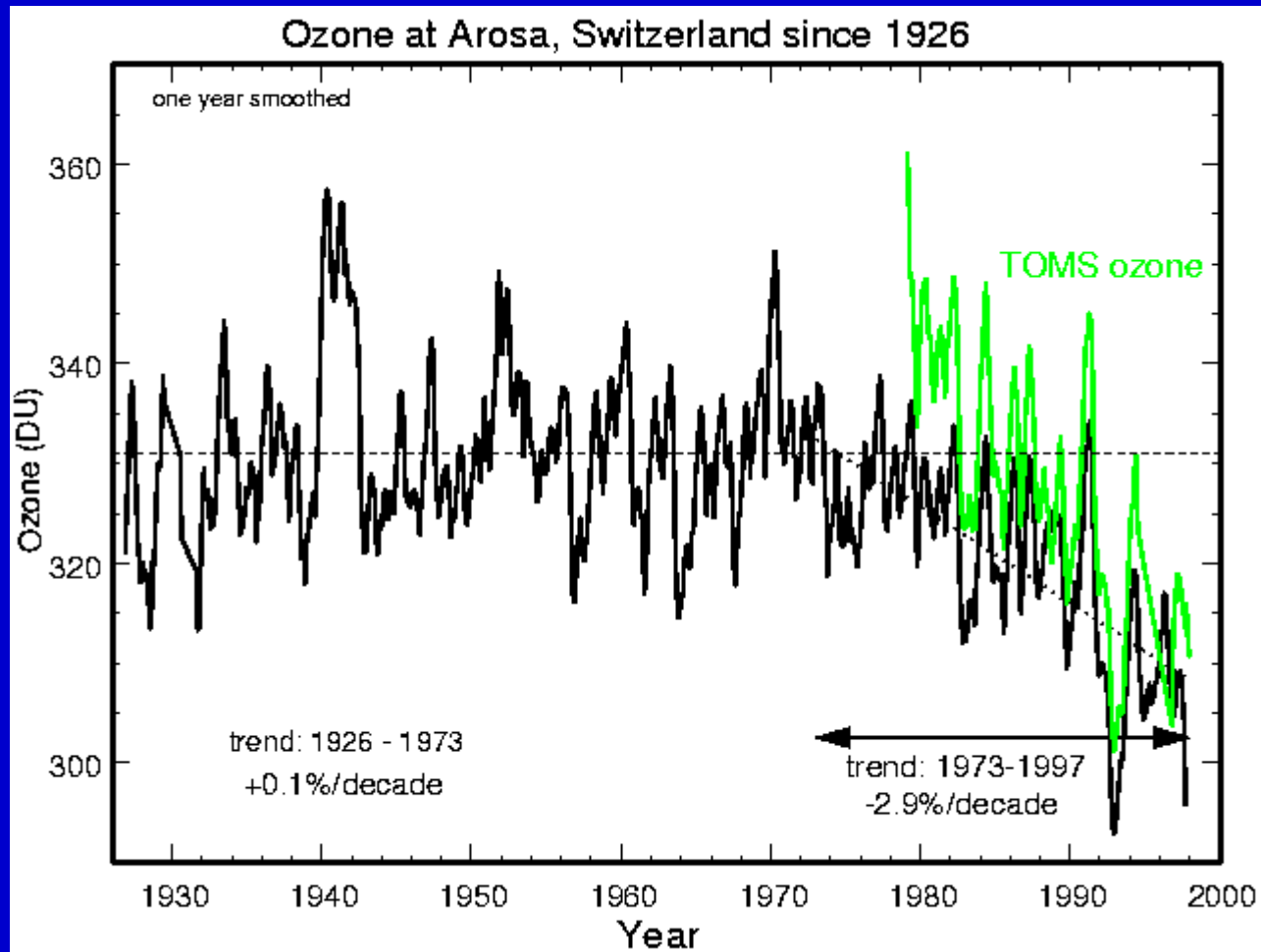


# Atmospheric Chemistry of the Ozone Layer

# Levels of Atmospheric Ozone have been Dropping



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?

