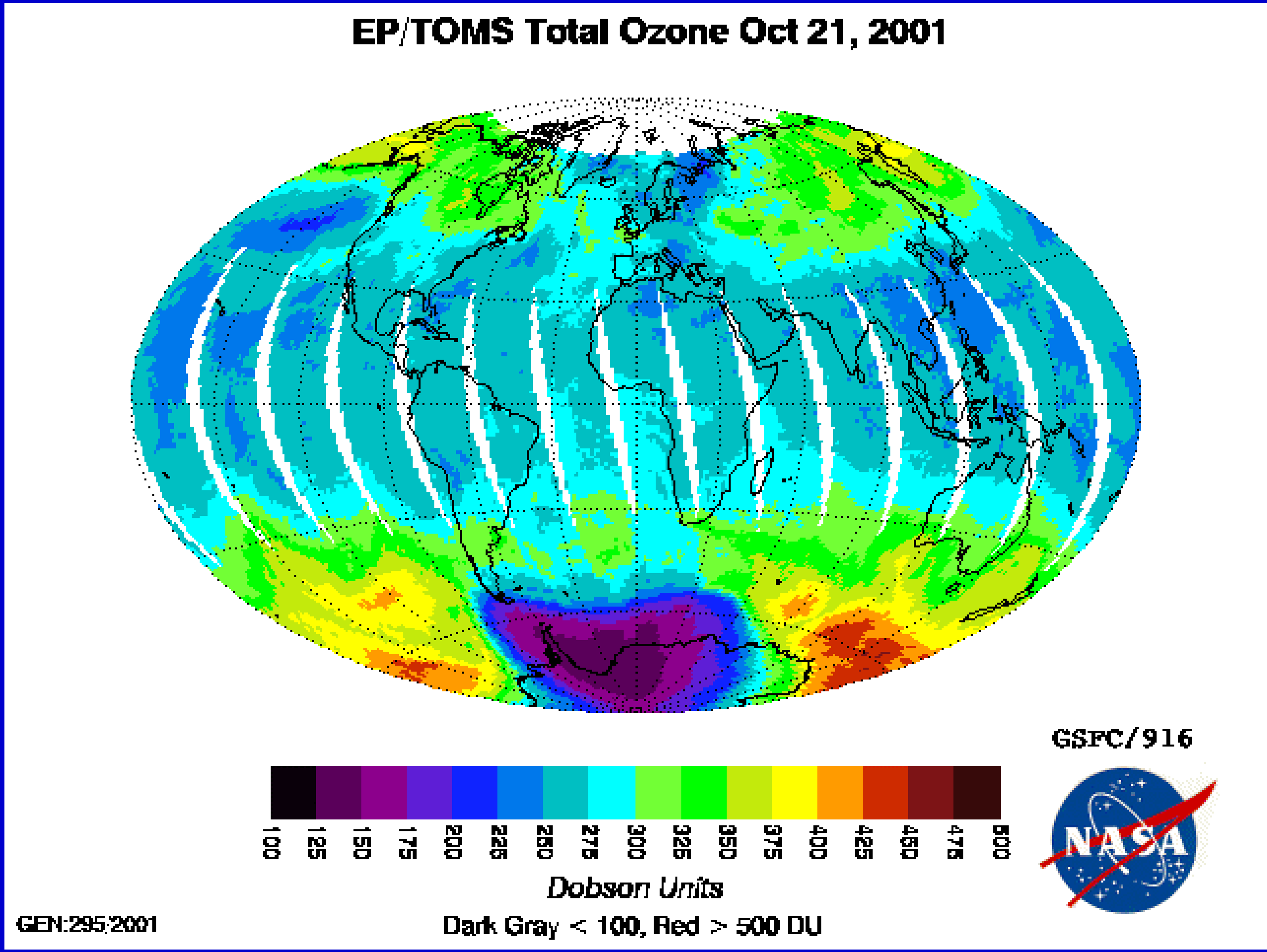
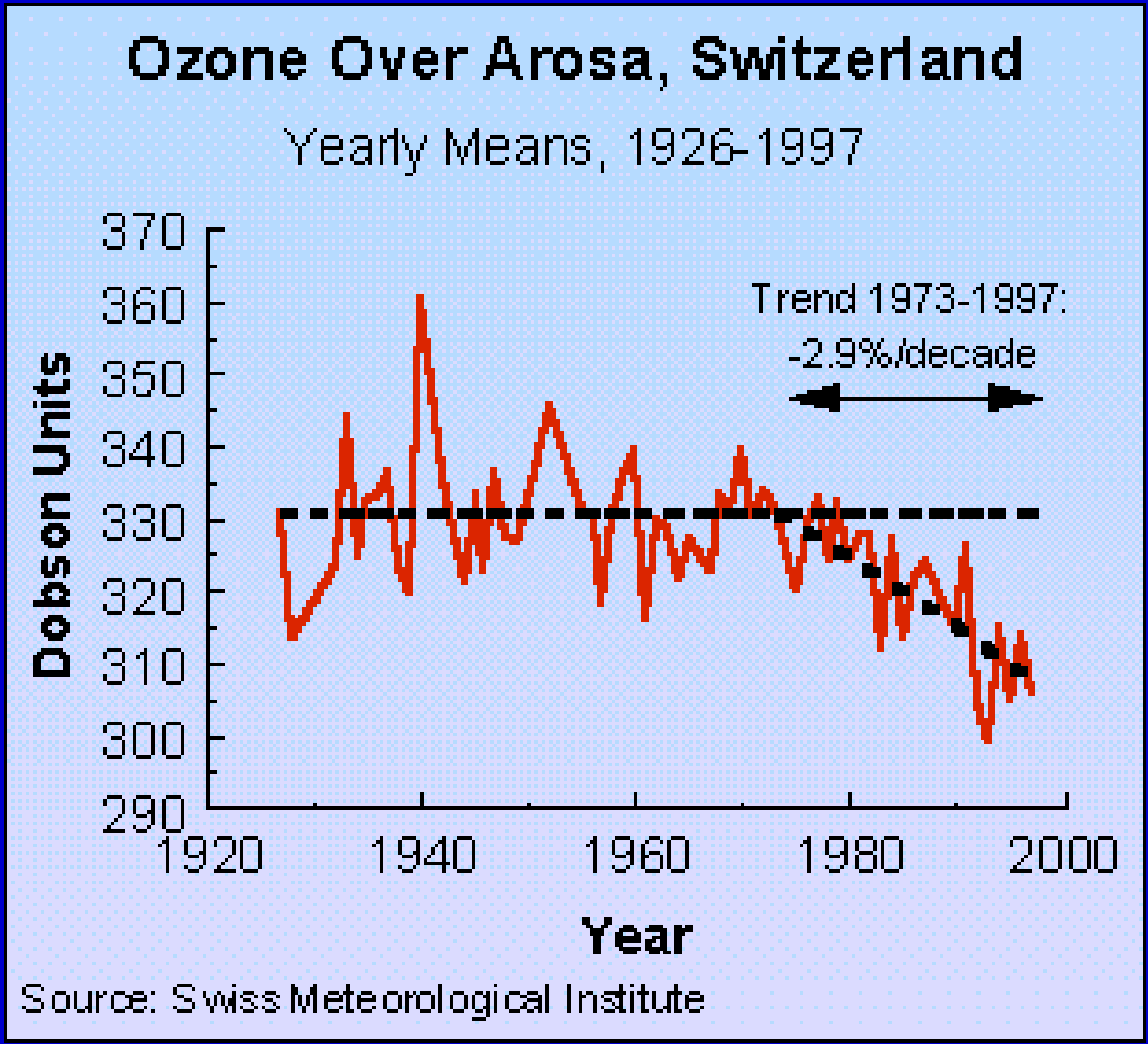
Atmospheric Chemistry of the Ozone Layer



