl + CH₃•
ClO• + NO₂• → ClONO₂

Useful background event
SST
worry about
N₂ + O₂ → 2 NO
and NO release from SSTs. There was an extensive study of photochemistry of this reaction

1974: Sherry Rowland + Mario Molina (UC - Irvine)
pointed to another possible problem:
CCl₂F₂ + hν → CClF₂ + Cl
\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2
\end{align*}
\]
Net rxn. O + O₃ → 2 O₂
Chlorofluorocarbons catalyze destruction of ozone
Source of CFCs (Freons (DuPont))
aerosol spray cans (propellant)
working fluids for air conditioners, refrigerators, heat pumps
Chemistry of CFCs

great resistance to chemical rxns.
no known reaction that destroys them
all CFCs manufactured are released to atmosphere eventually
one single Cl atom (from CFC) will destroy 100,000 $\text{O}_3$
molecules

The use of CFCs in aerosol cans was banned in US in 1978.
(Other uses of CFCs continued)
1984: A British group found a severe depletion of O₃ over Antarctica during Oct (Spring) - was confirmed by US satellite data
13 Monthly Variation of Total Ozone over Halley Bay, Antarctica

Figure 2.11
Loss of 50% of total overhead amount.
In 1993, $O_3 = 90$ DU.
(October)

Figure 2.10

Data from World Meteorological Organization (Ozone Report #23, American Chemical Society, Chemistry in Context, 1st ed. Copyright 1994 American Chemical Society, Washington, D.C. All Rights Reserved.
Instruments aboard NASA's ER-2 research airplane measured concentrations of chlorine monoxide and ozone simultaneously as the plane flew from Punta Arenas, Chile (53°S), to 72°S. The data shown above were collected on September 16, 1987. As the plane entered the ozone hole, concentrations of chlorine monoxide increased to about 500 times normal levels while ozone plummeted.
Chemistry of Ozone Hole Formation

Special winter conditions in lower stratosphere temporarily convert all chlorine stored as HCl and ClONO₂ into Cl• and ClO•. Conversion takes place on surface of ice crystals of H₂O and HNO₃ formed by OH• + NO₂•.

During winter (no light)
\[ \text{HCl + ClONO}_2 \xrightarrow{\text{surface of xtal}} \text{Cl}_2 + \text{HNO}_3 \]

Spring
\[ \text{Cl}_2 + hv \longrightarrow 2 \text{Cl}• \]

Also get winter
\[ \text{H}_2\text{O} + \text{ClONO}_2 \xrightarrow{\text{surface of xtal}} \text{HOCl} + \text{HNO}_3 \]

Spring
\[ \text{HOCl} + hv \longrightarrow \text{OH}• + \text{Cl}• \]
Figure 2.35 Reaction sequence responsible for Antarctic ozone hole.

The evolution of stratospheric chlorine chemistry with time above the Arctic in winter and spring. (Source: Redrawn from C. B. Webster et al., Science 261 (1993): 1130.)
Role of CFCs

Statospheric conc, of Cl = 3.5 ppb (0.6 ppb nat.)

no sink of CFCs in troposphere => rise to stratosphere

in stratosphere

\[ \text{CF}_2\text{Cl}_2 + hv \rightarrow \text{CF}_2\text{Cl}^* + \text{Cl}^* \]

T stratosphere of CFCs ~ 50 - 100 yr

Most action due to CFC - 11, CFC - 12 (‘hard’ CFCs, no H)
World wide O₃ concentrations appear to be decreasing at rate of ~ 1% / year

**So what?**
Biological Consequences of O₃ Depletion

Decrease in O₃ allows more UV-B to penetrate to earth’s surface.

1% decrease in O₃ $\Rightarrow$ 2% increase in UV-B at ground level.

![Graph showing incidence of skin cancer versus intensity of ultraviolet radiation](image)

Midlatitude effects

1972 - 1992  
6.6% decrease in O₃ in stratosphere

$\Rightarrow$ 11% increase in basal cell carcinogens

22% increase in squamous cell carcinogens

effect not seen yet (latency period)
Figure 2.30 Action spectrum of ultraviolet radiation damage to living tissue.

Figure 2.31 Variation with latitude of UV flux at 300 nm (dashed line) and death from skin cancer among white males in the United States (solid line) (excluding Alaska and Hawaii).

UVB harmful

Consequences
* ~ 2030  O₃ at Oslo, Leningrad decrease by 5%
  UV radiation increase 10%
  Skin cancer increase 10%
  [correlation between UV + skin cancer: skin cancer (ME) ~ \( \frac{1}{2} \) skin cancer (FL)]
  EPA estimates a nationwide increase of \( 40 \times 10^6 \) cancers between now and 2075. (\( 2 \times 10^5 \) deaths)
* destruction of phytoplankton in ocean
  oceanic food chain
  release of CO₂

Sensitivity to Ozone Reduction
\[
T \equiv \text{Transmission} = \frac{I}{I_0} = e^{-\varepsilon l}
\]
\[
\varepsilon = \varepsilon(\lambda)
\]
\[
\varepsilon l \quad \lambda = 310
\]
\[
10 \quad 290
\]
\[ dT = -\varepsilon e^{-l} \, dl \]
\[ dT / T = -\varepsilon dl = dl / l \]

1% decrease in l causes 1% decreases in T at 310
10% decrease in T at 290

If O₃ decreasing at 0.4 % / yr
O₃ loss / decade = 4% \(\Rightarrow\) 12% change in T at 300 nm
40% change in T at 290 nm

"Oh, for Pete's sake, let's just get some ozone and send it back up there!"

