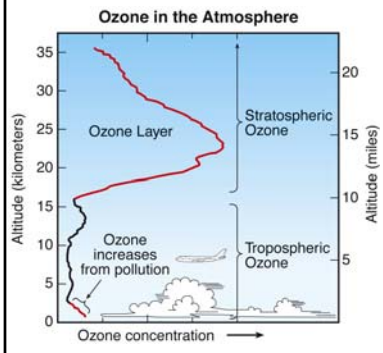
Stratospheric Chemistry

READING: Chapter 10 of text

- Mid-latitude Ozone Chemistry (and depletion)
- Polar Ozone Destruction (the Ozone Hole)

Stratospheric O_3: Overview



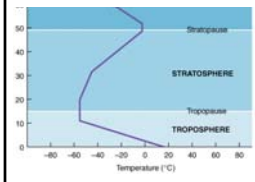
Most O_3 (90%) in stratosphere.

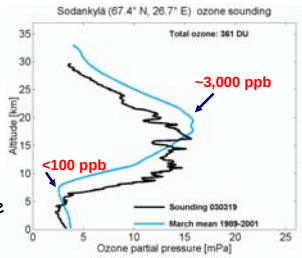
Remaining 10% in troposphere.

"Ozone layer" (15-30 km) is 3000 – 5000 ppb of O_3.

Surface O_3 ~ 40 – 100 ppb.

Stratospheric Ozone: Overview





- sustains terrestrial life by absorbing UV radiation
- impacts the atmospheric vertical temperature profile
- important role in Earth's overall radiative balance

Stratospheric Ozone: Motivating Questions

1. What are the natural production and loss mechanisms for stratospheric O_3?
2. What is the effect of anthropogenic emissions on stratospheric ozone, both past and future?
3. What are the mechanisms responsible for the drastic ozone decreases in the Antarctic?
4. What role, if any, does the stratospheric aerosol layer play in the gas-phase chemistry of the stratosphere?

Stratospheric Ozone—a brief history

1840's Ozone first discovered and measured in air by Schonbein who named it based on its smell.

1880-1900's: Hartley postulates the existence of a layer above the troposphere, where ozone is responsible for the absorption of solar UV between 200 and 300 nm.

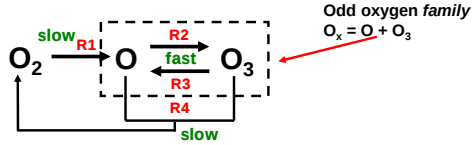
1913: Fabry and Buisson used UV measurements to estimate that if brought down to the surface at STP, O_3 would form a layer ~ 3 mm thick.

1920-25: Dobson first shows that T(z) in stratosphere not constant but increases with z and implicates O_3 absorption. Makes first extensive set of O_3 column measurements with his spectrophotometer

1930: Chapman proposed that O_3 continually produced in a cycle initiated by O_2 photolysis.

The Chapman mechanism

[R1] $O_2 + h\nu \rightarrow 2\,O$ $\lambda < 240$ nm
[R2] $O + O_2 + M \rightarrow O_3 + M$
[R3] $O_3 + h\nu \rightarrow O_2 + O$ $\lambda < 310$ nm
[R4] $O + O_3 \rightarrow 2O_2$



Mass balance for [O]:

$$\frac{d[O]}{dt} = 2j_{O2}[O_2] + j_{O3}[O_3] - k_2[O_2][O][M] - k_4[O_3][O] \sim 0$$

small small

Odd Oxygen Family: O_x

$[O_x] = [O] + [O_3] \cong [O_3]$

Mass balance for $[O_x]$: $\frac{d[O_x]}{dt} = 2j_{O2}[O_2] - 2k_4[O_3][O]$

- $[O_3]$ controlled by *slow net* production and loss via O_2 + hv (R1) and O + O_3 (R4)

  NOT by fast production and loss of O_3 from O + O_2 (R2) and O_3 + hv (R3)

- Effective O_3 lifetime $\cong \tau_{Ox}$:

  $\tau_{Ox} = [O_x]/2k_4[O][O_3] \cong 1/\ 2k_4[O]$

- In upper stratosphere τ_{Ox} short enough steady-state can be assumed: $2k_1[O_2] = 2k_4[O][O_3]$

$\therefore [O_3] = (k_1k_2/k_3k_4)^{1/2}\ C_{O2}N_{air}^{3/2}$

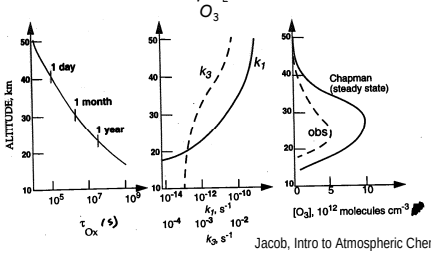
(where C_{O2} = [mole/mole] and N_{air} = air number density [cm^{-3}])

Vertical profiles

Reflects abundance of O atoms

Photolysis rate constants increase with altitude due to absorption of UV by O_2 and O_3

$[O_3]$ overestimated by a factor of 2



Jacob, Intro to Atmospheric Chemistry

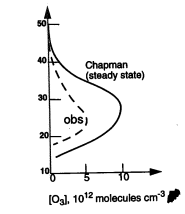
Questions

1. Why do ozone concentrations peak ~20 km altitude?
2. Where would you expect the highest ozone concentrations to be (equator vs. poles)?
3. The original Chapman mechanism included a fifth reaction:

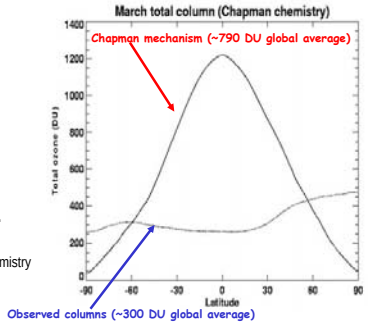
   $O + O + M \rightarrow O_2 + M$

   What would be the effect of this reaction on ozone? Where would it be most important?

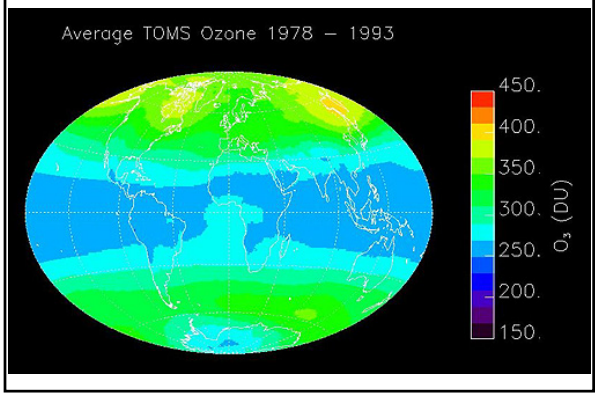
What's missing from the Chapman mechanism?



Jacob, Intro to Atmospheric Chemistry

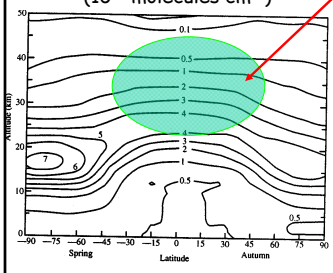


Average Ozone Column (Dobson units)



Vertical and latitudinal distribution of ozone

Ozone concentration
(10^{12} molecules cm^{-3})

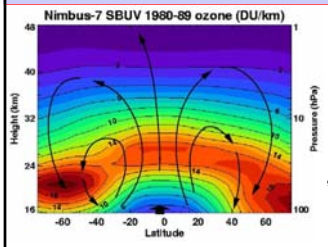


Region of largest production

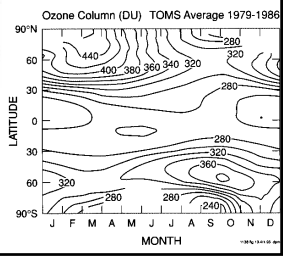
- Theory predict maximum O_3 production in the tropics
- But $[O_3]$ is not largest in the tropics
- To explain this (and low strat. H_2O) Brewer and Dobson suggested a circulation pattern