NASA "Total Ozone Mapping Spectrometer" http://toms.gsfc.nasa.gov/

Levels of Atmospheric Ozone have been Dropping



EPA - http://www.epa.gov/docs/ozone/science/arosa.html

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?

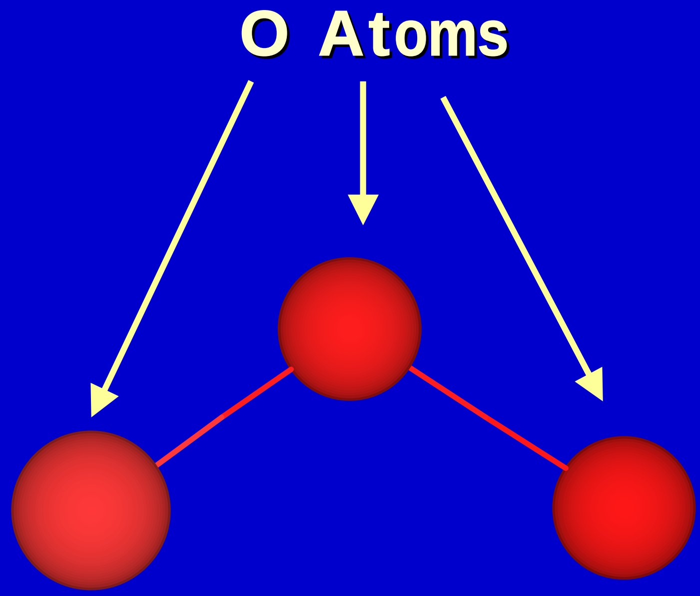
What is its purpose in the atmosphere?

What is its chemistry?

Why are levels of atmospheric ozone dropping?

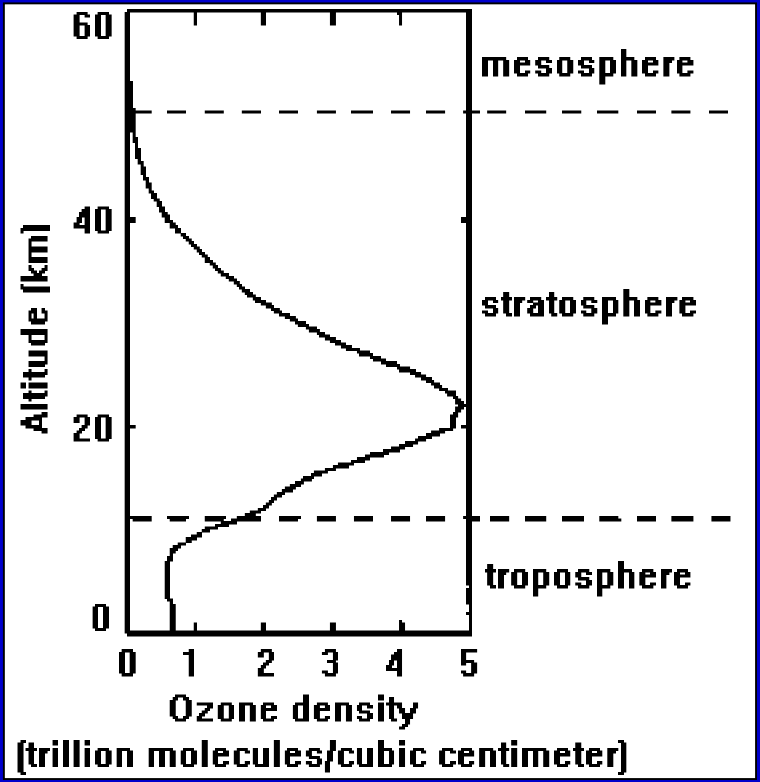
Finally, what is the Ozone Hole?

