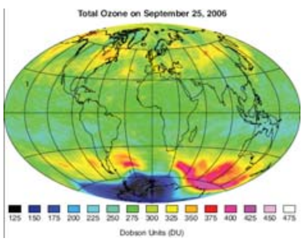
Chapter 2: Protecting the Ozone Layer

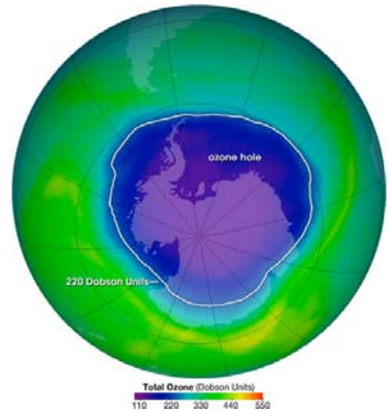


Why do we need to protect the ozone layer?

Isn't ozone hazardous to human health?

Why is the ozone layer getting smaller?

What can we do (if anything) to help stop the depletion of our ozone layer?



http://www.treehugger.com/clean-technology/ozone-layer-shifting-more-uv-radiation-in-tropics-and-antarctica-predicted-by-physicists.html

The Dobson unit (or DU)

The unit measures the ozone in a column above a specific location on earth.

If the ozone in the column were compressed at specified conditions of temperature and pressure, it would form a layer.

A layer 1 mm thick corresponds to 100 DU.

Ozone Formation

$$\text{Energy} + 3\,O_2 \xrightarrow{\text{Electrical arcs}} 2\,O_3$$

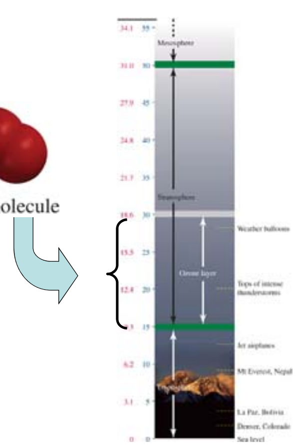
Energy must be absorbed (endothermic) for this reaction to occur.

Ozone is an **allotropic** form of oxygen.

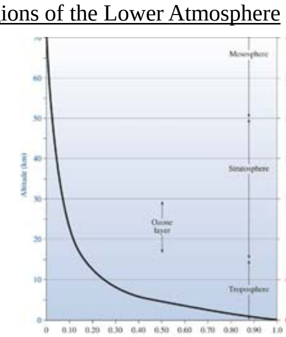
Allotrope - forms of the same element that differ in their chemical structure and therefore their properties.

Element	Allotropes
oxygen	O_2, O_3
carbon	graphite, diamond, buckminister fullerenes

2.1



The Regions of the Lower Atmosphere



Atmospheric pressure decreases with altitude.

2.1

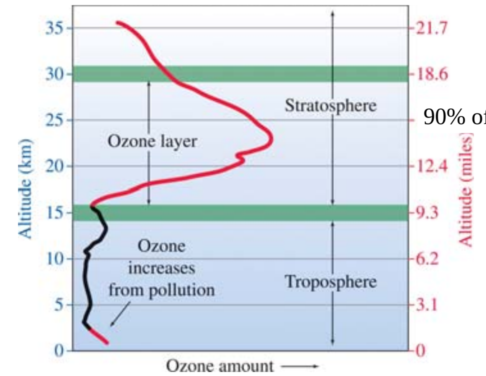
Have you ever been in a plane landing in Denver, CO?

You may have experienced being thrust forward as the plane uses more energy to stop. There are fewer air molecules at that height, reducing the amount of friction, so a greater amount of energy is needed to stop the plane.

Why does it take longer to cook an egg in Denver than it does in New Orleans?

There is less air pressure at higher altitudes. Water boils when the vapor pressure of the water molecules exceeds that of the localized air pressure. Because there is less air pressure at higher altitudes, water boils at a temperature *less than* 100^{o}C. More energy must be supplied (longer time) at a lower temperature to cook the egg.

2.1

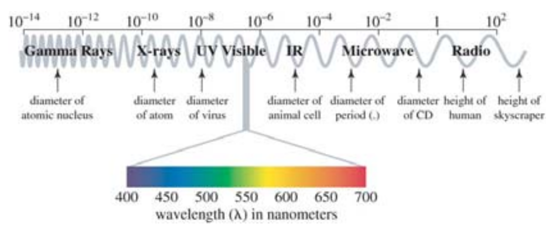


90% of all O_3

The ozone layer is a region in the stratosphere with maximum. Max: 12000 ppb ozone concentration.