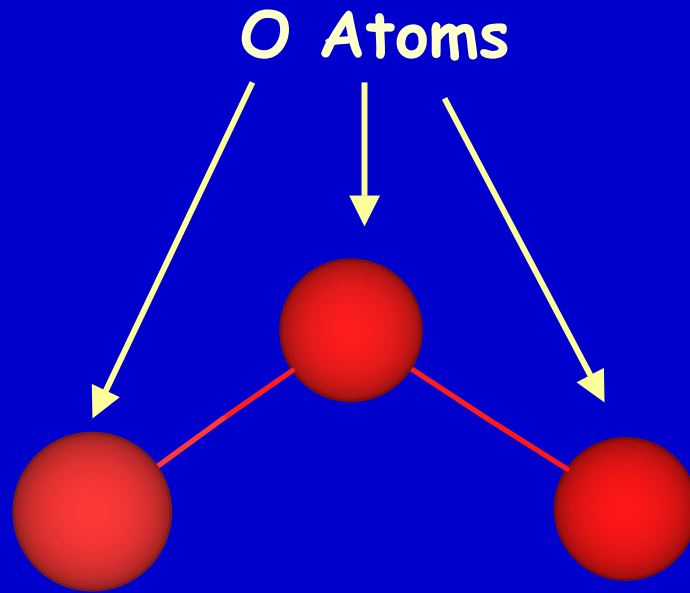
What is its purpose in the atmosphere?

What is its chemistry?

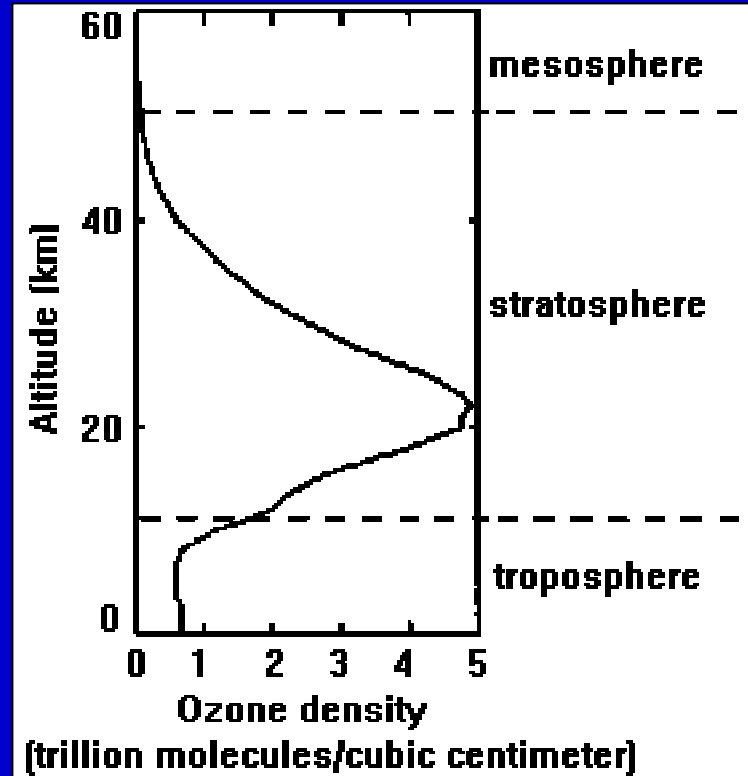
Why are levels of atmospheric ozone dropping?

Finally, what is the Ozone Hole?