Structure of Ozone



O_3

Where is ozone found in the atmosphere ?

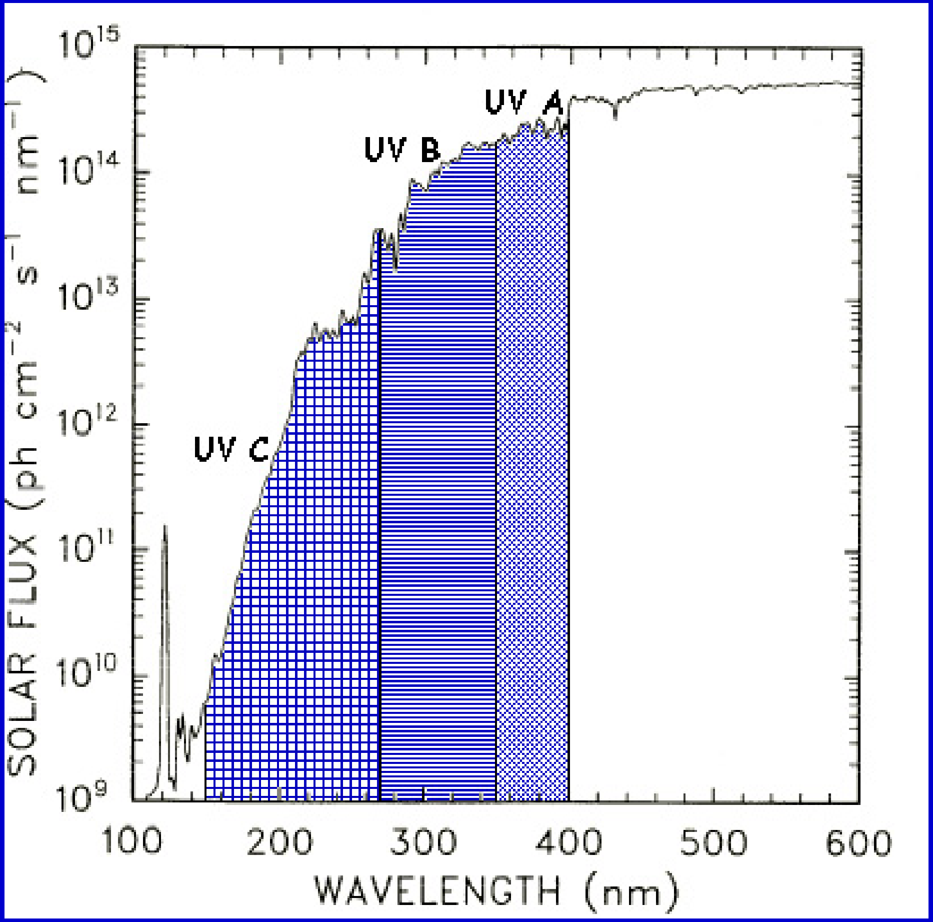


NASA Goddard Space Flight Center

Note, higher concentration in stratosphere, compared with troposphere