2.1

Radiation from the sun covers a large range in the *electromagnetic spectrum*

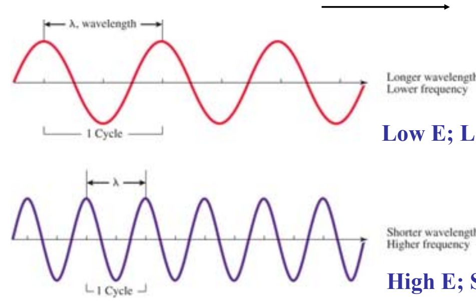


The various types of radiation seem different to our senses, yet they *differ only in their respective λ and ν.*

2.4

The Nature of Light

$c = 3\times 10^8$ m/s



Low E; Large λ

High E; Small λ

Wavelength (λ) = distance between successive peaks (nm).

Frequency (ν) = # of waves passing a fixed point per second

2.4

The wavelength and frequency of electromagnetic radiation are related by: $c = \lambda\nu$

where $c = 3 \times 10^8$ m/s (the speed of light)

You can consider a ray of light as a 'stream of ' energy packets, too.

The energy of a "packet of energy" (= photon) of electromagnetic radiation is calculated by:

$$E = \frac{hc}{\lambda} \quad \text{or} \quad E = h\nu$$

where $h = 6.626\times 10^{-34}$ J.s (Planck's constant)

Energy and frequency are *directly related* –higher frequency means higher energy.

Energy and wavelength are *inversely related* –higher wavelength means lesser energy.

2.5

What is the energy associated with a photon of light with a wavelength of 240 nm?

$$c = \lambda \nu$$

$$\nu = \frac{c}{\lambda}$$

$$\nu = \frac{3 \times 10^{8}\,\mathrm{m/s}}{240\mathrm{nm}}$$

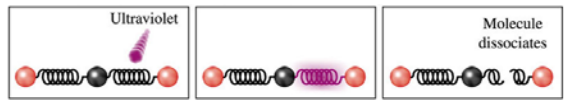
What is the energy associated with a photon of light with a wavelength of 240 nm?

$E = h\nu$

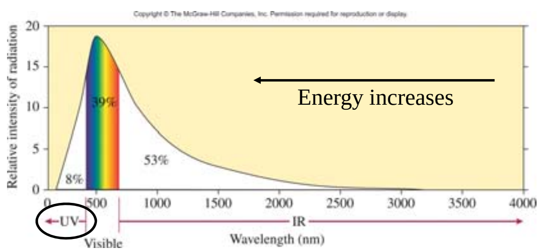
$E = (6.63 \times 10^{-34}\ \mathrm{J{\cdot}s})\ (1.3 \times 10^{15}\ \mathrm{s^{-1}})$

$E = 8.6 \times 10^{-19}\ \mathrm{J}$

UV radiation has sufficient energy to cause molecular bonds to break



These rays have varying energies. Energy of an 'energy packet' from a certain ray in inversely proportional to It's wave length.



Short λ range: includes UV (ultraviolet), X-rays, and gamma rays.

Visible: λ = 700–400 nm

Infrared (IR): longest of the visible spectrum; heat ray absorptions cause molecules to bend and stretch.

Microwaves: cause molecules . to rotate.

2.4

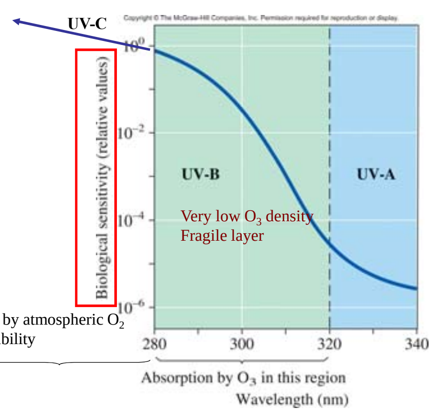
Table 2.4 Types of UV Radiation

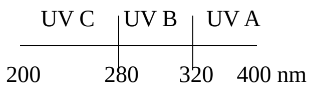
Type	Wavelength	Relative Energy	Comments
UV-A	320–400 nm	Lowest energy	Least damaging and reaches the Earth's surface in greatest amount
UV-B	280–320 nm	Higher energy than UV-A but less energetic than UV-C	More damaging than UV-A but less damaging than UV-C. Most UV-B is absorbed by O_3 in the stratosphere
UV-C	200–280 nm	Highest energy	Most damaging but not a problem because it is totally absorbed by O_2 and O_3 in the stratosphere

UV C | UV B | UV A

200 280 320 400 nm

2.6





A least energetic, least damaging; reaches earth's surface.