Figure is compilation of available measurements from 1960s

Brewer-Dobson circulation

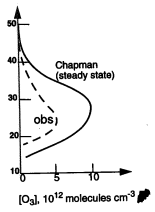


- Rising tropospheric air with low ozone
- B-D circulation transports O_3 from tropics to mid-high latitudes

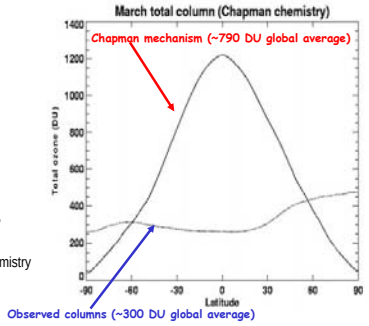


- O_3 max occur at high latitudes in late winter/early spring ← descending branch of the B-D circulation
- Virtually no seasonal change in the tropics but strong seasonal cycle in extratropics

What's missing from the Chapman mechanism?



Jacob, Intro to Atmospheric Chemistry



Catalytic chemical cycles

Altitudes >30 km (need O)

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\text{Net: } O + O_3 \rightarrow 2O_2$$

Altitudes < 30 km

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O_3 \rightarrow X + 2\,O_2$$
$$\text{Net: } O_3 + O_3 \rightarrow 3O_2$$

Catalysts:

X = OH, NO, Cl, Br

Hydrogen oxide (HO_x) radical family

$HO_x = H + OH + HO_2$

From troposphere and CH_4 oxidation

- Initiation: $H_2O + O(^1D) \rightarrow 2OH$
- Propagation through cycling of HO_x radical family (example):

  $OH + O_3 \rightarrow HO_2 + O_2$

  $HO_2 + O_3 \rightarrow OH + 2O_2$

  Net: $2O_3 \rightarrow 3O_2$
- Termination (example):

  $OH + HO_2 \rightarrow H_2O + O_2$

HO_x is a catalyst for O_3 loss but not the only one…

HO_x sources in the stratosphere

$O_3 + hv \rightarrow O(^1D) + O_2$

$O(^1D) + M \rightarrow O + M$

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

Small fraction of $O(^1D)$ 1/15,000 (25 km) reacts with H_2O, CH_4, or H_2 to form HO_x:

$H_2O + O(^1D) \rightarrow 2OH$

$CH_4 + O(^1D) \rightarrow OH + CH_3$

$H_2 + O(^1D) \rightarrow OH + H$

H_2O ~ 3-6 ppmv; CH_4 ~1-1.5 ppmv; H_2 ~ 0.5 ppmv

Stratospheric OH Profile

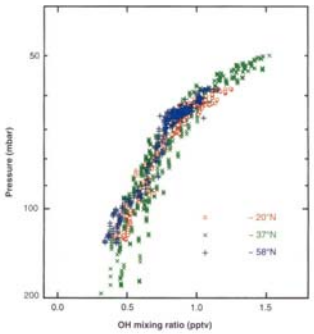
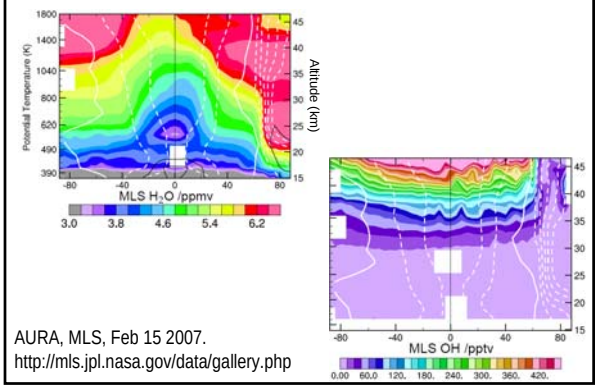


Fig. 1. Altitude profiles of [OH] measured during the SPADE campaign. The data have been normalized to 30° SZA by using the measured diurnal behavior. Despite the large increase in the concentrations of O_3 and NO_y observed between 20° and 60°N latitude, little variation in [OH] is observed at a given altitude.