Role of Ozone

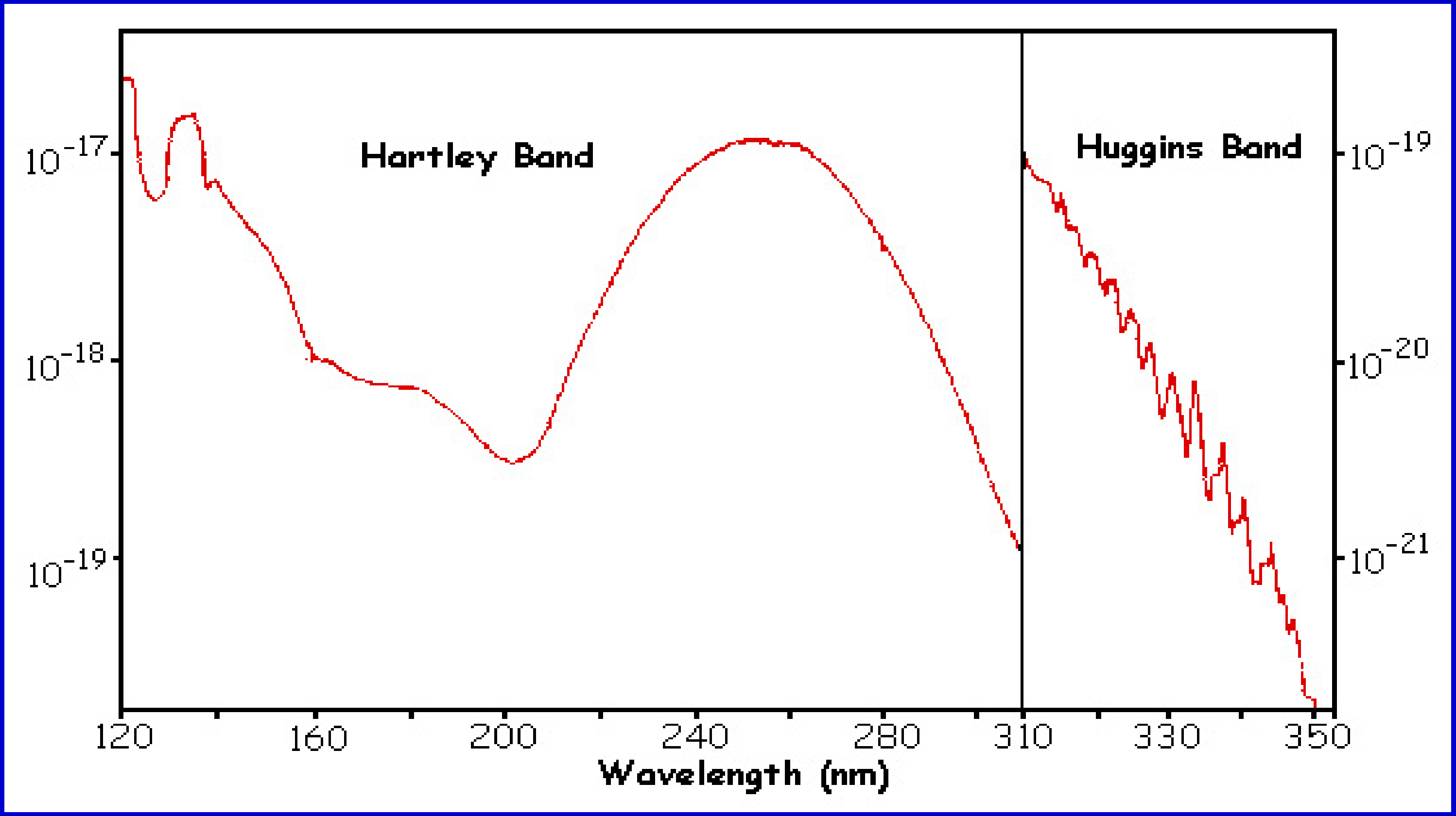
Solar Flux



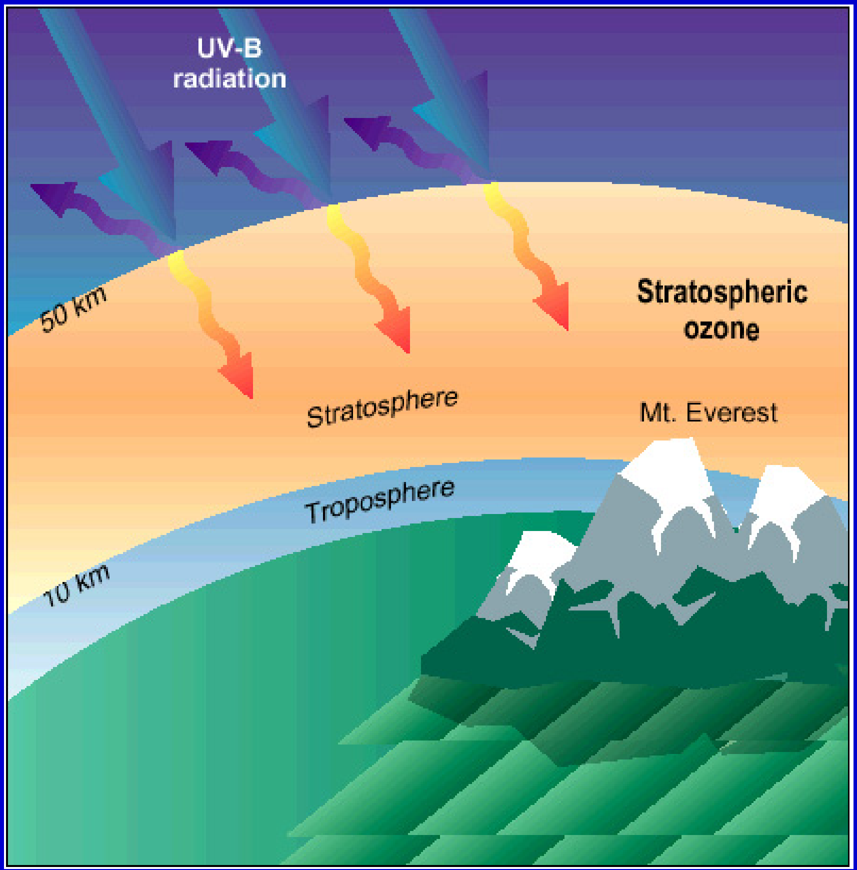
Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling - JPL Publication97-4