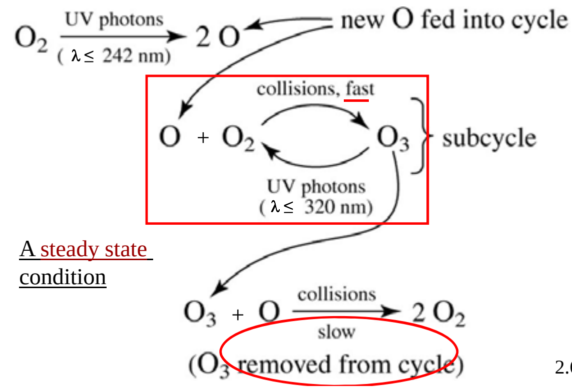
C most energetic, least problematic; O_2 in the atmosphere absorbs (consumes UV-C).

$$O_2 \xrightarrow{UV;\lambda<240nm\ UVC} 2O$$

B moderately energetic, absorbed by O_3 in the stratosphere.

$$O_3 \xrightarrow{UV;\lambda<320nm,\ UVB} O_2 + O$$

The Chapman Cycle



2.6

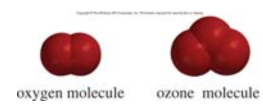
Any loss of O_3 *in the 'ozone layer'* would disrupt the beneficial subcycle reducing the amount of O_3 in the ozone layer. Such a loss allows the UV-B rays to reach the ground; leading to skin cancers etc.

The fragility of the ozone layer was recognized by an overwhelming majority of the worlds countries and steps were taken to minimize the man made factors leading to the depletion of the ozone concentration in the stratosphere following the *Precautionary Principle*.

$$O_2 \xrightarrow{UV;\lambda<240nm} 2O$$

$$O_3 \xrightarrow{UV;\lambda<320nm} O_2 + O$$

Which molecule is easier to break? O_2 or O_3?



Why?

Answer lies in the nature of atoms of elements and how atoms are held (bonded) together in molecules.

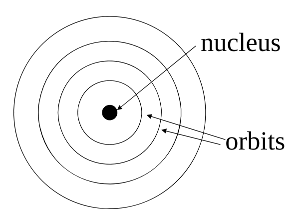
Structure of the Atom:

Atom: heavy positively charged small region (nucleus) and a soft negatively charged large region.

Nucleus: protons (positive charge) + neutrons (both equally heavy particles): virtually all mass in nucleus.

Mass of Electron – (1/1800)×mass of proton
Charge of electron = equal and opposite to proton

#protons = # electrons ; atom overall neutral.



An electron in an orbit acquires the energy of the orbit of residence.

Energy of orbits increases with the radius.

Table 2.1 Properties of Subatomic Particles

Particle	Relative Charge	Relative Mass	Actual Mass, kg
Proton	+1	1	1.67×10^{-27}
Neutron	0	1	1.67×10^{-27}
Electron	−1	0*	9.11×10^{-31}

* The relative mass of the electron is not actually zero, but is so small that it appears as zero when expressed to the nearest whole number.

6
C
12.01

Atomic number (Z)

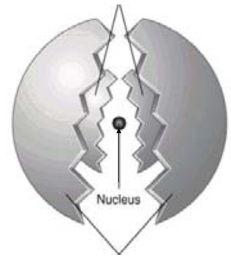
– The number of protons (nuclear charge)

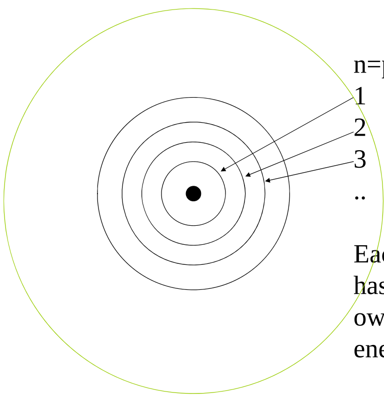
(A – Number the protons and neutrons)

Atomic Mass

– Mass of the protons and neutrons (amu)