# Structure of Ozone



# Where is ozone found in the atmosphere ?

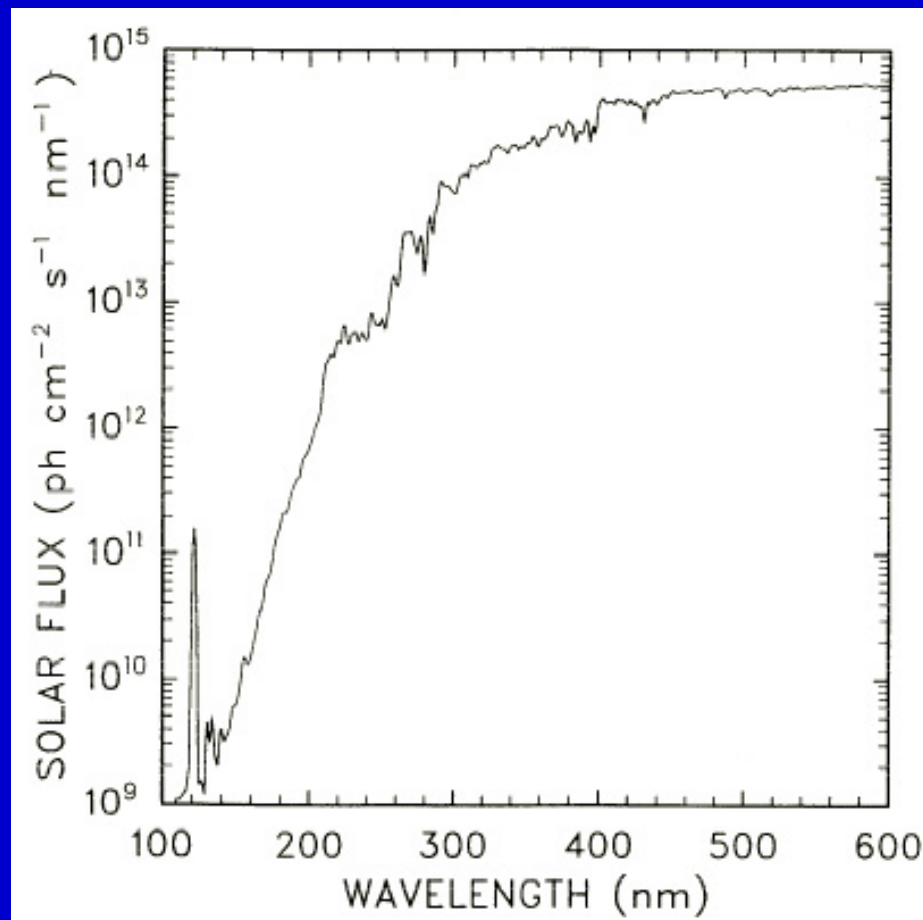


NASA Goddard Space Flight Center

Note, higher concentration in