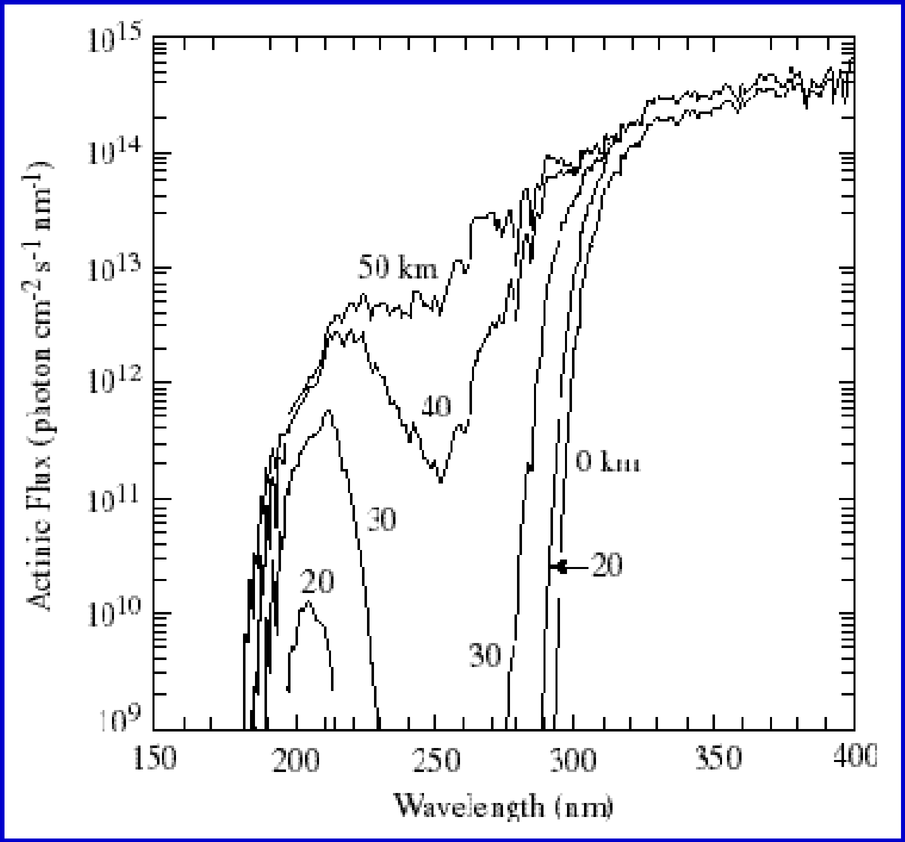
Role of Ozone

Absorption Spectrum of Ozone



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?

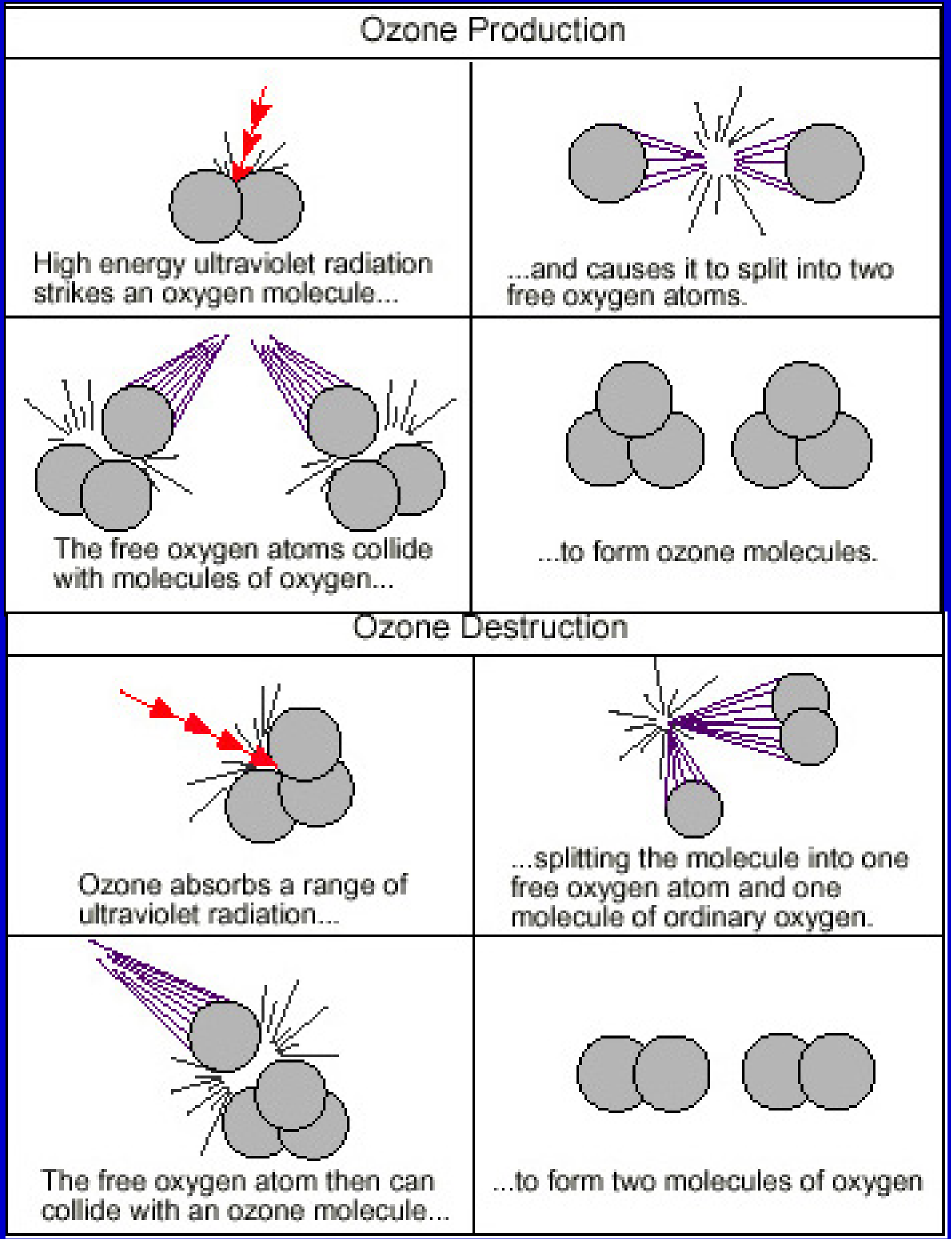
Chapman mechanism

$$O_2 + h\nu \rightarrow O + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O_3 + h\nu' \rightarrow O + O_2$$