2.2

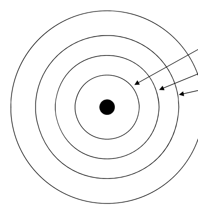




n=principal quantum number

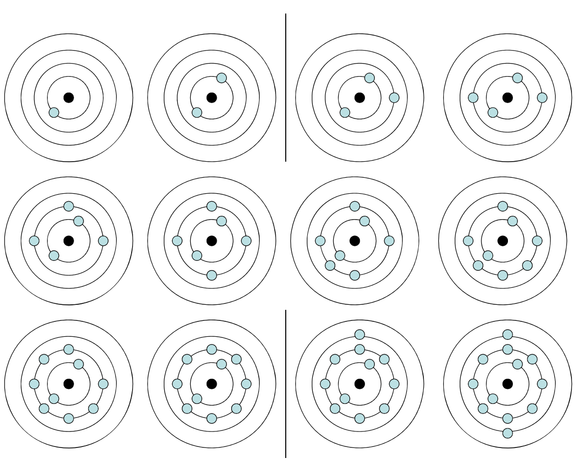
1
2
3
..

Each allowed state has a unique n and it's own energy – energy levels



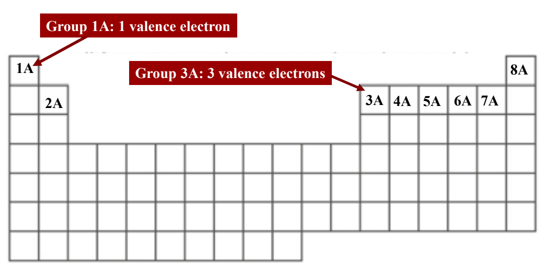
max # electrons

2
8
18
.
.



The electrons in the outermost energy levels are called **valence electrons**.

The group number (of the representative elements) on the periodic table tells you the number of valence electrons.



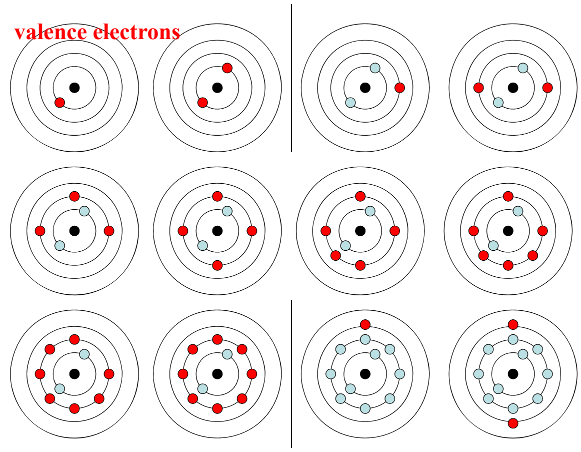
2.2

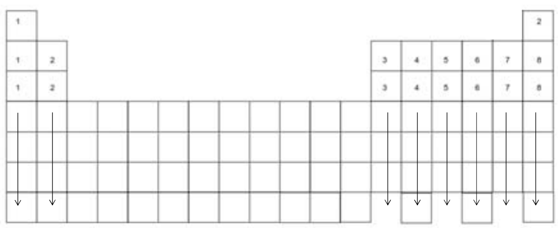
The electrons in the outermost energy levels are called **valence electrons**.

The valence electrons determine the properties of the elements.

Atoms with similar valence shell occupations behave similarly.

8 electrons in valence shell make it very stable – i.e. would like to stay or reach an 8 - electron environment; (stable octet)





Isotopes are two or more forms of the same element (same number of protons) whose atoms differ in number of neutrons, and hence in mass.

Isotopes of carbon: C-12, C-13, C-14
also written as: ^{12}C ^{13}C ^{14}C

Or more completely as: $^{12}_{6}C$, $^{13}_{6}C$, $^{12}_{6}C$

2.2

Most matter exist as compounds – formed by bonding of elements.

Atoms of elements makes bonds with other atoms, so that they would acquire/mimic the stable octet (except for H – in which case it is a duet)

Lewis structure of atoms:

H He

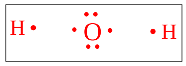
Li Be B C N O F Ne

The # of valence electrons on an atom = group #.