stratosphere, compared with troposphere

# Role of Ozone

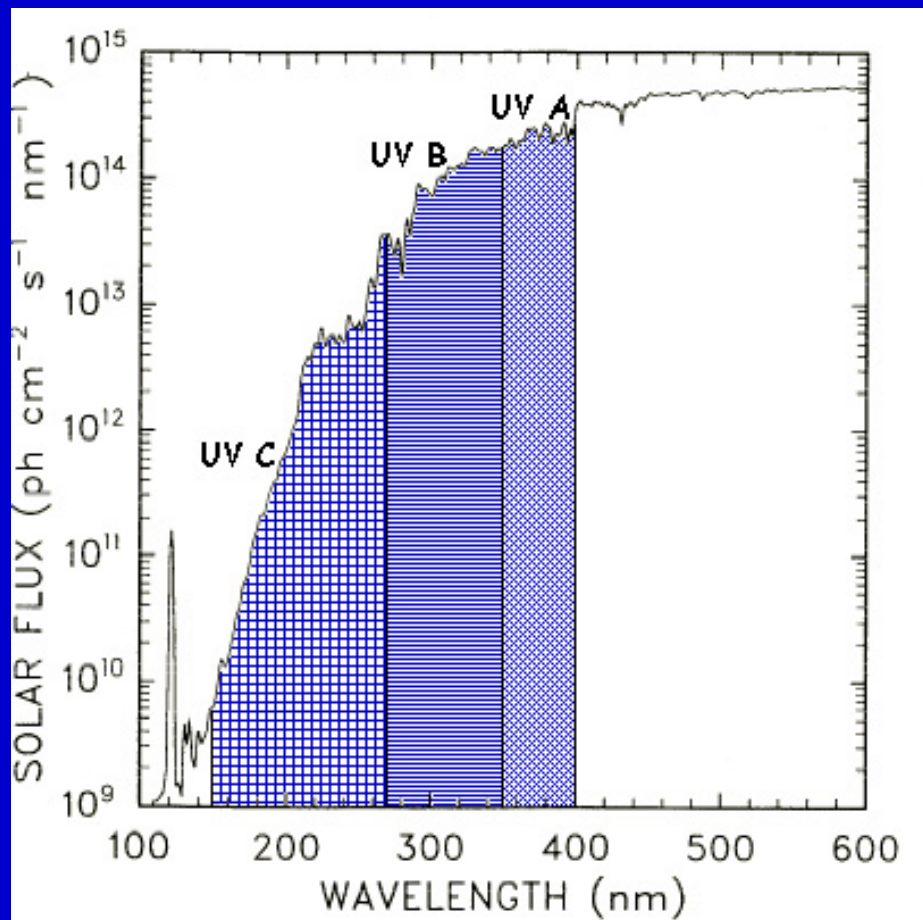
## Solar Flux



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