$$O + O_3 \rightarrow 2\,O_2$$



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

Kinetics of Chapman Mechanism

$O_2 + h\nu \rightarrow O + O$ k_1

$O + O_2 + M \rightarrow O_3 + M$ k_2

$O_3 + h\nu' \rightarrow O + O_2$ k_3

$O + O_3 \rightarrow 2\ O_2$ k_4

Rate of formation of O and O_3

$$d[O]/dt = 2k_1[O_2]-k_2[O][O_2][M] + k_3[O_3] - k_4[O][O_3]$$

$$d[O_3]/dt = k_2[O][O_2][M] - k_3[O_3]-k_4[O][O_3]$$

Steady-State Approximation

$$d[O]/dt = d[O_3]/dt = 0$$

Kinetics of Chapman Mechanism

$$d[O_3]/dt = k_2[O][O_2][M] - k_3[O_3] - k_4[O]\,[O_3] = 0$$

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

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

Kinetics of Chapman Mechanism

Can re-write $[O_3]$ as:

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

(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:

$$\frac{k_3}{k_4[O]} >> 1 \quad + \quad [O_3] = \frac{k_2[O_2][M]/k_4}{k_3/(k_4[O]) + 1}$$

Hence,

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

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

$O_2 + h\nu \rightarrow O + O$	k_1
$O + O_2 + M \rightarrow O_3 + M$	k_2
$O_3 + h\nu' \rightarrow O + O_2$	k_3
$O + O_3 \rightarrow 2\,O_2$	k_4

Competing Reactions

HO_x cycle

H, OH and HO_2 species formed by reaction of excited O atoms with H-containing atmospheric species like H_2O and CH_2

$$O_3 + h\nu' \rightarrow O + O_2$$

$$O + H_2O \rightarrow OH + OH$$

$$O + CH_4 \rightarrow CH_3 + OH$$

$$H_2O + h\nu \rightarrow H + OH$$

Reactions of HO_x species with O_3

$$OH + O_3 \rightarrow HO_2 + O_2$$

$$HO_2 + O \rightarrow OH + O_2$$

Net Reaction

$$O + O_3 \rightarrow 2O_2$$

"Ozone Depletion"

Competing Reactions

NO_x Cycle

NOx species are produced during the reaction of O atoms with N_2O (produced in the soil by bacteria)

$$O + N_2O \rightarrow 2\ NO$$

Reactions of NO_x species with O_3

$NO + O_3 \rightarrow NO_2 + O_2$

$NO_2 + O \rightarrow NO + O_2$

Net Reaction

$$O + O_3 \rightarrow 2O_2$$

"Ozone Depletion"

Competing Reactions

ClO_x cycle

ClO_x species are produced from chlorofluorocarbons (CFC's) and methyl chloride

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

Examples of CFC's : Freons ($CFCl_3$, CF_2Cl_2)

$$CCl_2F_2 + h\nu \rightarrow CF_2Cl + Cl$$

$$CCl_2F_2 + O \rightarrow CF_2Cl + ClO$$

Reactions of ClO_x species with O_3

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O \rightarrow Cl + O_2$

Net Reaction

$$O + O_3 \rightarrow 2O_2$$

"Ozone Depletion"

1995 Nobel Prize in Chemistry

Consequences of Competing Reactions

Catalytic Reactions

catalyst intermediate

$$Cl + O_3 \rightarrow ClO + O_2$$

$$ClO + O \rightarrow Cl + O_2$$

intermediate catalyst

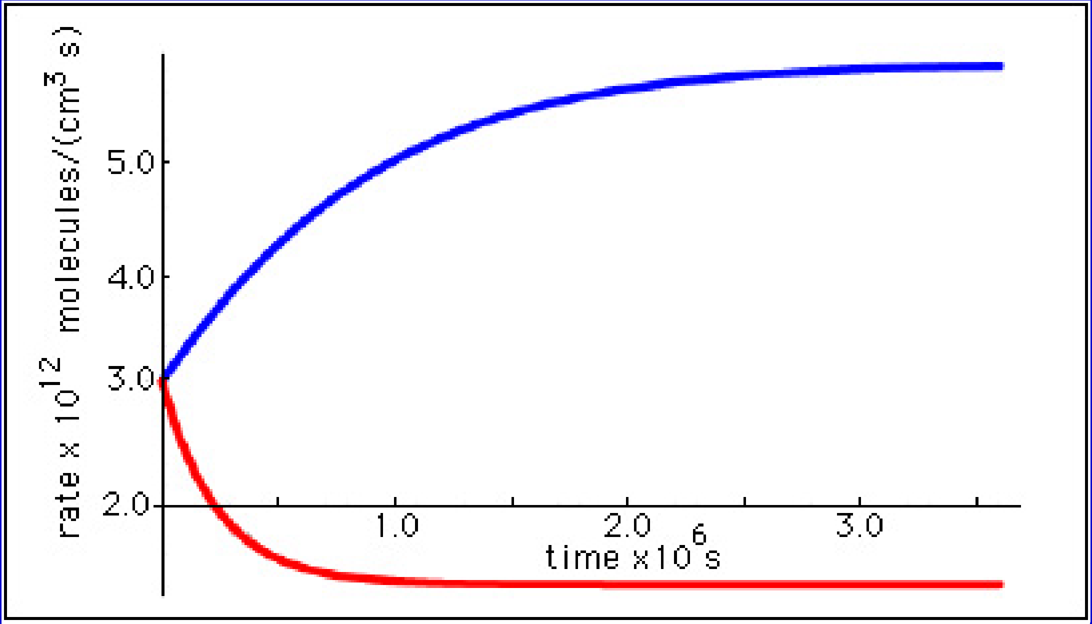
- lower activation energy

E_a for Chapman mechanism = 17.1 kJ/mol

E_a for ClO_x reaction = 2.1 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 occuring species (H_2O, N_2O, CH_4)

Artificial, “man-made” species

CFC’s (CCl_3F, CCl_2F_2, etc.)