THE INERT GAS ELEMENT ARRANGEMENT STABLE OCTET (duet for He)

Representing molecules with Lewis structures:

Consider water, H_2O:

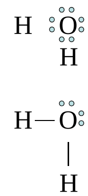


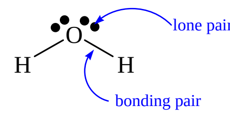
1. Find sum of valence electrons:
   1 O atom × 6 valence electrons per atom = 6
   \+ 2 H atoms × 1 valence electron per atom = 2
   8 valence electrons

2. Arrange the electrons in pairs; use whatever electron pairs needed to connect the atoms, then distribute the remaining electron pairs so that the **octet rule** is satisfied:

2.3

(6+2) e's



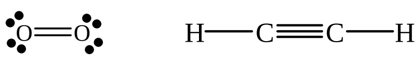


2. Arrange the electrons in pairs; use whatever electron pairs needed to connect the atoms, then distribute the remaining electron pairs so that the **octet rule** is satisfied:

2.3

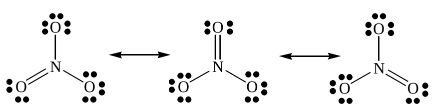
Representing molecules with **Lewis structures**:

Multiple bonds



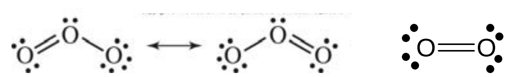
Double bond **Triple bond**

Occasionally, a single Lewis structure does not adequately represent the true structure of a molecule, so we use **resonance forms**:



2.3

O_3 O_2



1-1/2 bonds between O,O
Less strong

2 bonds between O,O
More strong

Which molecule is easier to break? O_2 or O_3?

Representing molecules with Lewis structures:

Typical **valence/valency** for selected atoms = the # of bonds an atom typically forms

Element	Typical valence	Classification
H, X (X= F, Cl, Br, I)	1	monovalent
O	2	divalent
N	3	trivalent
C	4	tetravalent

2.3

Lewis structures

1. Determine the sum of valence electrons.
2. Use a pair of electrons to form a bond between each pair of bonded atoms.
3. Arrange the remaining electrons to satisfy octet rule (duet rule for H).
4. Assign formal charges.

Formal charge = # v. e. – [# nonbonding e^- + ½ bonding e^-]

3.3

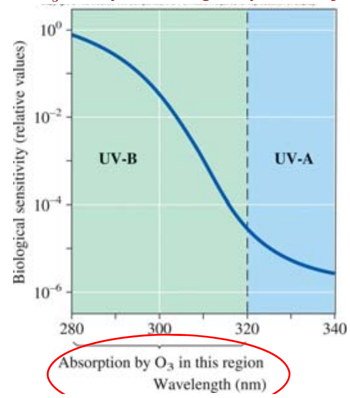
Table 2.4 Types of UV Radiation

Type	Wavelength	Relative Energy	Comments
UV-A	320–400 nm	Lowest energy	Least damaging and reaches the Earth's surface in greatest amount
UV-B	280–320 nm	Higher energy than UV-A but less energetic than UV-C	More damaging than UV-A but less damaging than UV-C. Most UV-B is absorbed by O_3 in the stratosphere
UV-C	200–280 nm	Highest energy	Most damaging but not a problem because it is totally absorbed by O_2 and O_3 in the stratosphere

x% loss of O_3 would result in 2x% increase damage.
Long days (closer to the equator) detrimental.

2.6

A very low O_3 density in the Fragile layer offers protection.



Biological Effects of Ultraviolet Radiation

The consequences depend primarily on:

1. The energy of the radiation.
2. The exposure time.
3. The organism sensitivity

The most deadly form of skin cancer, **melanoma**, is linked with the intensity of UV radiation and the latitude at which you live.

An Australian product uses "smart bottle" technology; bottle color changes from white to **blue** when exposed to UV light.

2.7

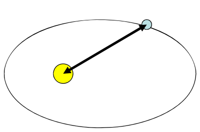
Table 02.05

Table 2.5 The UV Index

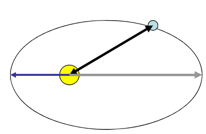
Exposure Category	Index	Tips to Avoid Harmful Exposure to UV
LOW	< 2	Wear sunglasses on bright days. Be aware that snow and water can reflect the Sun's rays. If you burn easily, cover up and use sunscreen.
MODERATE	3–5	Take precautions, such as covering up, if you will be outside. Stay in shade near midday when the Sun is strongest.
HIGH	6–7	Protect against sunburn. Reduce time in the Sun between 10 AM and 4 PM. Cover up, wear a hat and sunglasses, and use sunscreen.
VERY HIGH	8–10	Take extra precautions against sunburn, as unprotected skin will be damaged and can burn quickly. Minimize Sun exposure between 10 AM and 4 PM. Otherwise, seek shade, cover up, wear a hat and sunglasses, and use sunscreen.
EXTREME	11+	Take all precautions against sunburn, as unprotected skin can burn in minutes. Be aware that white sand and other bright surfaces reflect UV and will increase UV exposure. Avoid the Sun between 10 AM and 4 PM. Seek shade, cover up, wear a hat and sunglasses, and use sunscreen.

