Atmospheric Chemistry of the Ozone Layer

EP/TOMS Total Ozone Oct 21, 2001

Levels of Atmospheric Ozone have been Dropping

Ozone Over Arosa, Switzerland
Yearly Means, 1926-1997

Trend 1973-1997: -2.9%/decade

Source: Swiss Meteorological Institute

Decreasing Level of atmospheric ozone is harmful

There has been an increase in the number of cases of skin cancer and cataracts

Evidence of damage to plant and marine life
What is ozone?
Where in the atmosphere is it found?
What is its purpose in the atmosphere?
What is its chemistry?
Why are levels of atmospheric ozone dropping?
Finally, what is the Ozone Hole?
Structure of Ozone

O Atoms

$O_3$
Where is ozone found in the atmosphere?

Note, higher concentration in stratosphere, compared with troposphere.

NASA Goddard Space Flight Center
Role of Ozone

Solar Flux

Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling - JPL Publication 97-4
Role of Ozone

Absorption Spectrum of Ozone

![Absorption Spectrum of Ozone](image)
Role of Ozone

"The Ozone Depletion Phenomenon", Beyond Discovery, National Academy of Sciences
Role of Ozone

UV A (~400 to 350 nm) not absorbed by earth's atmosphere

UV B (~ 350 to 270 nm) partially absorbed by earth's atmosphere

UV C (~270 to 150 nm) completely absorbed by earth's atmosphere

UV B is harmful to life on earth
**How is ozone production and destruction?**

**Chapman mechanism**

\[
\text{O}_2 + h\nu \rightarrow O + O
\]

\[
O + O_2 + M \rightarrow O_3 + M
\]

\[
O_3 + h\nu' \rightarrow O + O_2
\]

\[
O + O_3 \rightarrow 2\text{ O}_2
\]

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"Ozone: What is it and why do we care about it?", NASA Facts, Goddard Space Flight Center
Kinetics of Chapman Mechanism

\[ O_2 + h\nu \rightarrow O + O \quad k_1 \]
\[ O + O_2 + M \rightarrow O_3 + M \quad k_2 \]
\[ O_3 + h\nu' \rightarrow O + O_2 \quad k_3 \]
\[ O + O_3 \rightarrow 2 O_2 \quad k_4 \]

Rate of formation of \( O \) and \( O_3 \)

\[ \frac{d[O]}{dt} = 2k_1[O_2] - k_2[O][O_2][M] + k_3[O_3] - k_4[O][O_3] \]
\[ \frac{d[O_3]}{dt} = k_2[O][O_2][M] - k_3[O_3] - k_4[O][O_3] \]

Steady-State Approximation

\[ \frac{d[O]}{dt} = \frac{d[O_3]}{dt} = 0 \]
Kinetics of Chapman Mechanism

\[
\]

\[
k_2[O][O_2][M] = \{ k_3 + k_4[O] \} \ [O_3]
\]

\[
k_2[O][O_2][M]/\{ k_3 + k_4[O] \} = [O_3]
\]
Kinetics of Chapman Mechanism

Can re-write \([O_3]\) as:

\[
[O_3] = \frac{k_2[O][O_2][M]}{k_3 + k_4[O]}
\]

(Divide by \(k_4[O]\))

\[
[O_3] = \frac{k_2[O_2][M]/k_4}{k_3/(k_4[O]) + 1}
\]
Kinetics of Chapman Mechanism

Since the rate constants and concentration of species are known, can show that:

\[
\frac{k_3}{k_4 [O]} \gg 1
\]

Hence,

\[
[O_3] \approx \frac{k_2 [O_2][M][O]}{k_3}
\]

\[
[O_3] = \frac{k_2 [O_2][M]/k_4}{k_3/(k_4 [O]) + 1}
\]
Kinetics of Chapman Mechanism

\[ [O_3] \approx \frac{k_2 [O_2] [M] [O]}{k_3} \]

\([O_3]\) depends on rate of reaction 2 and the intensity of light \((k_3)\)

Reaction 2 is slow (termolecular); makes ozone “vulnerable” to ozone-depleting reactions

\[
\begin{align*}
O_2 + h\nu &\rightarrow O + O & \quad & k_1 \\
O + O_2 + M &\rightarrow O_3 + M & \quad & k_2 \\
O_3 + h\nu' &\rightarrow O + O_2 & \quad & k_3 \\
O + O_3 &\rightarrow 2 O_2 & \quad & k_4
\end{align*}
\]
Competing Reactions

\[ \text{HO}_x \text{ cycle} \]

H, OH and HO\(_2\) species formed by reaction of excited O atoms with H-containing atmospheric species like H\(_2\)O and CH\(_2\)

\[
\begin{align*}
O_3 + h\nu & \rightarrow O + O_2 \\
O + H_2O & \rightarrow OH + OH \\
O + CH_4 & \rightarrow CH_3 + OH \\
H_2O + h\nu & \rightarrow H + OH
\end{align*}
\]
Reactions of \( \text{HO}_x \) species with \( \text{O}_3 \)

\[
\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2
\]

\[
\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2
\]