# Role of Ozone

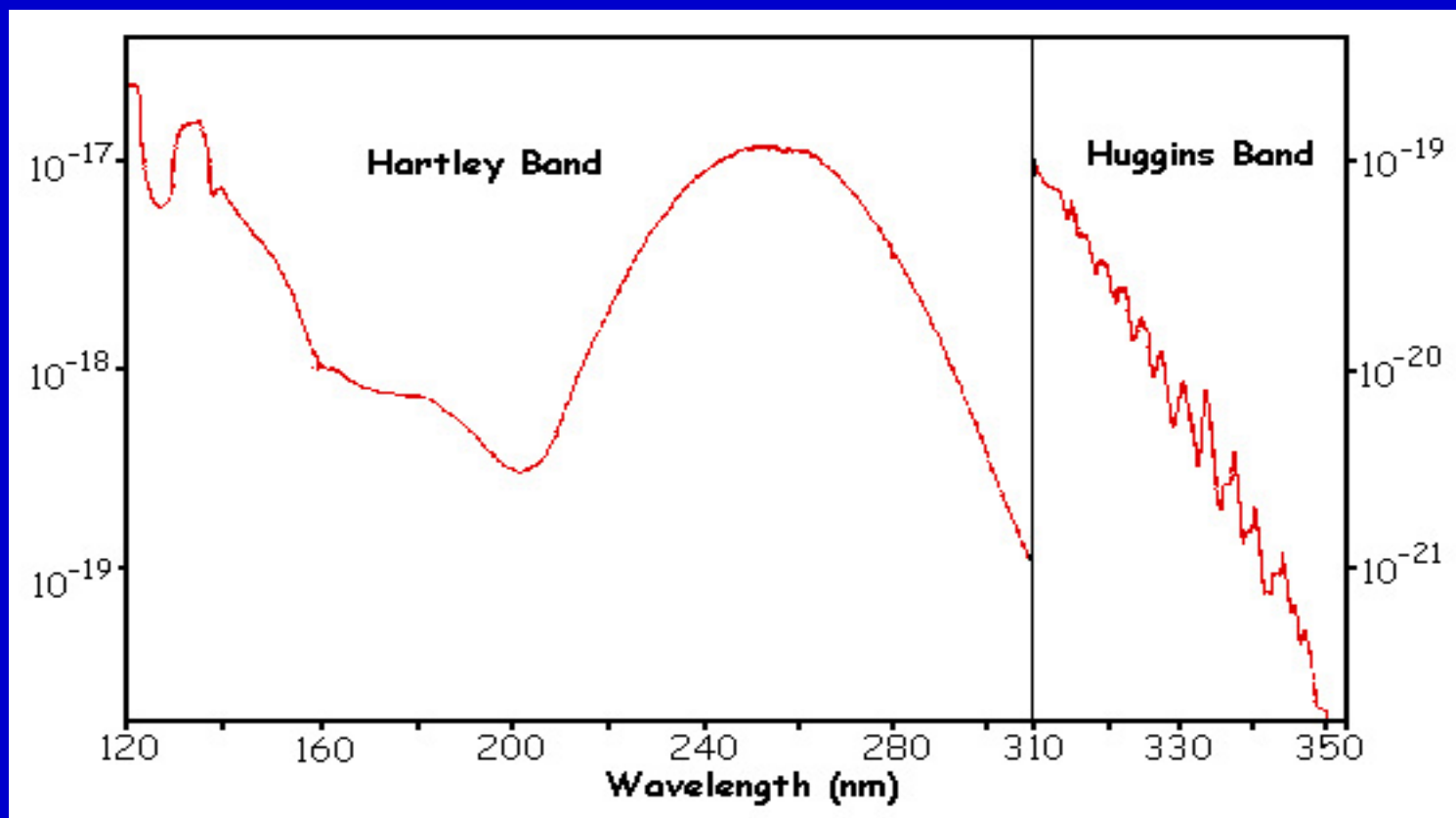
## Solar Flux



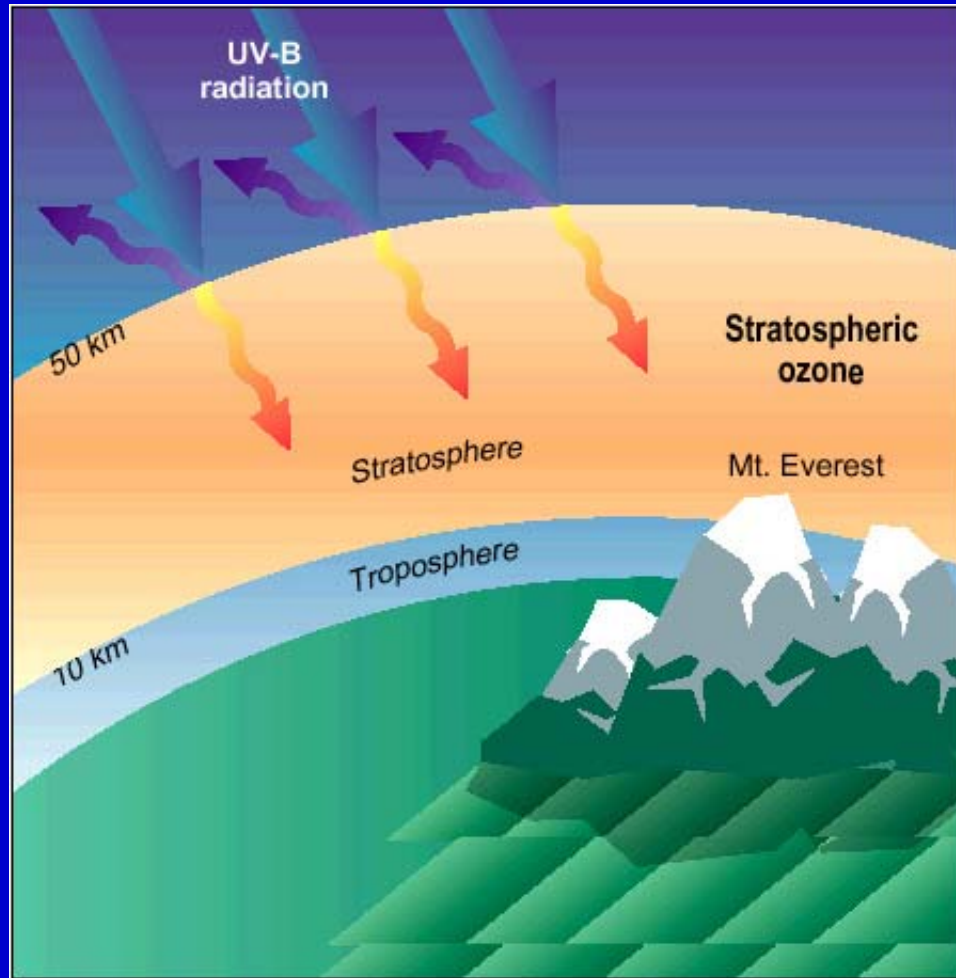
Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling - JPL Publication 97-4