CCl_4, $CHCl_3$

HBFC ($CHFBr_2$, CHF_2Br)

CH_3Br

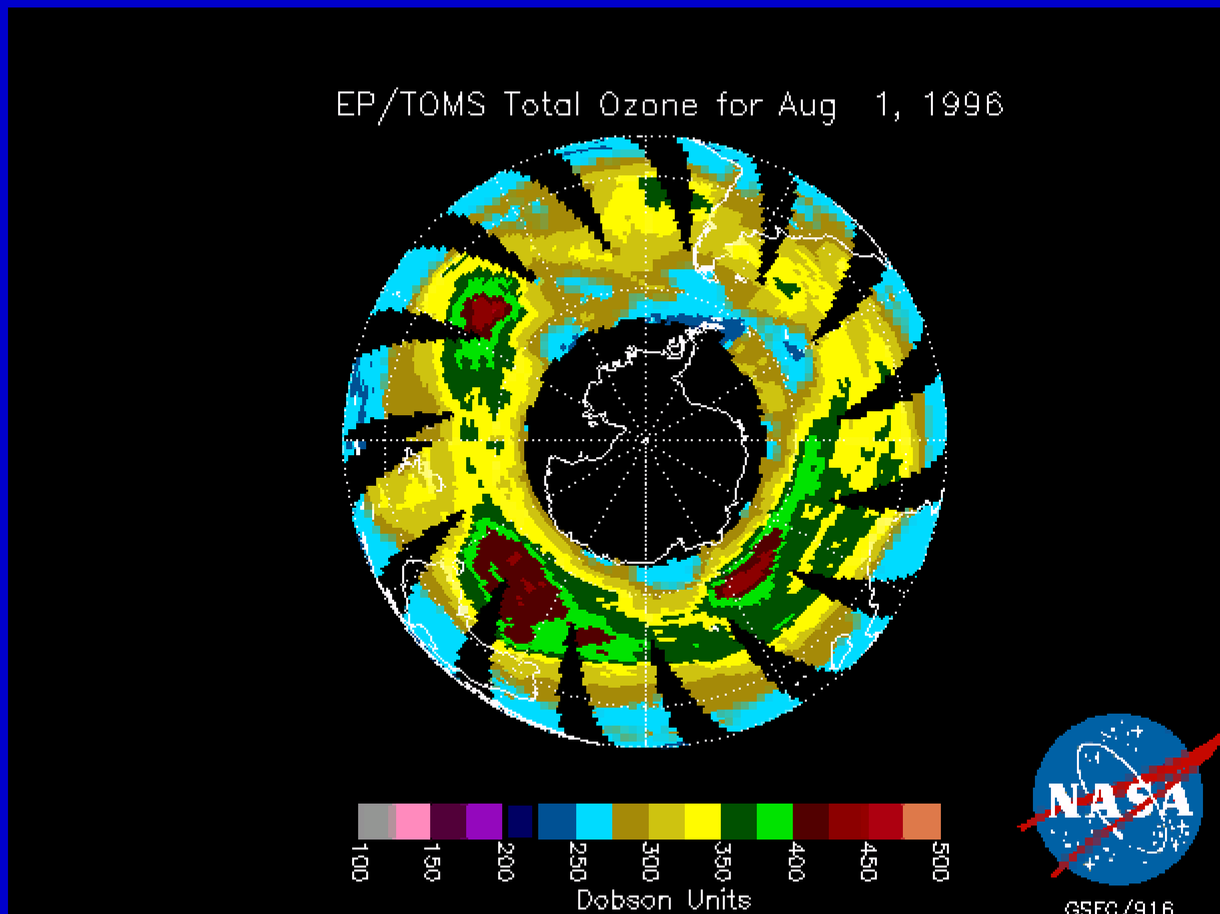
NO from supersonic aircrafts

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.