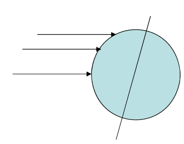
Source: U.S. EPA, 2009.

Reading assignment: Section 2.7 p. 82 -



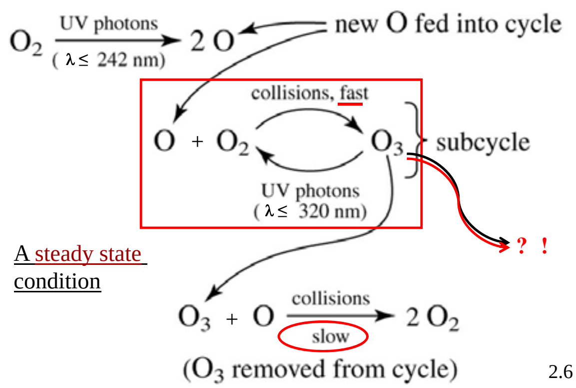
Ozone concentration – non uniform in the stratosphere





Ozone production is dependent on intensity of sunlight.

Distance, angle of rays, angle of earth with respect to rays (seasonal), sun-spots and also wind in stratosphere.



2.6

Materials & Processes reducing the O_3 Concentrations (natural):

Water vapor in stratosphere:

$H_2O \xrightarrow{light} H^\bullet + OH^\bullet$ Highly reactive free radicals *consume O_3 converting to O_2.*

(soil, bacteria) $N_2O + O^\bullet \rightarrow 2NO^\bullet$ *consumes* $O^\bullet$ reducing $O^\bullet$ (i.e. O) needed to produce ozone.

Materials & Processes reducing the O_3 Concentrations (*man-made*):

*Chlorofluorocarbons; **CFC** (C, F, Cl)*
Very stable substances (non toxic; boiling point -10 → -30°C; chemically inert/hard to break C-F,C-Cl bonds) – non-flammable, cheap, would last for long periods of time *in the troposphere*.

Reaches the ozone layer eventually.

Halons (C, Br; F and/or Cl but no H)
Similar to CFC's.

Used in:

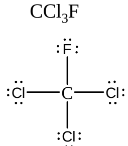
Refrigeration
Air conditioning
Foaming agent
Propellant (aerosols)

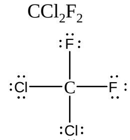
Very stable substances, non-flammable, cheap, would *last for long periods of time in the troposphere*.

Eventually enters the ozone layer.

How CFCs Interact with Ozone

CFC-11	**CFC-12**
Freon 11	Freon 12
trichlorofluoromethane	dichlorodifluoromethane
CCl_3F	CCl_2F_2





First, UV radiation breaks a carbon-halogen bond:

hν (λ < 220 nm) + $CCl_2F_2 \longrightarrow {}^\bullet CClF_2 + Cl^\bullet$ (free radicals)

2.9

The chlorine radical attacks an O_3 molecule:

$2\ \mathbf{Cl^\bullet} + 2O_3 \longrightarrow 2\ ClO^\bullet + 2\ O_2$

Then two chlorine monoxide radicals combine:

$2\ ClO^\bullet \longrightarrow ClOOCl$

The ClOOCl molecule then decomposes:

UV photon + $ClOOCl \longrightarrow ClOO^\bullet + \mathbf{Cl^\bullet}$

$ClOO^\bullet \longrightarrow \mathbf{Cl^\bullet} + O_2$

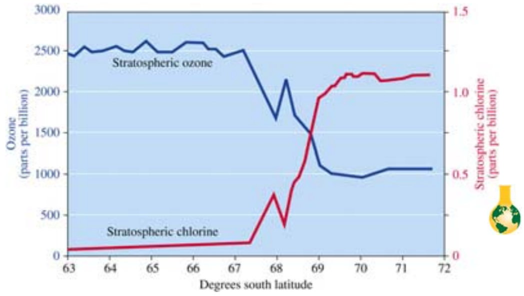
The 2Cl· radicals are free to attack more O_3

The net reaction is: $2\ O_3 \longrightarrow 3\ O_2$

The Cl· radicals are both **consumed and regenerated**; they act as **catalysts**

2.9

Experimental analyses show that as ClO$^{\bullet}$ concentrations increase, ozone concentration decreases (Antarctica) .