# Role of Ozone

## Absorption Spectrum of Ozone



# 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

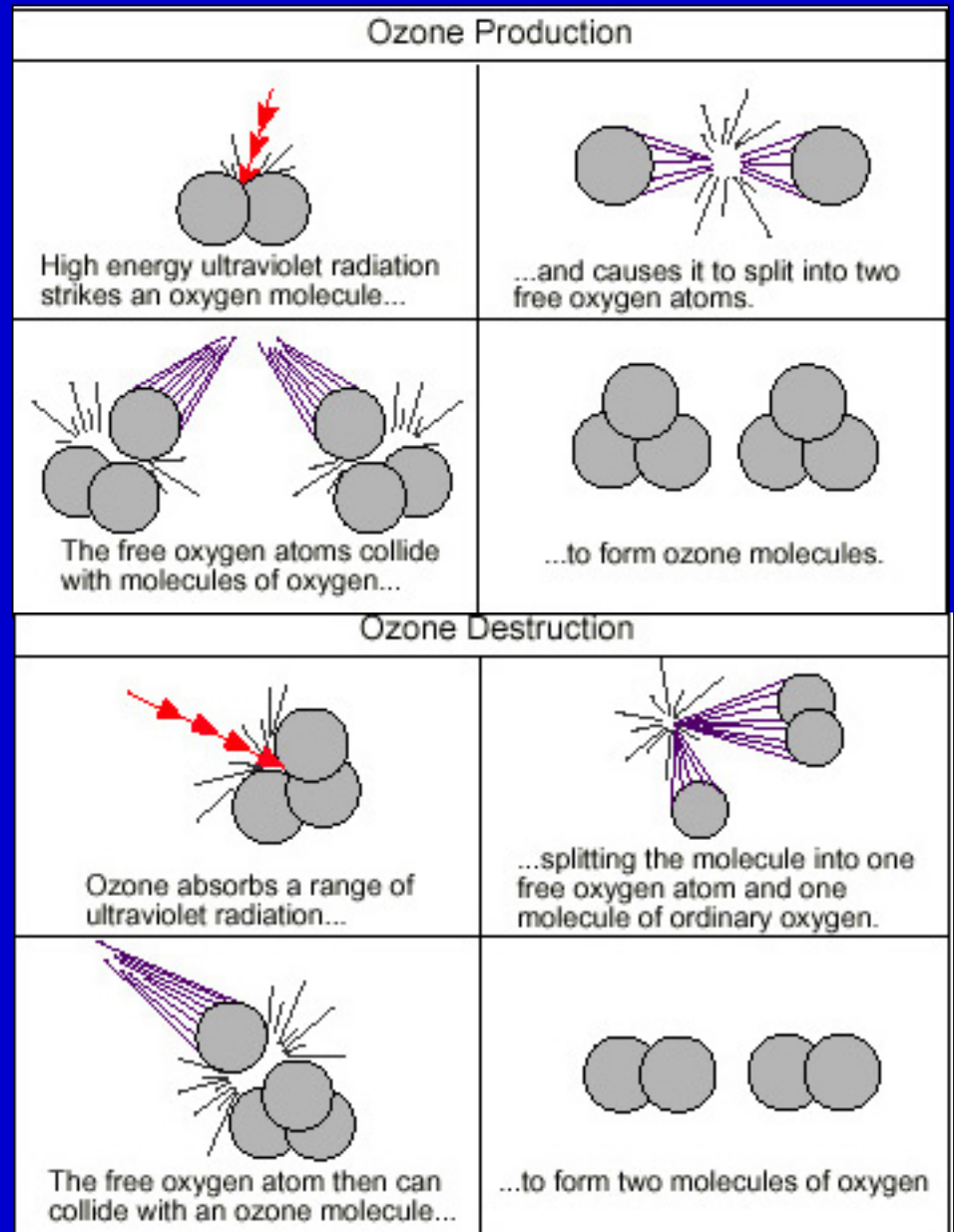
UV B (~ 350 to 270 nm) partially absorbed by earth's atmosphere

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

UV B is harmful to life on earth

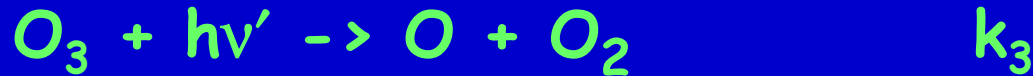
# How is ozone formed?

## Chapman mechanism



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

# Kinetics of Chapman Mechanism



Rate of formation of O and O<sub>3</sub>

$$d[\text{O}]/dt = 2k_1[\text{O}_2] - k_2[\text{O}][\text{O}_2][\text{M}] + k_3[\text{O}_3] - k_4[\text{O}][\text{O}_3]$$

$$d[\text{O}_3]/dt = k_2[\text{O}][\text{O}_2][\text{M}] - k_3[\text{O}_3] - k_4[\text{O}][\text{O}_3]$$

Steady-State Approximation

$$d[\text{O}]/dt = d[\text{O}_3]/dt = 0$$

# 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:

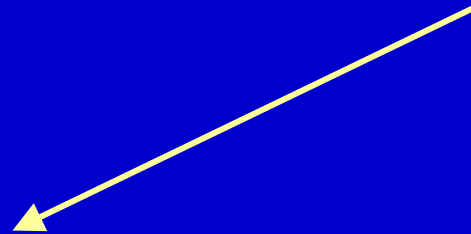
$$\frac{k_3}{k_4 [O]} \gg 1$$

+

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

Hence,

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

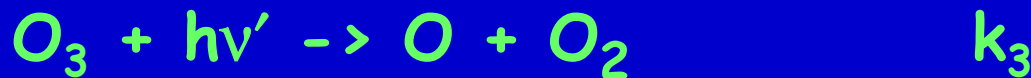


# Kinetics of Chapman Mechanism

$$[\text{O}_3] \approx \frac{k_2[\text{O}_2][\text{M}][\text{O}]}{k_3}$$

$[\text{O}_3]$  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



# Competing Reactions

## HO<sub>x</sub> cycle

H, OH and HO<sub>2</sub> species formed by reaction of excited O atoms with H-containing atmospheric species like H<sub>2</sub>O and CH<sub>4</sub>