(©1976 by Sidney Harris—American Scientist Magazine.)

What's so funny about this industrialist's answer to the ozone problem? To check whether it is a reasonable solution, suppose you determine the number of jumbo jet-loads of O₂ that would be required to replace 10% of the atmospheric ozone. Clearly, there are many different assumptions you might make and a variety of strategies you might use, but we offer some suggestions on how to proceed.

a. Let's focus on the region of the atmosphere between 10 and 50 km above the Earth's surface. Use Figure 2.9 to estimate the ozone concentration in this region.
b. You need to know the total number of \( \text{O}_3 \) molecules in this region, and therefore must calculate its volume. The region in question is a spherical shell, 40 km thick. The volume of such a shell is equal to \( 4\pi r^2t \), where \( r \) is the average radius of the shell and \( t \) is its thickness. Since the shell of air surrounds the Earth, you need to include the radius of the Earth (6300 km) in your calculation. A drawing might help. If you express \( r \) and \( t \) in kilometers, the volume will be in cubic kilometers or \( \text{km}^3 \).

\[
v = 4\pi r^2t
\]
\[
= 4(3.14)(6300\text{ km})^2(40\text{ km})
\]

c. Now you can use the results from a. and b. to compute the number of \( \text{O}_3 \) molecules in this ozone-rich region (1 km\(^3\) = 10\(^9\) m\(^3\)).

d. You also need to find out the number of \( \text{O}_3 \) molecules that can be carried in a jumbo jet. This in turn requires knowledge of the volume of a plane. Let's assume the jet can be approximated by a cylinder with a radius \( r \) of 5 m (15 ft) and a length \( l \) of 65 m (200 ft). The volume of the cylinder is \( \pi r^2l \).

\[
v = \pi r^2l
\]
\[
= (3.14)(5\text{ m})^2(65\text{ m})
\]

e. At 25°C and 1 atmosphere pressure, 25 L of gas contain about \( 6 \times 10^{20} \) molecules. Use this information and your answer to d. to calculate the number of \( \text{O}_3 \) molecules that could be contained in a single jumbo jet under these conditions of temperature and pressure (\( 10^3 \text{ L} = 1 \text{ m}^3 \)).

f. Finally, use the results of c. and e. to find the number of jet-loads of \( \text{O}_3 \) that would be required to replenish 10% of the ozone molecules in this region.

Note: We got a final answer of 1.7 \( \times 10^7 \) or 170 million planeloads, but you might be skeptical of that, too.
Global CFC Use

Aerosols        25%
Rigid foam insulation (Styrofoam)   19%
Solvents        19%
Air conditioning       12%
Refrigerators       8%
Flexible foam       7%

CFC nomenclature

CFC - 12
CFC - 12  12 + 90 = 102  1C, 0H, 2F
CFC - 115  115 + 90 = 205  2C, 0H, 5F
   F   F
  |    |
F – C – C – Cl
  |    |
   F   F

O3 treaties

1987   Montreal accord
       reduce CFC production to 50% of 1986
       by 2000.

1990   London amendments
       phase out of CFCs by 2000

1992   Copenhagen agreement
       phase out of CFCs by 1996
Figure 2.38 Percentage ozone changes in the southern hemisphere (referenced to year 1965) for three different chlorofluorocarbon emission scenarios: (a) assuming constant CFC emissions at 1974 levels; (b) assuming CFC emission reductions as specified in the Montreal protocol of 1987; (c) assuming CFC emission reductions under the 1990 London revisions. Source: C. Bruehl and P. J. Crutzen (1988). Scenarios for possible changes in atmospheric temperatures and ozone concentrations due to man's activities as estimated with a one-dimensional coupled photochemical climate model, *Climate Dynamics* 2: 173–203. Copyright © 1988 by Springer-Verlag. Reprinted with permission.
Figure 2-18
Chlorinated compounds, N₂O increasing in atmosphere

The trace gases trichlorofluoromethane (CFC-11, or CFCl₃), dichlorodifluoromethane (CFC-12, or CF₂Cl₂), methylchloroform (CH₃CCl₃), carbon tetrachloride (CCl₄), and nitrous oxide (N₂O) have been measured since mid-1976 at the Barbados station of the Global Atmospheric Gases Experiment (GAGE). The graphs show the monthly means and monthly variances there. Qualitatively similar results are obtained from the other GAGE stations located in Tasmania, Samoa, Oregon, and Ireland. At each station each of these trace gases is measured four or more times daily at ground level. Source: R. Prinn, P. Simmonds, F. Alyea, D. Cunnold, A. Crawford, P. Fraser, R. Rasmussen, and R. Rosen.
$135 \times 10^9$ of equipment depends on CFCs
Other sources of chlorinated hydrocarbons in ozone layer
1.6 ppb CFCs
0.6 ppb natural sources
1.0 ppb other man-made compounds

**CFC Substitutes**

- **HCFC** (hydrochlorofluorocarbons) H atom makes it more biodegradable; but still contributes to O$_3$ decrease
- **HFC** no chlorine, but a greenhouse gas
- isobutene hydrocarbons flammability problems
- **halons** no substitutes