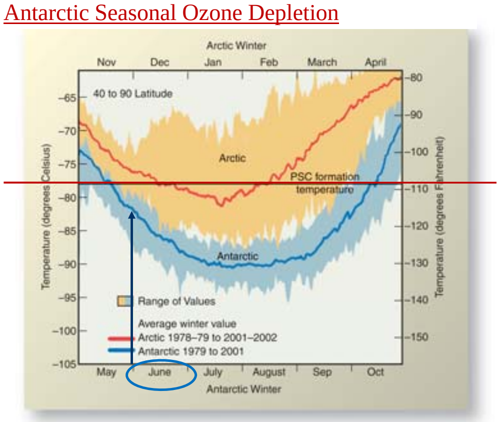
2.9

Other chlorinated compounds from natural sources do exist e.g $ClONO_2$ and HCl.

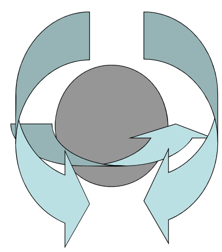
Unlike CFCs they are water soluble so hardly reaches the stratosphere due to rain.

Wherever HF is found there is HCl in the stratosphere implicating CFCs.

Antarctic Seasonal Ozone Depletion



Antarctic Seasonal Ozone Depletion



June-Sept. lower hemisphere coldest and darkest, -90°C.

Ice crystals in PSCs acts as a catalyst in the formation of very reactive HOCl and Cl_2 on the ice crystal surface from otherwise *less harmful* $ClONO_2$ and HCl.

End of Sept. sun comes up initiating Cl$^{\bullet}$ formation and triggering O_3 depleting reactions.

Antarctic Seasonal Ozone Depletion

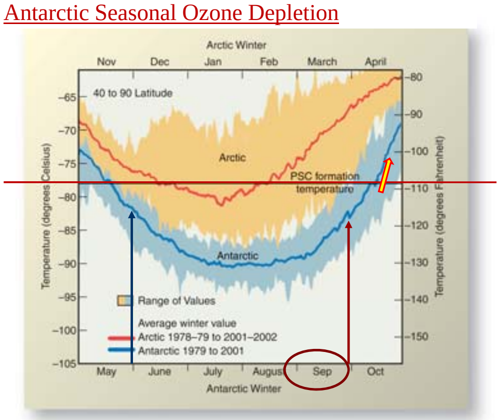
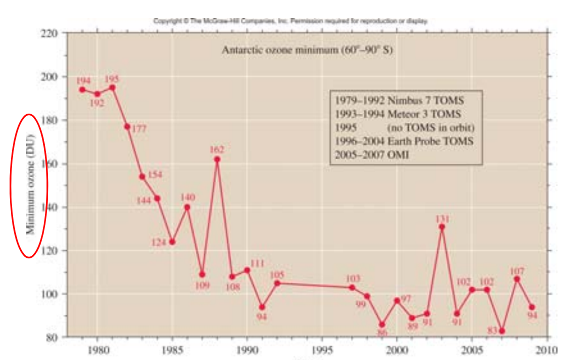
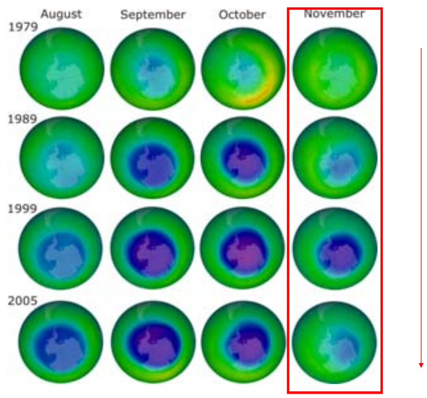
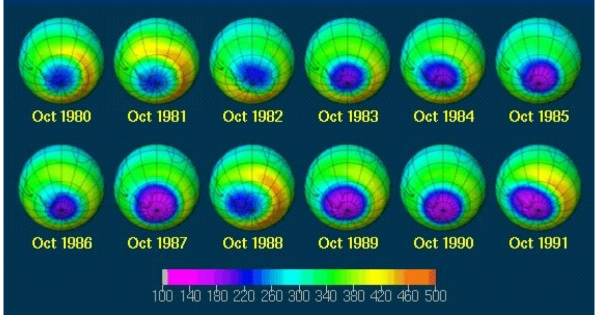