## Reactions of HO<sub>x</sub> species with O<sub>3</sub>



### Net Reaction



“Ozone Depletion”

# Competing Reactions

## NO<sub>x</sub> Cycle

NO<sub>x</sub> species are produced during the reaction of O atoms with N<sub>2</sub>O (produced in the soil by bacteria)



## Reactions of NO<sub>x</sub> species with O<sub>3</sub>



### Net Reaction



“Ozone Depletion”

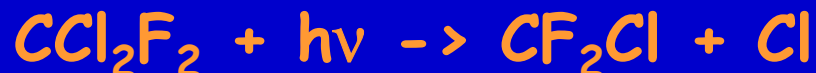
# Competing Reactions

## ClO<sub>x</sub> cycle

ClO<sub>x</sub> 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 (CFCl<sub>3</sub>, CF<sub>2</sub>Cl<sub>2</sub>)



## Reactions of ClO<sub>x</sub> species with O<sub>3</sub>



### Net Reaction

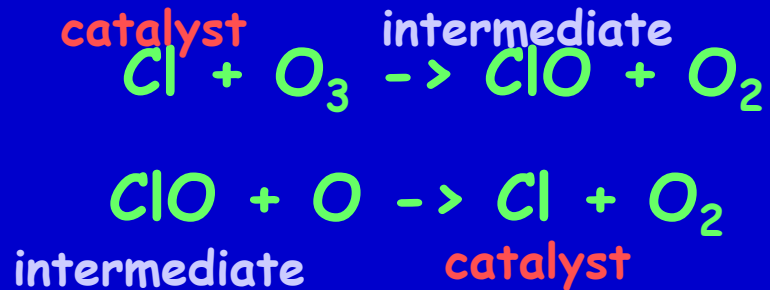


“Ozone Depletion”

1995 Nobel Prize in Chemistry

# Consequences of Competing Reactions

## Catalytic Reactions



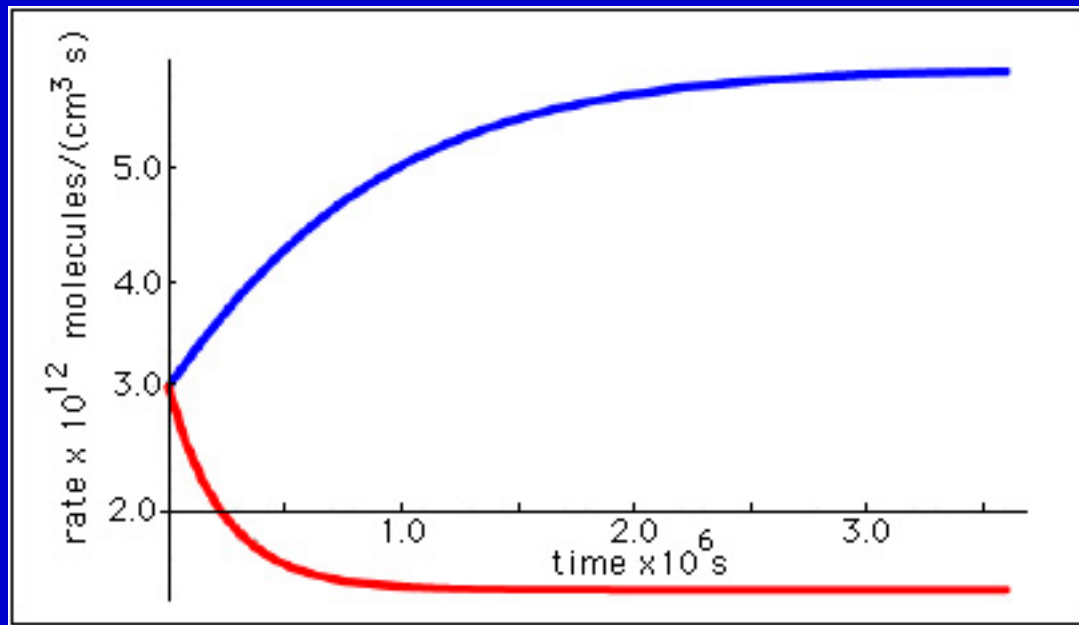
- lower activation energy

$E_a$  for Chapman mechanism = 17.1 kJ/mol

$E_a$  for  $\text{ClO}_x$  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 occurring species ( $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ )

Artificial, "man-made" species

CFC's ( $\text{CCl}_3\text{F}$ ,  $\text{CCl}_2\text{F}_2$ , etc.)

$\text{CCl}_4$ ,  $\text{CHCl}_3$

HBFC ( $\text{CHFBr}_2$ ,  $\text{CHF}_2\text{Br}$ )

$\text{CH}_3\text{Br}$

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.

QuickTime™ and a  
Animation decompressor  
are needed to see this picture.

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"

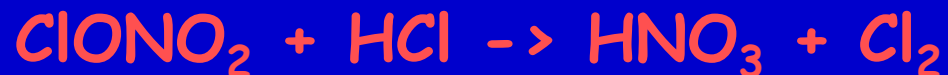
Air is trapped in the vortex along with ozone depleting species

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 Stratospheric Clouds

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



## Concentrations of Active Chlorine

The  $\text{Cl}_2$  and  $\text{HOCl}$  formed photodissociate to yield reactive  $\text{Cl}$  atoms



OZONE DEPLETION

# "Ingredients" for the formation of the Ozone Hole

The Antarctic vortex traps CFC's

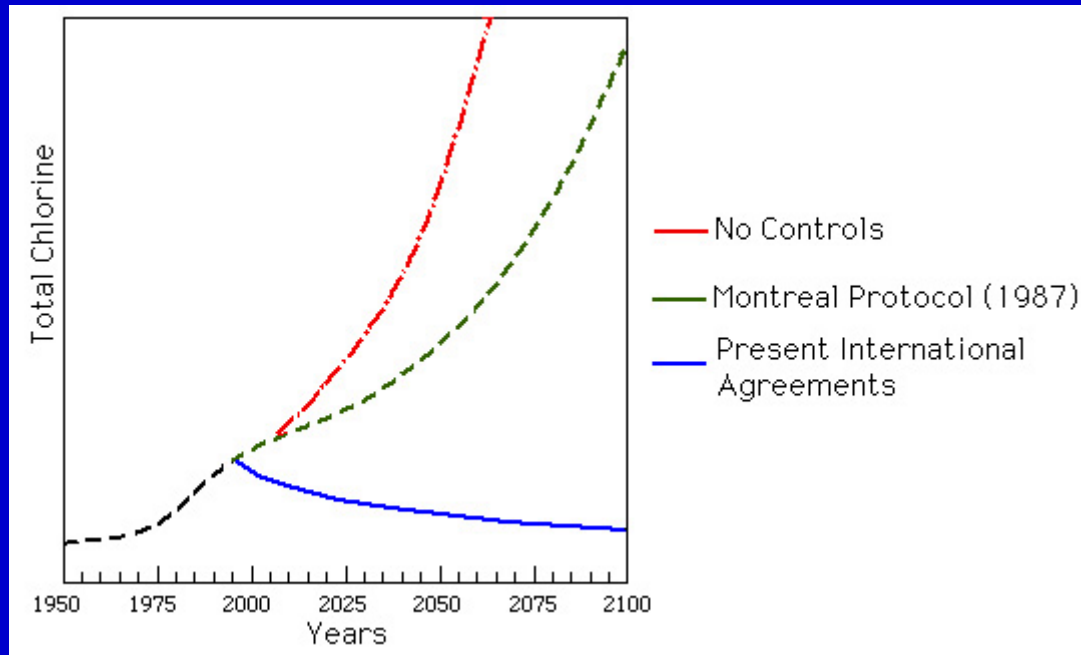
The low polar temperatures results in ice particles on which gas-solid reactions can occur efficiently

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

# 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

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(<http://www.gsfc.nasa.gov/>)

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[www.atm.ch.cam.ac.uk/tour/index.html](http://www.atm.ch.cam.ac.uk/tour/index.html)

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