Net Reaction

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

“Ozone Depletion”
Competing Reactions

$\text{NO}_x$ Cycle

$\text{NO}_x$ species are produced during the reaction of $O$ atoms with $\text{N}_2\text{O}$ (produced in the soil by bacteria)

$O + \text{N}_2\text{O} \rightarrow 2 \text{NO}$
Reactions of NO\textsubscript{x} species with O\textsubscript{3}

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

\[
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2
\]

Net Reaction

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

“Ozone Depletion”
Competing Reactions

$\text{ClO}_x$ cycle

$\text{ClO}_x$ species are produced from chlorofluorocarbons (CFC's) and methyl chloride

CFC's are artificially produced; methyl chloride is a naturally occurring chemical.

Examples of CFC's: Freons ($\text{CFCl}_3$, $\text{CF}_2\text{Cl}_2$)

$\text{CCl}_2\text{F}_2 + \text{hv} \rightarrow \text{CF}_2\text{Cl} + \text{Cl}$

$\text{CCl}_2\text{F}_2 + \text{O} \rightarrow \text{CF}_2\text{Cl} + \text{ClO}$
Reactions of ClO\textsubscript{x} species with O\textsubscript{3}

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]
\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]

Net Reaction

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

"Ozone Depletion"

1995 Nobel Prize in Chemistry
Consequences of Competing Reactions

Catalytic Reactions

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

\[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]

- lower activation energy

\[ E_a \text{ for Chapman mechanism} = 17.1 \text{ kJ/mol} \]

\[ E_a \text{ for } \text{ClO}_x \text{ reaction} = 2.1 \text{ kJ/mol} \]
Consequences of Competing Reactions

Effect of competing reaction on rate of ozone formation

Depleting reactions are NOT independent of each other; in fact all occur simultaneously

NET LOSS OF OZONE
Sources of ozone depleting molecules

Naturally occurring species (H₂O, N₂O, CH₄)

Artificial, “man-made” species

- CFC’s (CCl₃F, CCl₂F₂, etc.)
- CCl₄, CHCl₃
- HBFC (CHFBr₂, CHF₂Br)
- CH₃Br

NO from supersonic aircrafts

The artificial compounds have the most severe effect
What is the “Ozone Hole”? Every year, in October, a huge “hole” in atmospheric levels of ozone is observed over the Antarctic.

You will have to wait to see this movie in class.

EP/TOMS Total Ozone for Aug 1, 1996

August 1 '96 - Dec 15 '96

NASA Goddard Space Flight Center
Why does the Ozone Hole form over the Antarctic and why in spring?

The Antarctic Vortex

Polar Stratospheric Clouds

Concentrations of Active Chlorine
The Antarctic Vortex

In the winter, the air around the S. Pole cools and circulate west creating a "vortex"

Air is trapped in the vortex along with ozone depleting species

Heat from outside is "shut off", prolonging the duration of low stratospheric temperatures.
Polar Stratospheric Clouds

Low stratospheric temperatures result in “ice clouds” called Polar Stratospheric Clouds

The surface of the ice clouds serve as reaction sites for heterogeneous gas-surface reactions

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{HNO}_3 + \text{Cl}_2
\]

\[
\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HOCl}
\]
Concentrations of Active Chlorine

The Cl₂ and HOCl formed photodissociate to yield reactive Cl atoms

\[ \text{Cl}_2 + \text{hv} \rightarrow \text{Cl} + \text{Cl} \]

\[ \text{HOCl} + \text{hv} \rightarrow \text{Cl} + \text{OH} \]

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

OZONE DEPLETION
“Ingredients” for the formation of the Ozone Hole

The Antarctic vortex traps CFC’s

The low polar temperatures results in ice particles on which gas-solid reactions can occur efficiently

The same reactions in the gas phase have much higher activation energies. The higher $E_a$ and low temperatures result in very slow rates.

The onset of spring corresponds to higher light intensities and hence photolysis of Cl containing species
Annual growth in the Antarctic Ozone Hole

University of Cambridge “The Ozone Hole Tour” http://www.atm.ch.cam.ac.uk
What is being done to reduce ozone depletion?

Montreal Protocol and subsequent treaties ban world-wide usage of ozone depleting substances.

Assuming full compliance expect that ozone levels will return to "natural" levels ~2050.

http://www.nobel.se/announcement-95/announcement95-chemistry.html
References

NASA Goddard Space Flight Center
(http://www.gsfc.nasa.gov/)

EPA (www.epa.gov)

Center for Atmospheric Science, Cambridge University
www.atm.ch.cam.ac.uk/tour/index.html

Chemical Kinetics and Dynamics, Ch 15, J. Steinfeld, J. Francisco, W. Hase