August 1 ‘96 - Dec 15 ‘96

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 Stratopsheric Clouds

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

$$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$$

$$ClONO_2 + H_2O \rightarrow HNO_3 + HOCl$$

Concentrations of Active Chlorine

The Cl_2 and HOCl formed photodissociate to yield reactive Cl atoms

$$Cl_2 + h\nu \rightarrow Cl + Cl$$

$$HOCl + h\nu \rightarrow Cl + OH$$

$$Cl + O_3 \rightarrow ClO + O_2$$

OZONE DEPLETION

“Ingredients” for the formation of the Ozone Hole

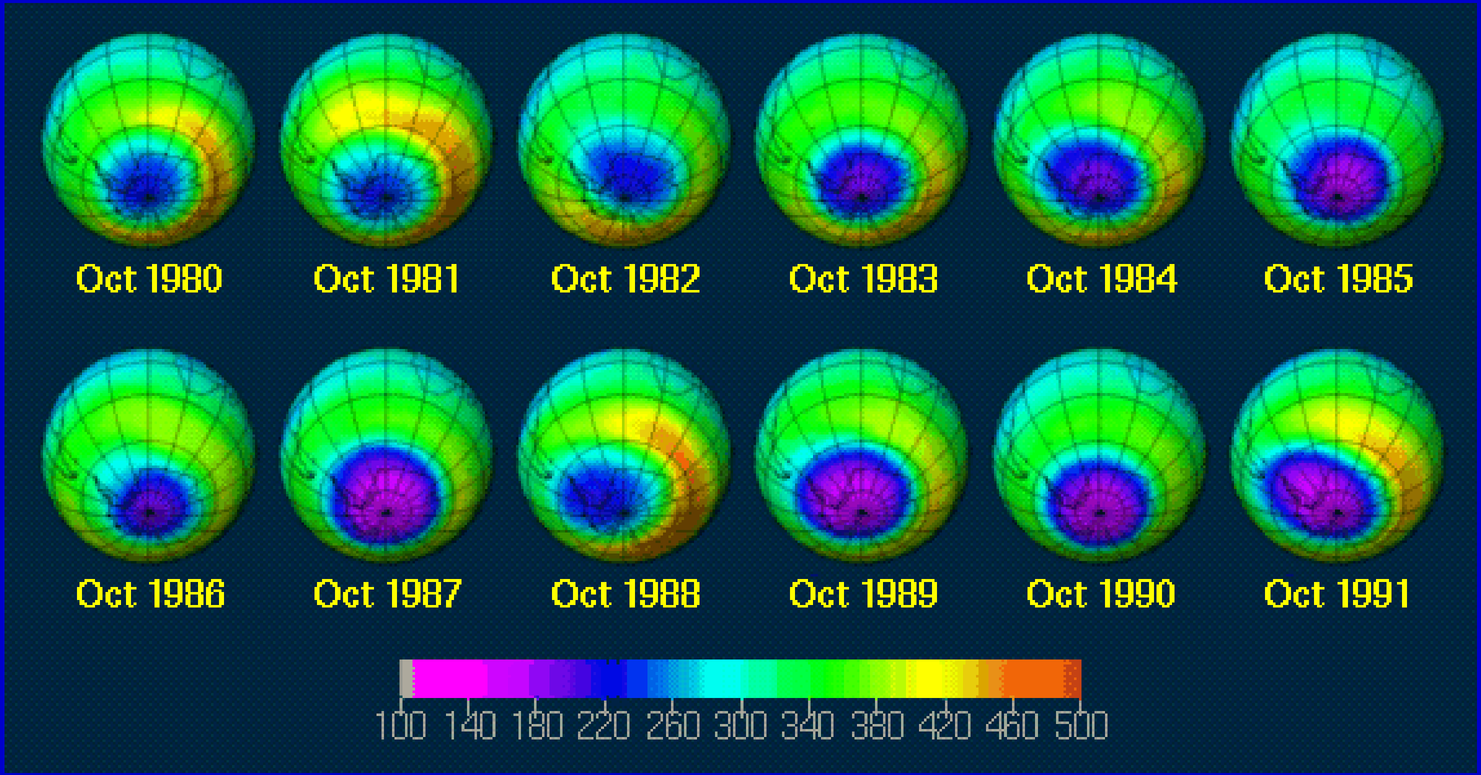
The Antarctic vortex traps CFC’s

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

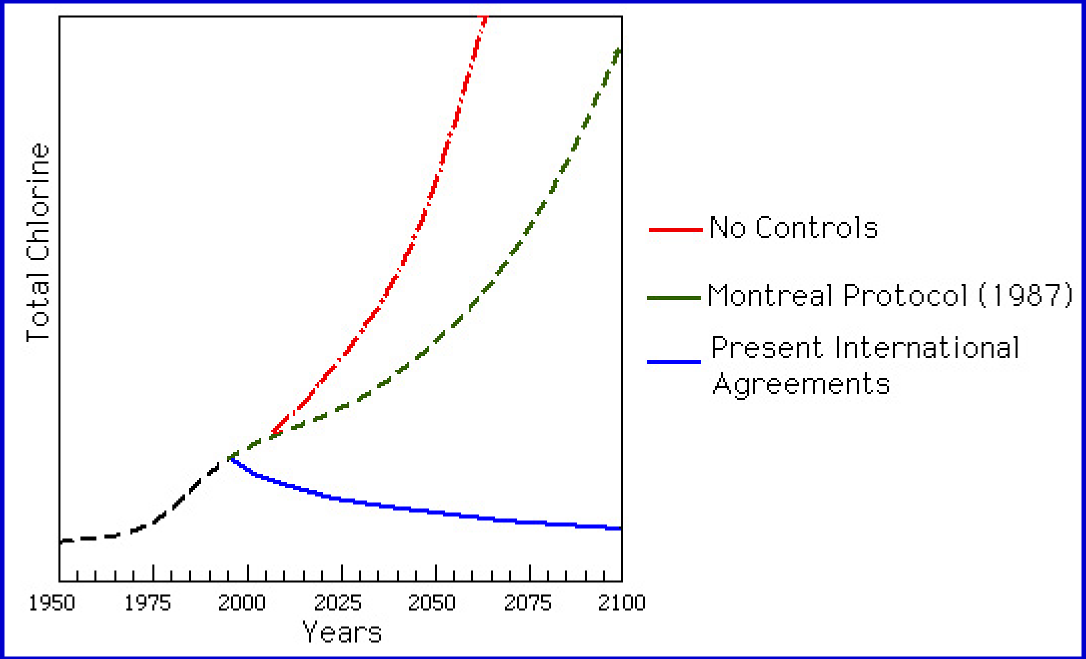
Annual growth in the Antarctic Ozone Hole



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



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

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

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