Wennberg, et al Science 1994

Satellite observations of H_2O and OH in the stratosphere



AURA, MLS, Feb 15 2007.
http://mls.jpl.nasa.gov/data/gallery.php

Nitrogen oxide (NO_x) radical family

$NO_x = NO + NO_2$

- Initiation $N_2O + O(^1D) \rightarrow 2NO$
- Propagation

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + h\nu \rightarrow NO + O$
$O + O_2 + M \rightarrow O_3 + M$
Null cycle

$NO + O_3 \rightarrow NO_2 + O_2$
$NO_2 + O \rightarrow NO + O_2$
Net $O_3 + O \rightarrow 2O_2$

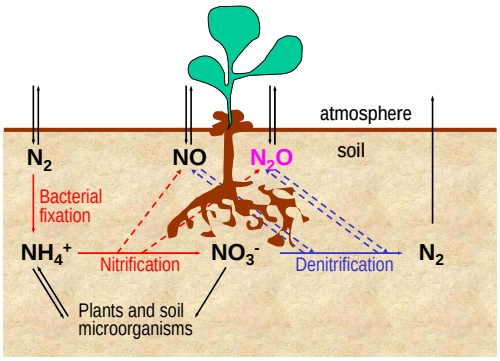
- Termination

$NO_2 + OH + M \rightarrow HNO_3 + M$
$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$

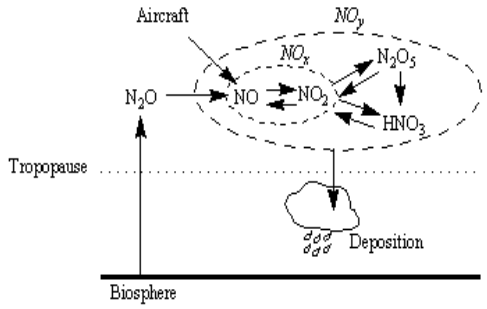
Recycling

$HNO_3 + h\nu \rightarrow NO_2 + OH$
$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$

Biological source of N_2O in the troposphere

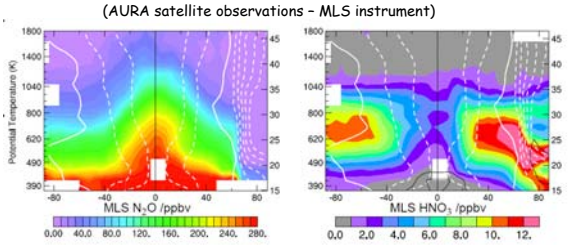


Cycling of NO_x and NO_y



N_2O and HNO_3 distribution in the stratosphere

(AURA satellite observations – MLS instrument)



Feb 15 2007

http://mls.jpl.nasa.gov/data/gallery.php

What have we learned about NO_y?

- **Production:**

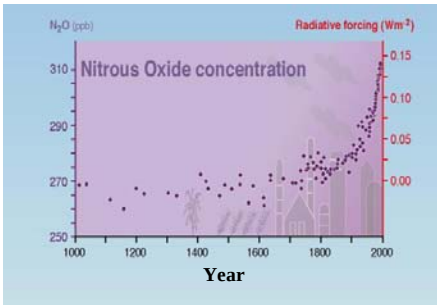
  $N_2O + O(^1D)$ - well understood natural source

- **Loss:** *via transport from stratosphere to troposphere*. Residence time for air in stratosphere is 1-2 years. Loss rate well constrained

- **Cycling:** O_3 loss related to NO_x/NO_y ratio.

NO_x catalytic cycle reconciled Chapman theory with observations…1995 Nobel Prize

Human Influence on Stratospheric NO_x



IPCC SYR Figure 2-1

Questions

1. Of the ozone loss mechanisms we have examined so far, can any operate at night?

2. A minor oxidation pathway for NO is

   $HO_2 + NO \rightarrow OH + NO_2$

What is the net effect of this reaction on ozone?