Fig02.14



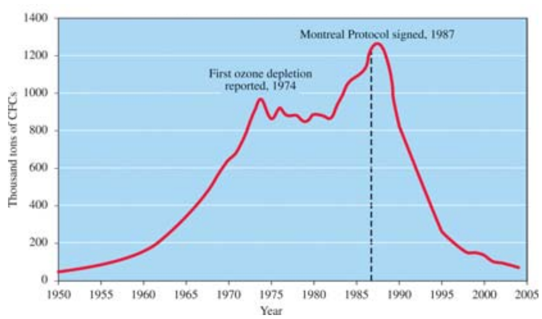


http://i110.photobucket.com/albums/n92/gengar_thegrin/HA/ozone1.png

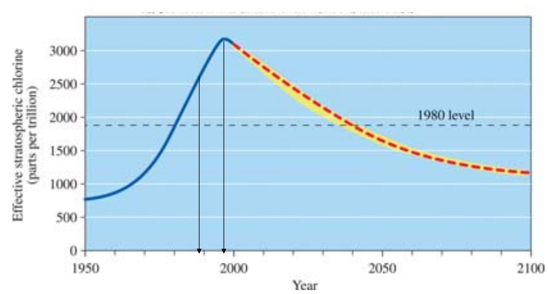


http://www.soest.hawaii.edu/GG/ASK/ozonehole.html

Montreal Protocol - 1987

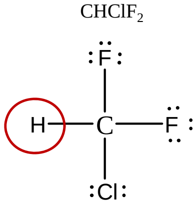


CFCs would be phased.

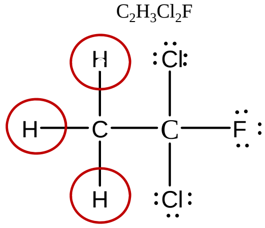


HCFCs are alternatives to CFCs: they decompose *more* readily in the troposphere so they will not accumulate to the same extent in the stratosphere.

HCFC-22
chlorodifluoromethane
$CHClF_2$



HCFC-141b
dichlorofluoroethane
$C_2H_3Cl_2F$



2.12

Chemical feature of HCFC.

Less C-Cl bonds, lowering the stability and their' lifetime in troposphere. Increase C- H bonds. Replace C-Cl with C-H.

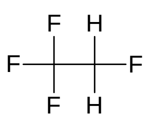
This lowers the desirable characters of these materials that made it so useful in air-conditioning and refrigeration.

low chemical stability, more flammable due to presence of higher proportion of H.

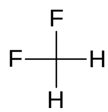
HCFCs would be phased out as well.

Hydrofluorocarbons, HFCs

Replaces HCFCs



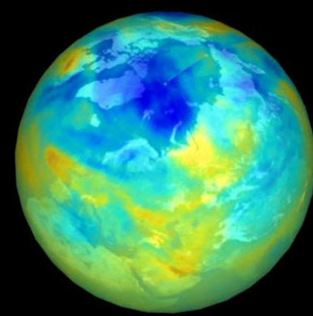
HFC-125



HFC-32

HFCs are however is a green house gas (next chapter).

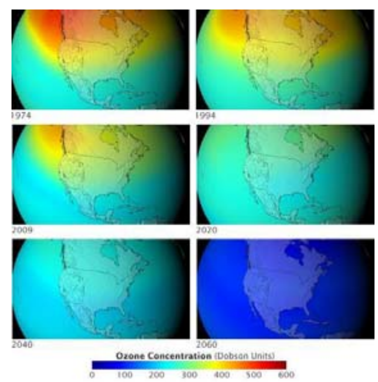
More UV Radiation in Tropics and Antarctica Predicted by Physicists



http://www.treehugger.com/clean-technology/ozone-layer-shifting-more-uv-radiation-in-tropics-and-antarctica-predicted-by-physicists.html

Ozone Layer: Wikipedia posting with a NASA animation

NASA *projections* of stratospheric ozone concentrations ***if*** chlorofluorocarbons had not been banned

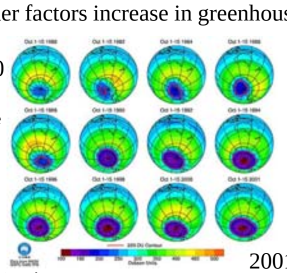


http://en.wikipedia.org/wiki/File:Future_ozone_layer_concentrations.jpg

Ozone hole can close by 2050

The hole in the ozone layer over Antarctica may close within 50 years, as the level of destructive ozone-depleting CFCs in the atmosphere would decline if the Montreal protocols were followed other factors increase in greenhouse gases were removed.

1980



2001

The hole in the ozone layer above Antarctica is seen in a series of satellite images over a 21-year time span

http://www.tribuneindia.com/2002/20020919/science.htm