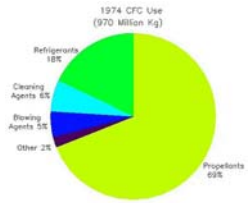
Anthropogenic perturbations to stratospheric ozone

$$X + O_3 \rightarrow XO + O_2$$
$$XO + O \rightarrow X + O_2$$
$$\text{Net: } O + O_3 \rightarrow 2O_2$$

Catalysts:

X = OH ← increasing CH_4 from troposphere
X = NO ← increasing N_2O from troposphere, supersonic fleet
X = Cl, Br ← Chlorofluorocarbons (CFCs) - Freons

"wonder gas" CFCs were invented in 1928



Use of CFCs increases rapidly

Chlorofluorocarbons (CFCs)

Used as refrigerants and as propellants in spray cans

Non-toxic, non-flammable, stable gases that are easily compressed.

Thought to be ideal…due to safety and durability.

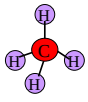
"Aerosol" Spray Cans: NOT SAME AS ATMOSPHERIC AEROSOL PARTICLES

Chlorofluorocarbons (CFCs)

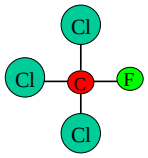
organic molecules where the H atoms have been completely replaced by fluorine and chlorine (synthetic molecules- entirely artificial)

Examples:

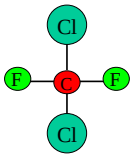
Methane



CFC11



CFC12



Chlorofluorocarbons and Halons

Halocarbon= halogen-containing organic compounds

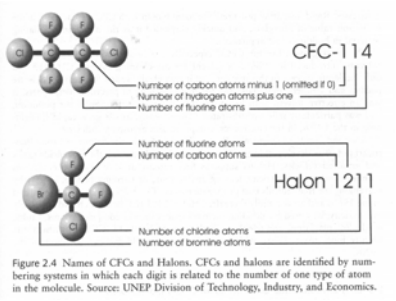


Figure 2.4 Names of CFCs and Halons. CFCs and halons are identified by numbering systems in which each digit is related to the number of one type of atom in the molecule. Source: UNEP Division of Technology, Industry, and Economics.

Halocarbon containing C, Cl and F

Br containing halocarbon

CATALYTIC CYCLES FOR OZONE LOSS:

Chlorine (ClOx = Cl + ClO) radicals

- Initiation:

  $CCl_3F + h\nu \rightarrow CCl_2F + Cl$

  $CCl_2F + h\nu \rightarrow CFCl + Cl$

  wavelengths<230 nm

- Propagation:

  $Cl + O_3 \rightarrow ClO + O_2$

  $ClO + O \rightarrow Cl + O_2$

  Net: $O_3 + O \rightarrow 2O_2$

  O_3 loss rate:

  $$\frac{d[O_x]}{dt} = -2k[ClO][O]$$

  Chain length > 10 (10^3 in upper stratosphere)

- Termination:

  $Cl + CH_4 \rightarrow HCl + CH_3$

  $ClO + NO_2 + M \rightarrow ClONO_2 + M$

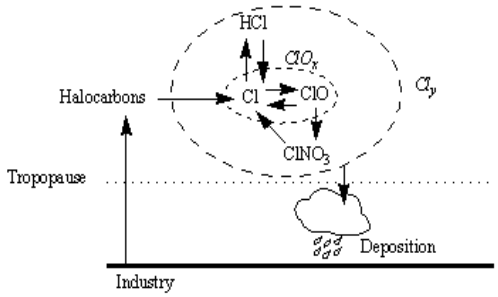
Recycling:

$HCl + OH \rightarrow Cl + H_2O$

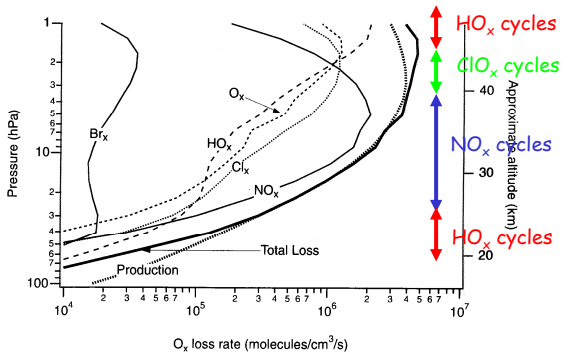
$ClONO_2 + h\nu \rightarrow ClO + NO_2$

Molina & Rowland, 1974 …1995 Nobel Prize

Cycling of ClO_x and Cl_y



Vertical distribution of O_x catalytic loss cycles



Early Warning Signs

Stratospheric sink for chlorofluoromethanes : chlorine atomc-atalysed destruction of ozone

Mario J. Molina & F. S. Rowland

Department of Chemistry, University of California, Irvine, California 92664

Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.

photolytic dissociation to $CFCl_3$ + Cl and to CF_2Cl + respectively at altitudes of 20–40 km. Each of the reactions cre two odd-electron species—one Cl atom and one free radi The dissociated chlorofluoromethanes can be traced to t ultimate sinks. An extensive catalytic chain reaction lea to the net destruction of O_3 and O occurs in the stratosphere

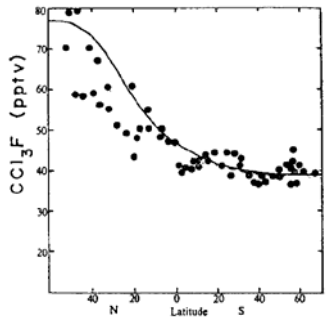
$$Cl + O_3 \rightarrow ClO + O_2$$
$$ClO + O \rightarrow Cl + O_2$$

This has important chemical consequences. Under n conditions in the Earth's atmospheric ozone layer, (2) is slower of the reactions because there is a much lower con

Nature, June 28, 1974

Molina, Rowland, and Crutzen win Nobel Prize in 1994

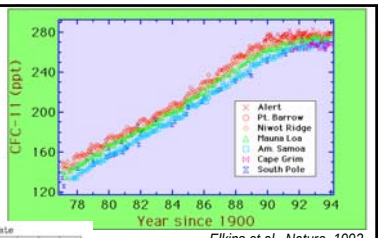
CCl_3F measurements in 1971: cruise from England to Antactica



CFC-11

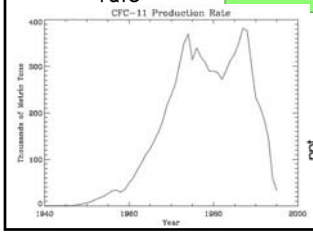
J. E. Lovelock, R. J. Maggs and R. J. Wade, Halogenated hydrocarbons in and over the Atlantic, Nature, 241, 194-196 (1973)

1970-1994: rapid increase in CFC-11 atmospheric levels

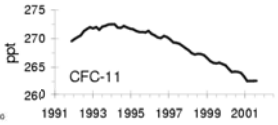


Elkins et al., Nature, 1993.

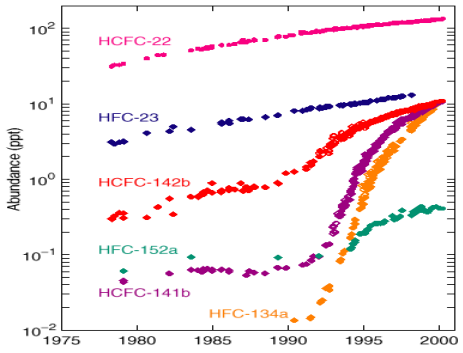
CFC-11 production rate



1994-today: CFC-11 is decreasing



Recent Rise in HCFC's (CFC Replacements)



Coupling Between HO_x, NO_x, and ClO_x Cycles

What is the effect of increasing stratospheric NO_x on the rate of ClO_x-catalyzed ozone loss?

Give an example of how HO_x and NO_x are coupled.

How might an increase in OH affect ClO_x cycles?